

**ENGINEERED 2D CARBON NITRIDE BASED
NANOCOMPOSITES FOR SOLAR ENERGY
CONVERSION APPLICATIONS**

BY

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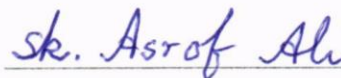
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Dedicated to my mother

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LIST OF ABBREVIATIONS

HER	:	Hydrogen Evolution Reaction
PR	:	Photoreforming
IEA	:	International Energy Agency
ΔG°	:	Gibbs Free Energy
EQE	:	External Quantum Efficiency
FGs	:	Functional Groups
EG	:	Ethylene Glycol
PECR	:	Photoelectrochemical-reforming
HMF	:	5-Hydroxymethylfurfural
HRG	:	Highly Reduce Graphene Oxide
CB	:	Conduction Band
VB	:	Valence Bond
LSV	:	Linear Sweep Voltammetry
EIS	:	Electrochemical Impedance Spectroscopy
UV-Vis/DRS	:	UV-Vis/diffuse Reflectance Spectroscopy
2D	:	Two Dimensional
OPV	:	Organic Photovoltaic
PSC	:	Perovskite Solar Cells
STH	:	Solar to Hydrogen Efficiency
e^-/h^+	:	Electron / Hole

ABSTRACT

Full Name : [Muhammad Ashraf]

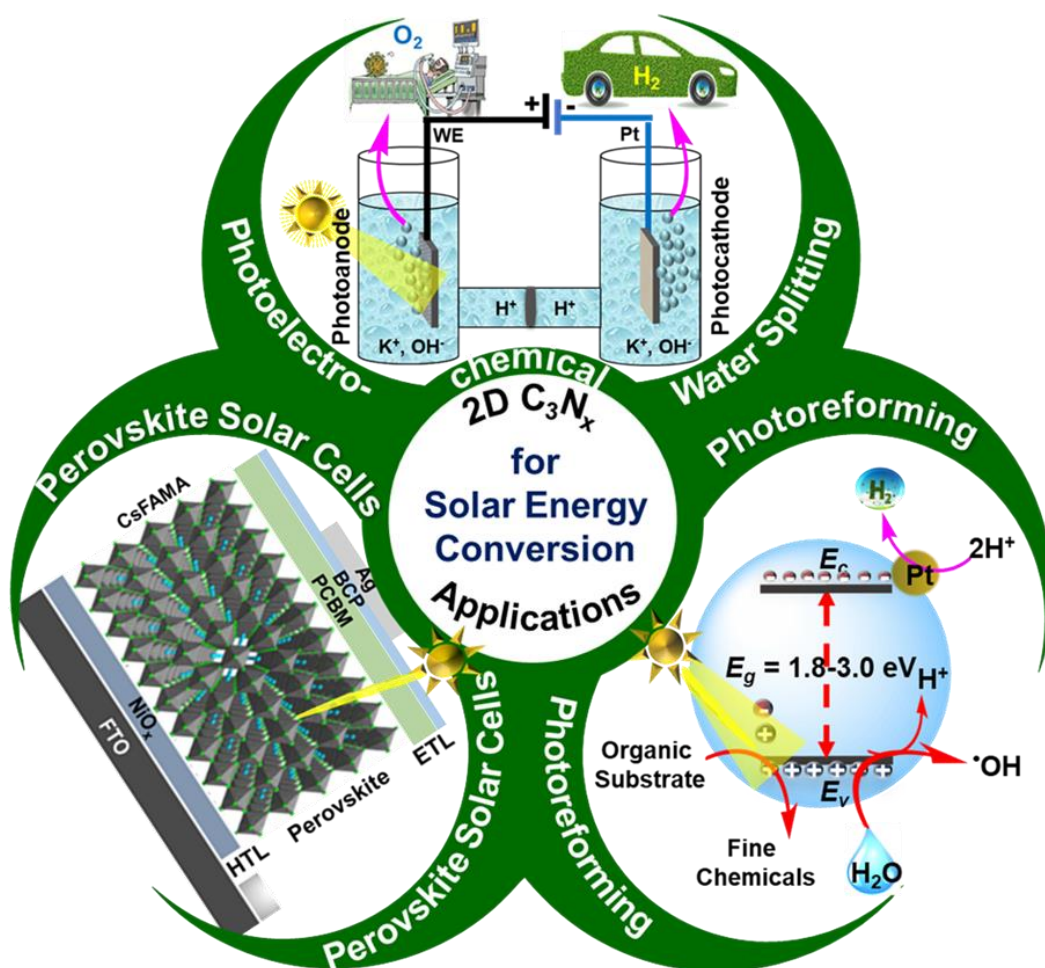
Thesis Title : [Engineered 2D Carbon Nitride based Nanocomposites for Solar Energy Conversion Applications]

Major Field : [Chemistry]

Date of Degree : [May/2022]

Solar energy harvesting is a well-established field of green energy research to encounter the upcoming demand of future energy and environmental sustainability, as the existing fossil fuels burning cause tremendous anthropogenic devastations. The main objective of my Ph.D dissertation is to engineer the two dimensional (2D) carbon nitride (C_3N_x) based nanocomposites, which can directly address the advancement of key challenges in solar energy conversion applications such as (1) Photocatalytic and photoelectrochemical (PEC) hydrogen generation, oxygen evolution and overall water splitting, (2) Photoreforming of plastic- or biomass-derived waste into organic valuables and “green” H_2 fuel (3) Organic photovoltaic (OPV) / perovskite solar cells (PSC). The surface functionalization and morphological investigation of the synthesized 2D C_3N_x based nanocomposites photocatalyst were carried out with the help of field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), and high-resolution transmission electron microscopy (HR-TEM), respectively. The structural elucidation were accomplished with the help of X-Ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance spectroscopy (NMR), mass spectrometry, and Raman analysis. The optical properties such as charge recombination behaviors of the photoinduced electrons/holes, optical band gaps and band positions were investigated with

the help of ultraviolet- visible spectroscopy (UV-vis)/diffuse reflectance spectroscopy (DRS) and room temperature photoluminescence (PL) spectroscopy. The photoelectrochemical techniques such as linear sweep voltammetry (LSV), chronoamperometry ($I-t$), electrochemical impedance spectroscopy (EIS) were used to measure the performance of the as synthesized 2D C_3N_x based nanocomposites for solar energy harvesting applications in terms of photocurrent densities(mA/cm^2), stability and solar to hydrogen (STH) efficiencies. Lastly, to fully understand the solar to sustainable energy technologies, we proposed overall mechanistic insights for each application. The overall research activities were performed at the laboratory scale, and we successfully developed the engineered 2D C_3N_x based nanocomposites for solar energy harvesting applications.



Graphical Abstract

ملخص الرسالة

الاسم الكامل: محمد أشرف

عنوان الرسالة: تصنيع مركبات نانوية ثنائية الأبعاد تعتمد على نيتريد الكربون لتطبيقات تحويل الطاقة الشمسية
التخصص: كيمياء

تاريخ الدرجة العلمية: مايو / 2022

يعد حصاد الطاقة الشمسية مجالاً راسخاً لأبحاث الطاقة الخضراء لتلبية الطلب القادم على الطاقة المستقبلية والاستدامة البيئية ، حيث يتسبب حرق الوقود الأحفوري الحالي في حدوث دمار هائل من صنع الإنسان . الهدف الرئيس من أطروحة الدكتوراه الخاصة بي هو تصنيع مركبات نانوية ثنائية الأبعاد القائمة على نيتريد الكربون والتي يمكن أن تعالج بشكل مباشر تقدم التحديات الرئيسية في تطبيقات تحويل الطاقة الشمسية مثل

1. التحفيز الضوئي والكهروضوئي لتوليد الهيدروجين و الأكسجين وانقسام الماء بشكل عام .
 2. التشكيل الضوئي للنفايات البلاستيكية أو المشتقة من الكتلة الحيوية إلى مواد عضوية ذات قيمة ووقود الهيدرجين الأخضر.
 3. الخلايا الضوئية العضوية / خلايا بيروفسكايت الشمسية.
- تم إجراء التهيئة السطحية والتحقيق المورفولوجي للمحفز الضوئي ثنائي الأبعاد القائم على المركبات النانوية لنيتريد الكربون بمساعدة المجهر الإلكتروني لمسح الانبعاث الميداني، والتحليل الطيفي للتشتيت الطاقى، والفحص المجهرى الإلكتروني عالي الدقة ، على التوالي. تم إنجاز التوصيف البنىوى بمساعدة تحليل حيود الأشعة السينية، والتحليل الطيفي للإلكترون الضوئي بالأشعة السينية، والتحليل الطيفي للرنين المغناطيسي النووي وقياس الطيف الكتلي ، وتحليل رامان.

تم فحص الخصائص الضوئية مثل عملية إعادة تركيب الشحنات الإلكترونية / الثقوب الضوئية ، وفجوات النطاق البصري ومواضع الشريط الطاقى بمساعدة التحليل الطيفي المرئي فوق البنفسجي / مطياف الانعكاس المنتشر و التحليل الطيفي للتألق الضوئي عند درجة حرارة الغرفة.

تم استخدام التقنيات الكهروكيميائية الضوئية مثل قياس الفولت الخطي، وقياس التيار الزمني، والتحليل الطيفي للمقاومة الكهروكيميائية لقياس أداء المركبات النانوية ثنائية الأبعاد C_3N_x لتطبيقات حصاد الطاقة الشمسية من حيث كثافات التيار الضوئي، والاستقرار وكفاءة عملية تحويل الطاقة الشمسية إلى الهيدروجين. أخيرًا ، لفهم اليات تحويل الطاقة الشمسية إلى الطاقة المستدامة، اقترحنا اليات شاملة لكل تطبيق. تم إجراء الأنشطة البحثية الشاملة على نطاق المختبر، ونجحنا في تطوير المركبات النانوية ثنائية الأبعاد القائمة على نيتريد الكربون C_3N_x لتطبيقات حصاد الطاقة الشمسية.

CHAPTER 1

Introduction

The energy systems used to meet the sustainable economic demands have transformed dramatically since the industrial revolution. Figure 1.1a shows the energy transformation worldwide as reported by the United States energy information administration (US-EIA). This indicates that the primary energy sources coming from non-renewable sources comprise of petroleum (37%), coal (11%), natural gas (32%) and nuclear electric power (8%). These accounts to around 89% share in the total energy system. The left over, 11% is fulfilled by the renewable energy resources such as the solar energy, biomass energy, hydrothermal energy, and geothermal energy sources^[1,2]. However, in the recent decades, global energy demand has been drastically increasing due to the expansion in population and rapid industrialization. It is estimated that energy demands will double by the year 2050^[3]. As discussed above and indicated in Figure 1.1a, the major portion of the current worldwide energy supply is still met through conventional fossil fuels (non-renewable energy sources) which are exhausting and expected to deplete in the near future (Figure 1.1b). In addition, the fossil fuel based energy sources are accompanied by the release of non-eco-friendly gases so called greenhouse gases (Figure 1.1c)^[4]. The rapid depletion of fossil fuels and release of greenhouse gases, particularly carbon dioxide will result in both the energy crisis and environmental deterioration in future. These both factors are considered big threat to the sustainable development of our upcoming society^[5].

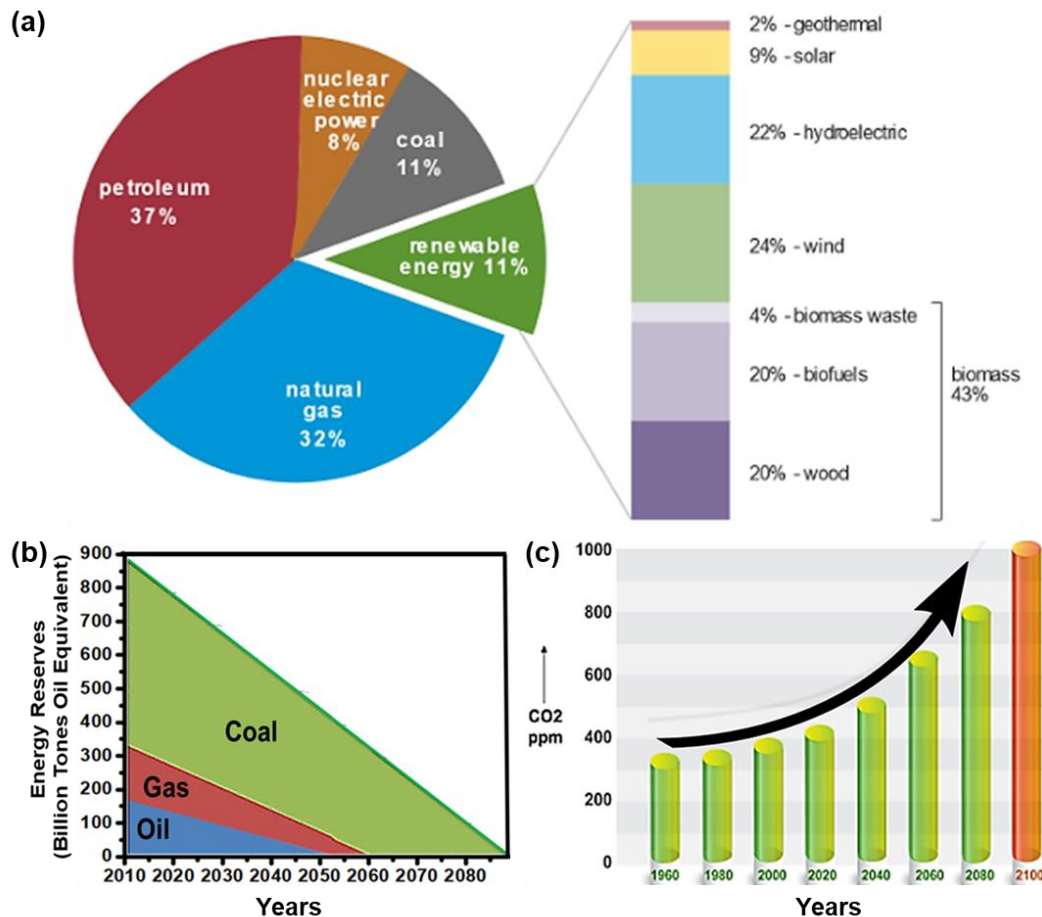


Figure 1. 1: The graphical presentation comparing the energy consumption produced by different resources worldwide during the year 2019 (Figure 1.1a). The diagram depicting the depletion of fossil fuel in future (Figure 1.1b) and rise in CO₂ in the environment (Figure 1.1c). Source: U.S. Energy Information Administration, Monthly Energy Review.

1.1 Renewable Energy on the Rise

The upward shift in total global CO₂ emissions have increased from 33.1 gigatons to 36.2 gigatons from 2010 to 2017 and are projected to rise further in future. In this contribution, almost 3.21×10^{13} kg of CO₂ was emitted to the atmosphere from these non-renewable energy resources^[6-9] and the release of CO₂ has increased its concentration >400 ppm, which was not noted in the past 450,000–600,000 years^[10,11]. In spite of these all challenges on brink, there is no regular mechanisms to capture CO₂ from the higher

atmosphere and its consumption is very slow in the lower atmosphere (biosphere). With an aim to develop technology that could actively consume the produced CO₂, may take another 400 years to several thousand years ^[12,13]. Arguably only this century CO₂ emission will remain in the earth atmosphere for another 500–2000 years ^[14,15].

Although, the nuclear energy and renewable energy produced from different sustainable sources are increasing by 2.5% per year but still the non-renewable sources (fossil fuels) will continue to contribute approximately 80% of the total energy supply until 2040 ^[16–18]. Based on these statistics, the researchers across the globe requires to answer two major challenges; (i) the replacement of non-renewable resources which may vanish in coming less than 100 year ^[9,19–24] by the efficient and cost effective renewable energy sources and (ii) the sustainability of environment which is at risk due to the massive consumption of fossil fuel that emits large volumes of greenhouse gases and contributes majorly for the global warming and other environmental impeachments. Particularly, the increase in CO₂ emission, researchers across the globe have shifted their interest on finding the alternative energy resources that are commercially viable, carbon neutral and environmentally friendly^[14,25–27]. In order to find the practical answers for above mentioned issues, the production of green, sustainable and renewable energy has become an imperative task for researchers in finding the new technologies or improving the existing methods to meet the future energy demands ^[28–30]. In this contribution, an enormous interest among the researchers and industries has developed about the utilization of renewable resources to fulfil the world energy requirements.^[31] As a result, the generation of renewable energy has experienced an increase from 51 quadrillion British thermal unit (BTU) in 2010 to 100 quadrillion BTU in 2022. There is an expected approximation that renewable energy would

increase to above 150 quadrillion BTU at the end of year 2030 (Figure 1.2a). The data (Figure 1.2a) also show the energy consumptions comparison in percentages for the years 2018 and 2050 ^[32,33]. These statistic stems the importance of renewable energy in future. Figure 1.2b indicates the different potential renewable energy resources available to meet the above-mentioned expectations. Among these renewable energy resources available, the solar energy leads from the front being abundant and almost available across all continents.

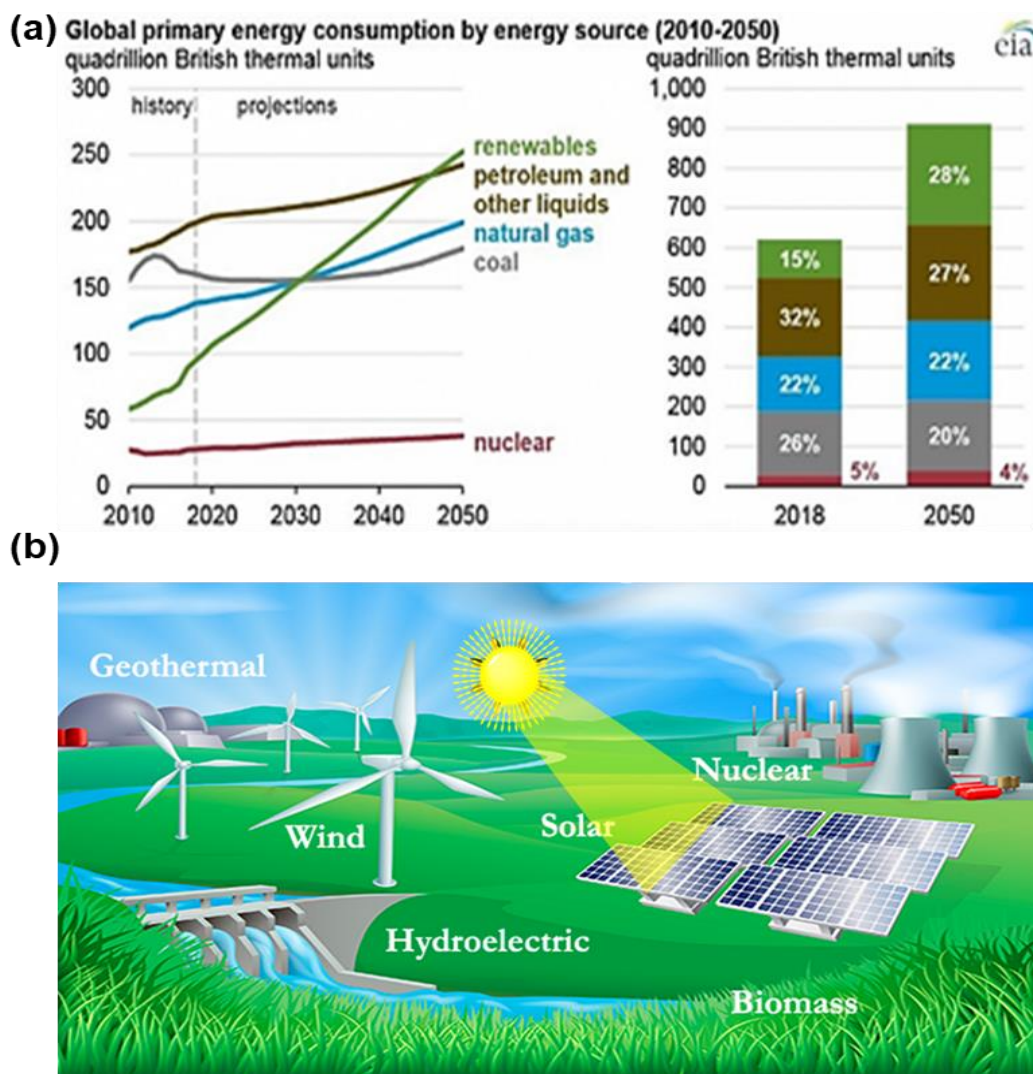


Figure 1. 2: (a) Renewable energy generation from 2010-2050. (b) A variety of energy sources shown which consumed in the world since 1990-2025^[33].

1.2 Solar Energy: A Great Substitute to Conventional Energy Sources

Also the solar energy or sunlight irradiation available on earth surface is by far the largest renewable power source ^[34]. The total solar energy received our earth surface every year from sun light irradiation is about 1.2×10^5 tera watt (TW), which is about 6,000 times of our recent power consumption ^[19,35,36]. It should be noted that the solar spectrum comprises approximately 7% of UV region, 44% of visible light region and 49% of the IR region as indicated by the solar spectrum distribution ratios in Figure 1.3 ^[37].

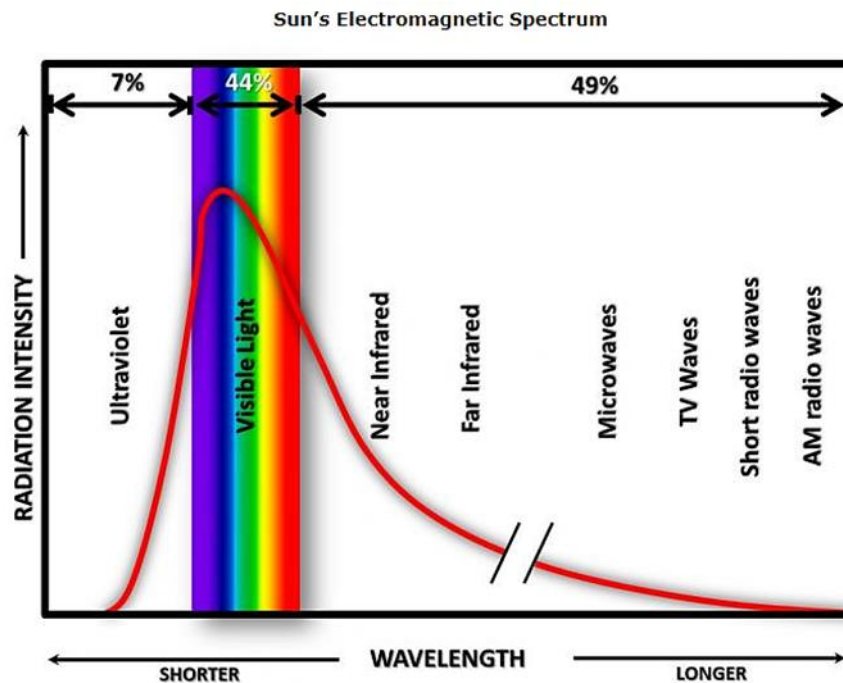


Figure 1. 3: Illustration of spectral irradiance for sun light spectrum ^[38,39].

Sunlight energy can be directly utilized but it's both intermittent and diffuse nature, demands for an efficient and economically viable approach of converting it into electrical or chemical energy. ^[40,41] But realizing this dream in a sustainable way with least harmful impact on our planet has been still a longstanding challenge for the scientific community ^[42]. This is also partially because the available industrial systems that could potentially

utilize solar light are still on the initial stage and a lot of exploration and the development of research tools are needed to achieve the targeted goal ^[43]. Therefore, the researchers are trying to explore different protocols to fabricate devices capable of converting solar energy in a highly efficient, environmentally benign and economically viable way^[44]. Among these available approaches of converting sunlight energy in a sustainable fashion, three technologies have emerged namely; (i) photocatalytic or photoelectrochemical water splitting into molecular hydrogen (H₂) fuel, (ii) photoreforming of plastic- or biomass-derived waste into organic valuables and “green” H₂ fuel and (iii) organic photovoltaics in the form of perovskite solar cells ^[45]. In this research, we will discuss the different technologies available to harvest and convert solar energy into industrially viable chemical energy options. We would introduce the basic principles and focus on the mechanistic insights of the above mentioned three emerging solar energy conversion technologies. This would particularly help novice to understand the basic principle as well as design of new projects. In the last section, we will discuss the role of nanostructured materials in improving the efficiencies of devices resulting from these technologies. Finally, we will conclude the review with recent advances and future prospects of these technologies for their potential use on industrial scale.

1.3 Research Objectives

The primary theme of this proposed study was to synthesize and engineered 2D C₃N_x based nanocomposites, which possess enhanced optical properties. These 2D C₃N_x based nanocomposites were further investigated for solar energy harvesting applications such as (1) Photocatalytic and photoelectrochemical (PEC) hydrogen generation, oxygen evolution and overall water splitting, (2) Photoreforming of plastic- or biomass-derived waste into

organic valuables and “green” H₂ fuel (3) Organic photovoltaic (OPV) / perovskite solar cells (PSC). The major objectives achieved are listed as follow.

1.3.1 Synthesis and Engineering of C₃N_x

The purpose of this objective was to synthesize and engineered 2D C₃N_x based nanocomposites for solar energy conversion applications. We successfully developed different C:N ratio 2D C₃N_x based nanocomposites i.e. (i) C₃N₃, Melon, C₃N₄, C₃N₅ (ii) HRG@Melon (iii) C₃N₃/Ni₂P, and (iv) C₃N₃/Cu, by various synthetic techniques for photoinduced solar energy conversion applications.

1.3.2 Optimization of Reaction Conditions

Optimized various reaction parameters such as the effect of time, temperature, the concentration of the precursors and other chemical reagents to achieve engineered 2D C₃N_x based nanocomposites.

1.3.3 Characterizations of 2D C₃N_x based Nanocomposites.

The physicochemical properties of the engineered 2D C₃N_x based nanocomposites were explored by various characterization techniques. The morphology of the as prepared photocatalysts were characterized using spectroscopic, X-ray and electron microscopy techniques. The structure of the as-prepared engineered 2D C₃N_x based nanocomposites, were measured by X-ray diffractometer (XRD), Rigaku mini flex II X-ray diffractometer between 20 and 90° 2 θ with a scan rate of 0.02° 2 θ s⁻¹ using Cu-K α radiation source (λ = 1.5414 Å). Fourier transform infrared spectroscopy (FT-IR, Nicolet Avatar-330) was used to investigate surface functional groups and optical properties of synthesized engineered 2D C₃N_x based nanocomposites. BET measurements were accomplished by a

gas absorption setup Autosorb-6G from Quantachrome with nitrogen gas for analysis. During the measurements process, the temperature was set as -196.15 °C. Quantachrome ASiQWin 3.0 software was used to perform data evolution. Raman spectrometer (Tag no.340326 RR-1115) with charge-coupled device (CCD) detector in the spectrum window of 30–2000 cm^{-1} using green type laser ($\lambda = 532 \text{ nm}$) with an intensity of 50% and an exposure time of 15 s was used for Raman spectra. UV-vis diffuse reflectance spectroscopy was recorded in the range of 200 nm to 800 nm using Cary 500 UV-vis NIR spectrophotometer in Ulbricht sphere compared with BaSO_4 white reflectance standard. Field-emission scanning electron microscopy was performed using an FE-SEM (Tescan Lyra-3) at 20 kV for chemical analysis. The energy dispersion spectrum (EDS) analysis of our samples was carried out on a Lyra 3 attachment to the FESEM using the LINK INCA program system. XPS measurements were carried out on an Axis Ultra DLD imaging photoelectron spectrometer. Measurements were carried out using the Hybrid mode with 10 mA and 15 kV at the Al anode. The analysis area was $700 \mu\text{m} \times 300 \mu\text{m}$ (i.e., X-ray spot size). Survey spectra were measured at a pass energy of 80 and elemental spectra at 20 pass energy of the analyzer. All spectra were charge corrected to a binding energy of 284.8 eV for the C 1s line corresponding to adventitious aliphatic carbon. Measurements were evaluated using the CasaXPS software. Powdered samples were prepared by placing one drop (10 μL) of a diluted NP solution in ethanol (0.1 mg mL^{-1}) on a carbon-coated copper grid and by letting it dry at room temperature for transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and electron dispersive X-ray spectroscopy (EDXS). TEM, and EDX measurements were carried out with an FEI TECNAI F30 S-TWIN transmission electron microscope equipped with a field emission gun and working at 300

kV. TEM images and nano electron diffraction (NED) patterns were obtained with a CCD camera (16-bit 4.096×4.096 pixel GATAN ULTRASCAN4000) and acquired using the Gatan Digital Micrograph software. ICP-OES analysis were done by using microanalysis service at chemistry Department in KFUPM through on thermos Scientific iCAP 700 spectrometer to identify quantification of bulk Ni and P contents presence in engineered 2D C_3N_x based nanocomposites, which was degassed in $H_2O_2:H_2SO_4$ of 2:1 overnight before measurements.

1.3.4 Solar Energy Conversion Setup and Measurements.

To study the Photocatalytic, PEC water splitting and PEC reforming performance we make complete setup, consist of solar simulator, monochromator, photoelectrochemical cell, and Potentiostat. Prior to PEC water splitting measurements, proper training is conducted. All PEC measurements were conducted with a three-electrode system using a Gamry Potentiostat (600+). A Pt wire electrode and an Ag/AgCl (saturated KCl) electrode were used as counter and reference electrodes. All potentials were converted to reverse hydrogen electrode (RHE) values using the equation

$$V_{RHE} = V_{Ag/AgCl} + 0.059 \text{ pH} + 0.197$$

Mott-Schottky measurements were performed in optimized aqueous solution using the same Potentiostat at 2000 Hz. Photocurrents were measured at 1.23 V vs. RHE under illumination with a solar simulator (303 W Xe arc lamp, ozone free, equipped with air mass AM 1.5G and water filters) at a power density of 100 mW cm^{-2} , which was calibrated using a power meter (Model 919-P, Newport).

All electrodes were fabricated by drop casting on a fluorinated tin oxide (FTO) glass support. For each PEC reaction, 10 mg of the photocatalyst was suspended in a 2 mL of an equimolar mixture of ethanol and deionized (DI) for two hours using ultrasonication. 5 μ L of a 0.5% Nafion solution in (1:5) added as binder. 10 μ L of the prepared ink was drop casted on a $1 \times 1 \text{ cm}^2$ area of FTO and dried in an oven at 60 $^{\circ}\text{C}$. The dried electrodes were calcined at 350 $^{\circ}\text{C}$ under an argon atmosphere.

CHAPTER 2

Literature Review

2.1 Photocatalytic (PC) and Photoelectrochemical (PEC) Water Splitting

A typical photocatalytic system for water splitting features single semiconductor based photocatalyst in solution. Upon irradiation of solar light, the photocatalyst split water molecules ($2\text{H}_2\text{O}$) in to 2H_2 and O_2 . This results storing the solar energy in the form of chemical fuels ^[46]. Thermodynamically, to complete this chemical process, the electronic bandgap (E_g) value must be higher than 1.23 eV, corresponding to sum of the equilibrium redox potential for water splitting. Therefore, reaction experience very slow kinetics and oxidation of $2\text{H}_2\text{O}$ and reduction of H^+ observes substantial overpotentials ^[47,48]. Thus practically, a bandgap larger than around ~ 1.7 eV at room temperature is required to drive this reaction. In the recent couple of decades, tremendous efforts have been exercised to find appropriate semiconducting materials together with some suitable cocatalysts to perform half reactions. The hydrogen evolution reaction (HER) occur on the semiconductor surface upon coupling of two electrons ($2e^-$) with two electron deficient hydrogens normally called as two protons (2H^+). The oxygen evolution reaction (OER) needs the removal of $4e^-$ and 4H^+ from $2\text{H}_2\text{O}$ by a process normally proceeds at suitable rate at high over potentials because it involves the cleavage of four O-H bonds and the formation of the oxygen double bond ($\text{O}=\text{O}$). Mechanistically, the absorption of light triggers charge separation in semiconductor photocatalyst with the photogenerated

electrons transfer to the HER cocatalyst and hole (h^+) migrating to the cocatalyst, where OER takes place (Figure 2.1 a&b) ^[49,50].

But the fast recombination of charges and the sluggish kinetics related to both reactions especially in water oxidation reaction triggers the whole system insufficient in terms of quantum yield (QY) and solar -to-hydrogen (STH) generation efficiency. The conventional photocatalysts systems usually includes organic dyes (QuPh⁺-NA ^[51], eosin Y ^[52], fluorescein ^[53]) bulk semiconductors (such as TiO₂ ^[54], g-C₃N₄ ^[55], SrTiO₃ ^[56], Ta₂O₅, ^[57] other metal oxides ^[58], fluorides ^[59,60] and sulfides ^[61] (table 1), metal complexes (such as Ru ^[62], Ir ^[63], and Rh based complexes ^[64]) as an light absorbers. However, none from the above-mentioned systems are ideal candidate for overall water splitting. Thus, the overall water splitting system based on single semiconducting materials is challenging due to too low efficiencies for practical applications.^[65] Hence, many important studies were conducted with aim to optimize the individual driven half reactions using suitable sacrificial redox reagents. The focus was to investigate photocatalyst materials that can mediate the overall water splitting reaction. In this case, the possibility is to driven overall reaction solely by sunlight energy or using an external electric potential in the form of PEC to mediate the redox reaction ^[49].

PEC water splitting are ideal approaches to convert sunlight energy into chemical energy in the form of “green” H₂ fuel ^[66]. In this direction, the raw materials required (water & sunlight) are naturally abundant and economically viable. However, the biggest challenge associated with PEC water splitting is to synthesize or engineer a single photocatalytic system that can absorb in the visible portion of solar spectrum and access the excited state in which the electrons (e^-) and holes (h^+) energies match there redox potentials (reduction

of H^+ and oxidation of water).^[59] At the same time, it should be chemically stable under reaction conditions and able to efficiently separate the electrons (e^-) and holes (h^+) pair^[67]. Thermodynamically, splitting of water to H_2 and O_2 is an endothermic process having a positive value for the change in the Gibbs free energy (ΔG°) around 237 kJ mol^{-1} . This means for two electron process, H_2O can be electrolyzed under standard conditions through externally applied voltage of 1.23 eV ^[68]. The overall reaction *i.e.*, reduction of proton and oxidation of water can be presented by the following equations.



The water redox potential determines the necessary bandgap and the band edge positions for a semiconductor based photocatalyst in a photocatalytic and PEC water splitting for the production of H_2 fuel^[69].

The sluggish kinetics of the electrons (e^-) and holes (h^+) pair separation or fast charge recombination and propensity of semiconductors to undergo oxidative decomposition limits over-all water splitting under aqueous conditions^[70]. These issues can be improved by the proper design or engineering of photocatalysts used in PEC based water splitting approach. A conventional PEC cell consists of photoactive electrodes (anode or cathode) as a working electrode and the dark electrode naming counter electrode usually made of Pt disk, an external bias and solar light irradiation source as shown in Figure 2.1 c&d^[71]. The introduction of photoactive electrode reduces the voltage needed by applying solar power to replace some of the electric power^[72]. The combination of photoactive electrode and dark electrode immersed in the solution (electrolyte) comprises the basis of a conventional

PEC cell. But the typical integrated PEC cell consist of a photoanode, and photocathode sensitized using two distinct light absorbers ^[71,73]. In an ideal PEC cell, aqueous electrolyte at pH ~ 7 contacts the anode, and cathode, while the energy of solar light force water molecule to split into H₂ and O₂ at the two electrodes in a 2:1 molar ratio respectively ^[71,74]. During visible solar light irradiation, the photocatalytic materials of photoanode absorb photon with energy power in electron volt (eV) equal or greater than its bandgap, and generates e⁻ - h⁺ pairs ^[41]. The electrons generated upon solar light irradiation migrate to the active site of materials for reduction of protons into H₂ fuel while the h⁺ travelling to the counter electrode through an external circuit for the oxidation of water molecules into O₂ ^[71,75]. Therefore, this device (shown in figure 2.1e) is featured as a well-designed PEC cell in which both the photoanode, and photocathode can facilitate or mediate the overall splitting of water without sacrificial agents ^[71,76]. This device is an ideal choice for the efficient conversion of solar energy into H₂ fuel because only solar light as an input is needed to split water molecules into H₂ and O₂. Moreover, the two products H₂ and O₂ formed in distinct locations such that its separation is not needed, which is a practically viable advantage of this approach ^[74].

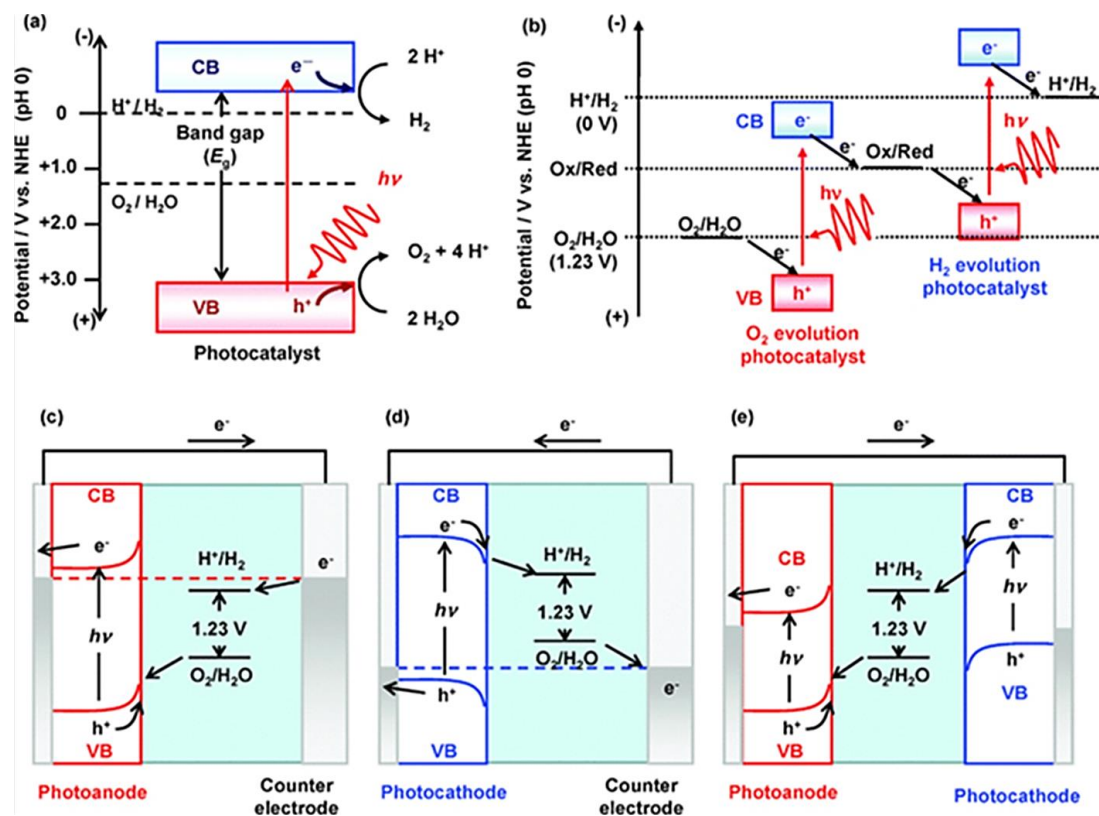


Figure 2. 1 (a&b) Schematic illustration of the basic PC mechanistic insights PEC systems (c&d) A conventional PEC cell consists of photoactive electrodes (anode or cathode) as a working electrode and the dark electrode naming counter electrode usually made of Pt disk, an external bias and solar light irradiation source (e) typical integrated PEC cell consist of a photoanode, and photocathode sensitized using two distinct light absorbers ^[48,71].

The first report of solar induced water splitting was demonstrated by Honda and Fujishima in 1972, using TiO₂ as a semiconductor photocatalyst ^[50,77]. In spite the good stability of TiO₂, its practical appliance as semiconductor photocatalyst is limited due to its wide bandgap i.e., 3.2 eV. It only absorbs ultraviolet (UV) photons of whole solar spectrum. The researchers started search for narrow bandgap (1.0 to 2.0 eV) materials that could harvest the visible spectrum of solar light ^[77–79]. In 1998 John Turner and his group did the first major breakthrough in the field of water splitting using GaInP₂ photocathode and a GaAs photovoltaic showed solar to hydrogen conversion efficiency up to 12.4% ^[80,81]. Since the discovery, the key photocathodes were made of GaInP₂ and InP, with the obtained

photocurrent densities of 30 mA cm^{-2} [80]. Parallely, other semiconductor materials shown in Table 2.1 such as Cu(In,Ga), (S,Se)₂, (CIGS) and CuInS₂ (CIS) were also used as photocathodes for solar induced water splitting. Among these materials combinations, some are already approaching the maximum theoretical efficiency for solar induced water splitting due to relevant bandgap positions [82]. Although, due to the high cost because indium (In) based materials InP and GaInP₂ are non-abundant earth elements, the large scale fabrication of these photoelectrodes is a big challenge [80,81]. Unfortunately, these conventional semiconductor electrode materials and devices did not achieve the target efficiency and the emerging trends shifted to the coupling of perovskite materials for the boosting efficiency of PEC systems. In this regard, Qui et al., explored other transition metals based photocatalyst which more abundant and economically viable. They reported a single perovskite solar cells in tandem with photoanode of Mo-doped BiVO₄ in PEC cell device and achieved solar to hydrogen (STH) conversion efficiency of unassisted water splitting around 6.2% with 10 hour stability [83]. The efficient systems for energy supply, requires the material which are cheap, abundant and environmentally benign and these materials in tandem dye sensitized solar cells (DSSC) photoelectrodes could be the perspective candidate for unassisted water splitting [84]. In this contribution, Sivula et al., fabricated a series of transition metal oxides based photoanode (WO₃ / Fe₂O₃) for the potential application for unassisted water splitting in combination with dye sensitized solar cells and achieved STH conversion efficiency 3.10% and 1.17% respectively [85]. This PEC tandem cells retained its stability up to 80% more than 8 hour. Wang and Park reported unassisted monolithic tandem cell without external bias that showed 5.7% STH conversion. It combined the high level transparency of BiVO₄ sensitized mesoporous WO₃ films/Pt

having single dye sensitized solar cells ^[86]. On the other side, coating of BiVO₄ onto porous WO₃ films maintained high transparency, letting enough photons to enter into dye sensitized photoanode. Likewise, porphyrin dye sensitized photoanode having cobalt electrolyte make up enough potential to accomplish wireless photocatalytic water splitting in tandem system ^[87]. Also, Mara Sero and Gimenez et al., reported a tandem device combined with CdS quantum dots modified TiO₂ photoanode coupled with DSSC for splitting of water with almost zero external bias. This system demonstrated STH conversion efficiency of over 0.78% with high stability ^[88]. Designing and constructing hybrid photoanodes with various range of light absorbers were essential for developing effective and efficient water splitting systems ^[88]. Recently, perovskites based materials have been widely applied as photocatalysts for water splitting applications ^[89]. The photocatalytic activity of perovskite is predominantly determined by B-site elements. In perovskite there are two main groups of elements which can act as an active site (B) of cation components. Among first group include these elements Ti⁴⁺, Ta⁵⁺, Nb⁵⁺, Zr⁴⁺, W⁶⁺, and Ce⁴⁺ elements having empty d orbitals. In second group include elements like Ga³⁺, Ge⁴⁺, In³⁺, Sb⁵⁺, and Sn⁴⁺ with filled d orbitals and typically considered as an excellent photocatalytic behavior for water splitting applications shown in Table 2.1 ^[90]

Table 2. 1: Some representative typical photocatalyst and their efficiencies for overall water splitting.

Hydrogen Evolution Photocatalysts	Oxygen Evolution Photocatalysts	Light source	Reaction condition	Efficiency AQY=	Ref
0.5 wt% Pt/TiO ₂ (anatase)	TiO ₂ (rutile)	400W Hg lamp	H ₂ O pH=11	-----	[54]
3 wt% Pt/C ₃ N ₄	0.5wt% PtO _x /WO ₃ or BiVO ₄	300W Xe lamp	H ₂ O pH=8.3, H ₂ O pH=3.0,	-----	[91]
0.5 wt% Pt/SrTiO ₂	1 wt% Pt/WO ₃	300W Xe lamp	H ₂ O	0.1% at 420 nm	[92]
0.5 wt% Pt/ZrO ₂ /TaON	0.5 wt% PtO _x /WO ₃	300W Xe lamp	H ₂ O	6.3% at 420 nm	[93]
0.4 wt% Pt/MgTa ₂ O ₆ - _x N _y /TaON	0.45 wt% PtO _x /WO ₃	300W Xe lamp	H ₂ O	6.8% at 420 nm	[58]
0.3 wt% Pt/SrTiO ₃ :Rh	BiVO ₄	300W Xe lamp	H ₂ O	2.1% at 420 nm	[94]
0.5 wt% Ru/SrTiO ₃ :Rh	0.5 wt% PtO _x /WO ₃	300W Xe lamp	H ₂ O pH=4.3	0.24% for H ₂ and 0.36% for O ₂ at 400 nm	[95]
1.0 wt% Ru/SrTiO ₃ :Rh	BiVO ₄	300W Xe lamp	H ₂ O pH=3.5	1.7% at 420 nm	[96]
1 wt% Ru/SrTiO ₃ :Rh	BiVO ₄	300W Xe lamp	H ₂ O pH=2.4	4.2% at 420 nm	[97]
0.7 wt% Ru/SrTiO ₃ :Rh	Bi ₄ NbO ₈ Cl	300W Xe lamp	H ₂ O pH=2.5	0.4% at 420 nm	[98]

To conclude, PEC water splitting is an emerging and promising pathway for solar to hydrogen technology that offers at ambient temperature potential of high conversion efficiency using cost-effective thin films or semiconducting nanomaterials ^[99]. Continued advancements in device designing, photocatalyst engineering, economically viable method for electrode fabrications, enhancing efficiency, durability and lowering overall cost of the

system are still crucial for the market viability. The present ongoing development in research of these advancements is making a necessary stride that could benefit from the intense synergies with the contemporary efforts in experimental and theoretical investigation of nanomaterials for solar conversion applications. Thus, it is suggested that the efficiency could be enhanced up to the targeted level by improving the absorption of sun light into visible region with better surface engineering. The lifetime and durability of materials could be improved by investigation of rugged materials and the surface protective coating of electrodes and materials. At last, the overall cost for H₂ production should be reduced by the use of inexpensive earth abundant materials and process and cell design [82].

Table 2. Some representative typical photoelectrochemical-cell reaction over various photoelectrodes and its efficiencies for water splitting.

Photoelectrode	Reaction condition	Surface Area (cm ²)	Light source	Applied Bias (V)	Efficiency QE=	Ref
TiO ₂	Fe ³⁺ Solution	1	400W Hg lamp	N/A	10%	[50]
TiO ₂	1 M NaOH/ 0.5 M H ₂ SO ₄	2	UV light	N/A	60 μ mol/8h	[78]
<i>n</i> -TiO ₂	5 M NaOH	0.2	150 W Xe lamp	0.6	ABPE= 1.08%	[79]
CM <i>n</i> -TiO ₂	5 M NaOH	0.2	150 W Xe lamp	0.3	ABPE= 8.35%	[79]
Pillar TiO ₂	1 M NaOH/ 0.5 M H ₂ SO ₄	0.2	UV light	N/A	37 μ mol/8h	[100]
Vis-WO ₃ /Vis-TiO ₂	0.05 M NaOH/ 0.025 M H ₂ SO ₄	2	UV light	N/A	39 μ mol/8h	[85]
Vis-WO ₃ /Vis-TiO ₂	1 M NaOH/ 0.5 M H ₂ SO ₄	2	AM 1.5	N/A	6 μ mol/8h	[85]
SrTiO ₃	9.5 M NaOH	0.25	Argon ion laser (351 nm)	N/A	11%	[77,101]
GaInP ₂ /GaAs	2 M NaOH	0.5	75 W Xe lamp	N/A	ABPE= 16.5%	[102]
InGaP/GaAs/Ge	2 M NaOH	2	AM 1.5	N/A	440 μ mol/8h	[81]
p- GaAs / <i>n</i> -GaAs/p-GaInP ₂ /	3 M H ₂ SO ₄	0.2	75 W Tungsten halogen lamp	0.3	ABPE= 12.4%	[80]

2.2 Photoreforming

Photoreforming (PR) has emerged as one of the most promising approach to utilize the low valued organic products i.e. municipality or agricultural waste (biopolymers) & plastics (synthetic polymers) to carbon neutral H_2 fuel and other value-added organic chemical products ^[103–105]. The direct photoreforming of raw organic and plastics waste will help in achieving the goals to maintain sustainable environment. At the same time, it will provide carbon neutral energy (H_2 fuel) from renewable source as an alternative to the conventional fossil fuels that are depleting and contributing to the global warming ^[71,106].

The whole PR process involves the following steps on the surface of semiconductor based photocatalyst: (i) absorption of photon, (ii) separation of charges and (iii) utilization of charges for the redox reactions to produce H_2 fuel and organic fine chemicals and (iv) photocatalyst surface activation recyclability. The overall PR processes is depicted in Figure 2 and discussed in the following section.

2.2.1 Absorption of Photon:

In the first step of PR process, photon absorption occurs on the surface of the photocatalyst that results in charges ($e^- - h^+$ pair) for the photoredox reactions ^[107]. A photocatalyst used is semiconductor material in which fully occupied valence energy band (VB) are separated from unoccupied energy band called conduction band (CB) that defines the band gap energy with a magnitude (E_g) starting from 1.0 eV to 4.0 eV ^[108,109]. When a light in the form of photons having energies equal or more than band gap (E_g) energy is irradiated on the surface of the semiconductor material, the electrons from the VB are excited to CB, leaving a vacancy in the form of hole (h^+) behind in the VB ^[106,108,110]. In simple words,

light having sufficient energy allows a semiconductor to behave like a conductor, which have mobile charge carriers taking part in chemical reactions. Semiconductor can be n-type (electron as their majority charge carriers) or p-type (hole as their majority charge carriers) ^[109,111]. On the other hand, band gap of semiconductor impacts the efficiency of light absorption and excitation of charges, therefore it can be either direct or indirect bandgap ^[112,113]. In direct band gap semiconductors such as CdS, carbon nitrides (CN_x) and rutile TiO₂, the momentum of an electron present in the VB similar to that of electron in the CB, therefore photo excitation occurs readily, and the photon absorption coefficients of the mentioned materials are normally high energy ^[113–117]. But in indirect band gap semiconductors such as Si or anatase TiO₂, the involvement of the electron in changing its momentum take place, as a result the excitation of electron from VB to CB of semiconductor occurs due to the interactive vibration of quantized lattice known as phonon. This multi-body excitation have lesser chances than direct transition and usually exhibited lower absorption coefficient and less effective photo-excitation ^[106,111–113]. Generally, the semiconductor materials having indirect band gap are exploited in energy harvesting or conversion applications ^[118]. However, due to poor optoelectronic features of most materials gives low optical conversion performance ^[119]. Therefore, wide range of strategies have been recently developed to increase the efficiency through doping or alloying, to enhance their optoelectronic properties by changing the band gap energy ^[120]. A key challenge in this regard is to investigate effective strategies to substantially improve optical transitions at band gap without sacrificing its intrinsic nature. The most efficient strategies until now is the nanostructure engineering or surface modifications ^[118,119].

2.2.2 Separation of Charges:

When the sunlight irradiation excites the charge carrier, they must be separated and transported onto the surface of the photocatalyst. While the electrostatic interaction behind the solar induced excited e^- - h^+ pair should be overcome first to recombine it ^[111]. The typical binding energies of semiconductor materials vary from 0.001 eV to 1 eV, depending on the type of semiconducting material. Once the e^- - h^+ have been separated, they can migrate to the photocatalyst surface. The usual gap that a charge carrier can travel before recombining with another carrier, or diffusion length, depends on the diffusion coefficient and lifetime of charge carriers within a given semiconductor ^[121].

Typically, the formation of semiconductor materials in the nanosized regime such as nanocomposites consist of multiphase or multicomponent heterojunctions is a very efficient strategy to engineer highly active photocatalytic systems ^[122]. There are several approaches developed in the recent past to inhibit the charge carriers recombination in most of the heterogeneous photocatalysts ^[123]. One prominent strategy is the decoration of semiconducting materials with metal nanoparticles ^[124]. In most cases, the fermi energy levels of the metal nanoparticles used are lower than that of the photocatalyst, facilitating electron transfer from photocatalyst to the metal using Schottky contact. The noble metals such as Pt, Au, Ag or Rh based metal or alloy nanoparticles are mostly used for charge separation ^[124,125]. This is because of their high catalytic efficiency. However, high cost and natural abundance limit their use for large scale appliance. Therefore naturally abundant or cost effective elements such as Co, Ni based nanoparticles were also explored recently ^[126,127]. These nanoparticles act as co-catalyst as electron reservoir or sink specially to separate electrons from photoexcited holes in the VB of photocatalyst

materials. In this process, these materials can also act as a better active site for the reduction of proton i.e., holes to generate H₂ fuel. Besides metal or alloy nanomaterials, metal oxides based nanoparticles have also been explored for charge carrier separation ^[128]. Another key approach to minimize the recombination of photoexcited electrons and holes is the formation of nanocomposite of photocatalyst semiconductors with carbon based materials especially graphene or its assemblies other conjugated nanomaterials ^[129]. Due to the high number of electron mobility in these conjugated frameworks, the photoexcited electron easily transferred from the CB of semiconductor to graphene or other conjugated frameworks and can be efficiently separated from photocatalyst surface ^[130].

However, once e⁻ or h⁺ becomes trapped in defects, it did not diffuse onto the surface of the photocatalyst, or fail to take part in a catalytic reaction and ultimately recombine ^[111]. The lifetimes for the charge carrier and recombination are almost similar and usually takes place on picosecond to nanosecond timescale. This makes charge separation or recombination a key factor in the efficiency of overall PR process ^[113]. Ultimately, the light induced excited charge carriers that have managed to diffuse to the surface of semiconductor, can be utilized for further redox reactions ^[106].

2.2.3 Utilization of Charge Carriers in Redox Reaction

(a) Involvement of Electrons in the Evolution of H₂:

In the PR process, electrons take part in the generation of H₂ fuel. Because the CB of the semiconductor to which the electrons have been excited required to have a greater negative potential than the reduction potential of H⁺ to H₂ (0 V vs. reversible hydrogen electrode, RHE) ^[112,114]. According to Sabatier principle, the active site on the surface of

photocatalyst should also have a low hydrogen binding energy to adsorb protons from electrolyte, whereas high enough to allow the desorption of the produced i.e. H₂ gas molecule ^[106]. However, some of the semiconductors have their own capability to reduce proton, therefore in most water splitting studies and PR process, a metal co-catalyst (Pd, Pt, Ni, Cu, Au or Co etc.) is used for effective H₂ production. The purpose of these co-catalysts is to efficiently facilitate charge separation and transport these charges through the formation of Schottky barrier. The most important, it can also act as an active site for the reduction of proton ^[106,114].

(b) Oxidation of Substrate:

In the PR process, after effective charge separation, holes (h⁺) move to participate in the oxidation of the substrate usually biomass or plastic. This involves both direct and indirect routes. Typically, semiconductors having strong oxidation potential of VB, normally greater than the +2.7 V vs RHE, like TiO₂ can generate very reactive hydroxyl (OH[•]) radicals. Then these OH[•] radicals can oxidize substrates in aqueous solution on or near to the photocatalyst surface, depending on the surface bound or free OH[•] radicals ^[111]. On the other hand, oxidation can also take place through direct migration of the holes to the surface of the photocatalyst and there reacts with the substrate adsorbed onto the surface of the photocatalyst. The VB of the semiconducting photocatalyst must have positive oxidation potential than the substrate to a particular product (substrate-dependent). Irrespective of direct or indirect nature of chemical reaction, oxidation often yields both a range of intermediate products (fine chemicals) and CO₂ ^[106,112,114].

2.2.4 Photocatalyst Activation:

During the PR process, sometime intermediate products could adsorb to the surface of the photocatalyst. This results in the decrease of the photoactivity of the photocatalyst or in some of the cases, it does not react further. This process is called deactivation of the photocatalysts. The typical deactivating molecules are carbonates and carboxylate species produced during the PR process. The process to regenerate the surface of the photocatalyst for better recyclability is called photocatalyst activation. the activation of the photocatalyst can be performed by continuous flushing the system with inert gas such as N_2 or Ar gas flow system [106,112].

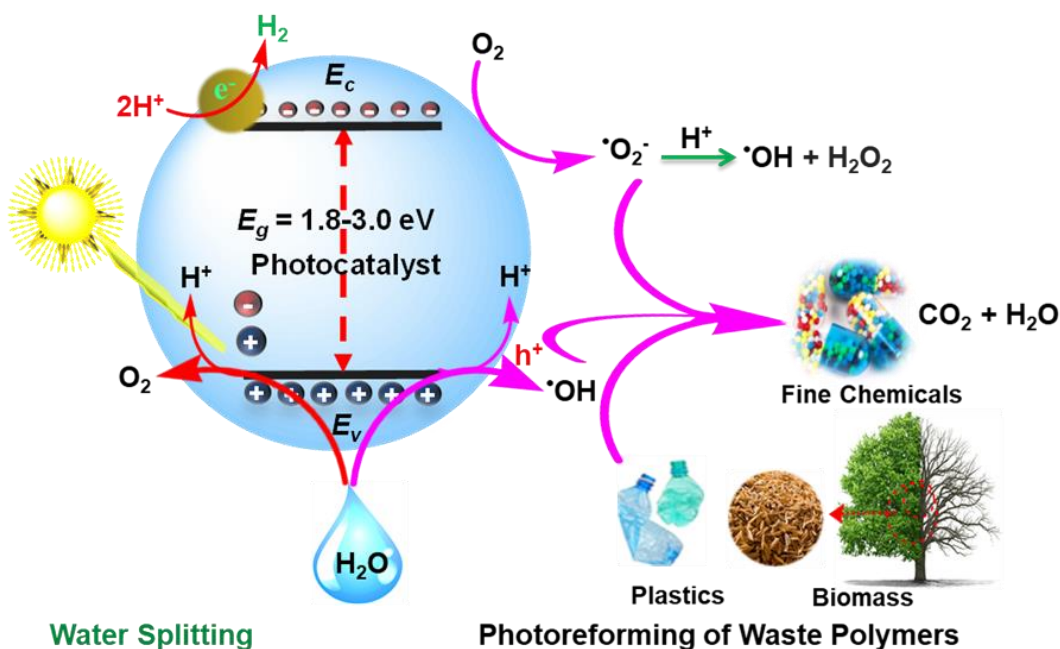


Figure 2. 2: Over-all mechanistic scheme of PR process which involve mainly five steps (1)Absorption of photon (2) separation of charges (3) Involvement of electrons in the evolution of H_2 (4) Oxidation of Substrate (5) Photocatalyst deactivation .Also showing comparison with water splitting

Photoreforming (PR) seems to be a new research roadmap for conversion of raw biomass to fuel and valuable chemicals, which is specifically environmentally benevolent,

strategically simple and emerging solar driven approach ^[131]. Plastic in due course initiates to break down when immersed in water and exposed to sunlight. However, this method can take numerous years. The process was expedited using photo-active material that accelerate breakdown of waste plastics and H₂O to sustainable H₂ fuel and valuable products. To photoreform the waste plastics, scientists innovate a photocatalyst made of low-cost cadmium sulfide semiconductor (CdS QDs) used under alkaline aqueous solution. The optimum size of the QDs that could provide high surface area and best efficiency must be below 5 nm ^[132].

In the first time in 1981 photoreforming (Table 2.3) of different plants extract was examine by T. Kawai and T. Sakata using Pt/TiO₂ as a photocatalyst. He achieved the similar rates of H₂ production for pure cellulose (0.004-0.018 mmol_{H2} g_{cat}⁻¹h⁻¹) using the same photocatalyst ^[133]. Enhanced performance of the photoreforming process was achieved in the basic solution, or upon mixing of RuO₂ as OER catalyst (0.058 mmol_{H2} g_{cat}⁻¹h⁻¹) and at elevated temperature (0.061 mmol_{H2} g_{cat}⁻¹h⁻¹) ^[134].

The solar energy promoted the reforming of cellulose from plant material using Pt/TiO₂ photocatalyst dispersed in H₂O at rates up to (0.095 mmol_{H2} g_{cat}⁻¹h⁻¹) ^[135]. Hydrogen production yield varies and depends on the nature of biomass waste. However, under similar set of conditions, aquatic plants show higher yields and rates then terrestrial plants owing to their lesser lignin gradient (3.3 mmol_{H2} g_{cat}⁻¹h⁻¹) ^[136]. The nature of the catalyst plays crucial role in the overall process. As an example, CdS/CdO_x photocatalyst showed high photoreforming using sunlight than other conventionally used photoactive materials. Wood, Bagasse, sawdust and grass offered Hydrogen generation yields and rates up to (5.3

mmol_{H2} g_{cat}⁻¹h⁻¹). Concentration of the alkaline solution enhanced the photocatalyst stability and biomass solubility ^[114].

Recently nanostructured semiconductor quantum dots (QDs) based materials attracted enormous attention due to their quantum yield, and photostability in various energy-based device applications ^[36,137]. Due to considerable increase in CO₂ emission, recently researchers from most of the developed countries shifted their interest on the alternative energy resources (hydrogen fuel), which is-cheaper, achievable and environmentally friendly ^[138]. One of such approaches is to PR for this purpose.

Table 2. 3. Certain examples of PR of waste plastic and raw lignocellulose.

Photocatalysts	Substrate	Conditions	Light source	Rate [mmol _{H2} g _{cat} ⁻¹ h ⁻¹]	Yield [mmol _{H2} g _{sub} ⁻¹]	EQE [%]	Ref
CdS/CdO _x	Plastic (PLA, PET, PUR)	10 M NaOH	AM 1.5G	4.13	2.17	5.15	^[132]
CdS/CdO _x	Beechwood	10 M KOH, 25 °C	AM 1.5G	5.0	1.3	n/a	^[114]
Co/CdS/CdO _x	wooden branch	10 M KOH, 25 °C	AM 1.5	5.31	0.49 (24 h)	n/a	^[114]
0.5 % Pt/TiO ₂	rice husk	H ₂ O	sunlight	0.095	n/a	n/a	^[135]
5 % Pt/TiO ₂	rice plant	5 M KOH	Xe	0.058	1.75 (10 h)	1.3	^[136]
4 % Pt/TiO ₂	cherry wood	5 M KOH	Xe	0.049	0.296 (10 h)	1.1	^[133]
4 % Pt/TiO ₂	Dutch clover	5 M KOH	Xe	0.047	0.284 (10 h)	1.1	^[133]

0.5 % Pt/TiO ₂	alfalfa stems	H ₂ O	UV	0.100	n/a	n/a	[135]
Co/CdS/CdO _x	sawdust	10 M KOH, 25 °C	AM 1.5	0.75	0.070 (24 h)	n/a	[114]
5 % Pt/TiO ₂	turf	5 M KOH	Xe	0.033	0.98 (10 h)	0.74	[136]
0.2 % Pt/TiO ₂	fescue grass	H ₂ O, 60 °C	Xe	0.061	0.076 (3 h)	n/a	[134]
4 % Pt/TiO ₂	goldenrod	5 M KOH	Xe	0.018	0.11 (10 h)	0.4	[136]
Co/CdS/CdO _x	bagasse	10 M KOH, 25 °C	AM 1.5	0.37	0.034 (24 h)	n/a	[114]
4 % Pt/TiO ₂	wakame seaweed	5 M KOH	Xe	0.055	0.332 (10 h)	1.2	[114]
4 % Pt/TiO ₂	water hyacinth	5 M KOH	Xe	0.034	0.202 (10 h)	0.7	[114]
5 % Pt/TiO ₂	laver	5 M KOH	Xe	0.111	3.32 (10 h)	3.3	[136]
Co/CdS/CdO _x	grass	10 M KOH, 25 °C	AM 1.5	1.0	0.093 (24 h)	n/a	[114]
5 % Pt/TiO ₂	chlorellaalgae	5 M KOH	Xe	0.090	2.7 (10 h)	2.0	[136]

2.3 Perovskite Solar Cells

Perovskite solar cells are a type of solar energy conversion devices that involves materials having a specific ABX₃ type of crystal structure ^[139]. Perovskite has two main categories; (i) halo alkane perovskite and (ii) organic/inorganic hybrid perovskite with ABX₃ crystal

structure ^[140]. In the formula ABX_3 , A is ascribed to the large cations of organic or inorganic such as methylammonium (MA^+ , $CH_3NH_3^+$) or formamidinium (FA^+ , $CH(NH_2)_2^+$) located in the vertex of *face centered cubic* (FCC) lattice ^[139]. In general formula, B corresponds to a small inorganic cation such as Pb^{2+} , Cu^{2+} , Sn^{2+} etc. whereas X_3 is attributed to ions which have the capability of bonding A and B such as I^- , Br^- and Cl^- etc. as shown in Figure 2.3b ^[139].

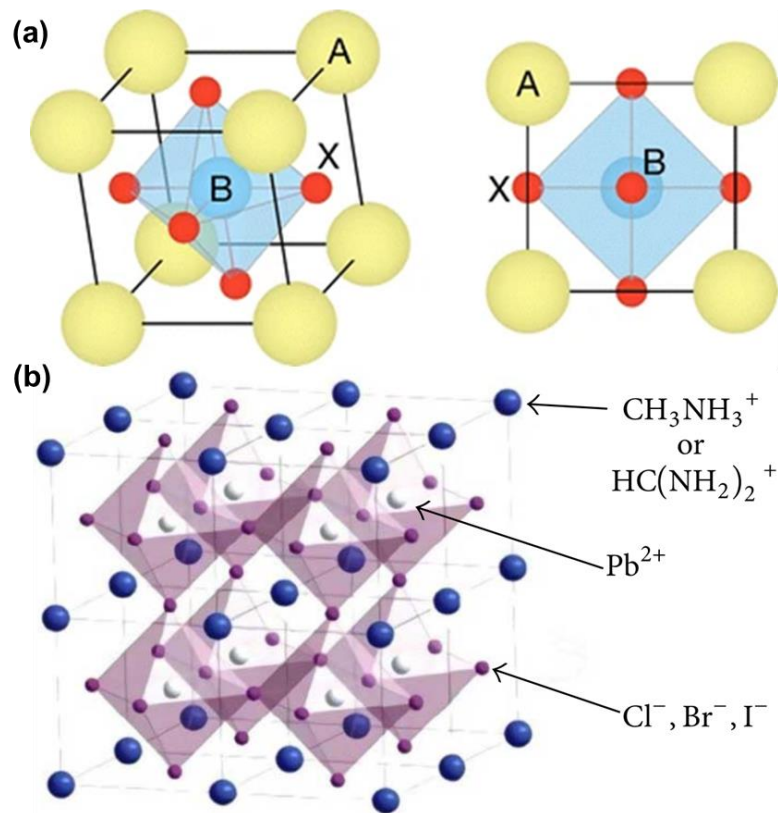


Figure 2. 3 (a) Two views of the cubic perovskite crystal structure for ABX_3 compounds. Atoms of type A (in yellow) are positioned at the cube corners, B atoms (in blue) at the cube center, and X atoms (in red) at cube faces. The B atoms are octahedrally coordinated by X, whereas the A atoms are 12-fold coordinated by X ^[139]. (b) Typical perovskite cubic lattice structure ^[140].

In the recent past, there is an immense interest to develop lead halide perovskite solar cells due to its ease of processing techniques and economically viable compared with typical traditional silicon solar cells ^[45,141]. In particular, lead -iodine perovskite ($CH_3NH_3PbI_3$) having a direct bandgap of 1.5 eV are considered one of the ideal sunlight absorbers due

to its high extinction coefficient, low binding energy of exciton, excellent charge carrier mobility, simple processing ability, and low cost ^[141,142]. The photon conversion efficiency of perovskite solar cells have reached over 25% and it is predicted that it could further increase by optimizing the parameters of the devices and developing new materials in future ^[143,144].

2.3.1 Structure of Perovskite Solar Cell:

The architecture of PSC devices consists of three key layers. The main layer is the perovskite material based absorber layer which is sandwich between electro transport layer (ETL) and hole transport layer (HTL) ^[145]. These three layers are packed in between two electrodes i.e. front contact and back contact as shown in the Figure 2.4 ^[141]. The perovskite materials absorb the sun light and generate $e^- - h^+$ pairs. The ETL and HTL permit the flow of specific and selective numbers of charge carriers to their corresponding electrodes. Beside the light absorber, HTL and ETL, there is a back contact layer and front contact layer ^[146,147]. The ETL is mostly fabricated by the materials such as cadmium sulfide (CdS), zinc oxide (ZnO), ^[148] zinc selenide (ZnSe), titanium dioxide (TiO₂), ^[149] Tin oxide (SnO₂), ^[150] cerium oxide (CeO_x), zinc oxy sulfide (ZnOS), [6,6]-phenyl C61-butyric acid methyl ester (PC₆₁BM) ^[151], ICBA ^[152] as shown in Figure 2.4 and Table 2.4 ^[153]. The HTL are mostly made of 2, 2', 7, 7'-tetrakis [N,N-di(4-methoxyphenyl-amino)- 9, 9' -spirobifluorene (Spiro-OMeTAD) which are the benchmark HTL material for PSC. However, the high cost of these benchmark HTL materials limits the utilization on large scale. Therefore, there is still room to explore new types of HTLs to replace the above mentioned material with that of cost competitive, enhanced stability and high reproducibility ^[145,154]. In this contribution, both inorganic or organic based HTL materials

are available ^[141]. The common inorganic HTL used materials are nickel oxide (NiO),^[155,156] cuprous thiocyanate (CuSCN),^[157] cuprous oxide (Cu₂O)^[158] whereas the most common organic based HTL materials are spiro-OMeTAD,^[159] poly [2,5-bis (3-tetradecylthiophene-2-yl) thieno [3, 2-b] thiophene (D-PBTTT-14), poly (3-hexylthiophene-2, 5-diyl) (P₃HT) and poly (3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS)^[160], PTAA ^[161,162], reduced graphene oxides (rGO),^[163] C₆₀^[164] etc. Mostly, gold (Au) is used as a back-contact layer. Due to its high cost, many efforts are made to replace the Au with inexpensive back contact layer such as Ni ^[141,153,154,165].

Three common types of PSCs systems have been developed, namely mesoporous PSCs (n-i-p), planar PSCs (n-i-p) and inverted planar PSCs (p-i-n) ^[145]. The architecture of all three types of PSCs are depicted in Figure 2.4b below.

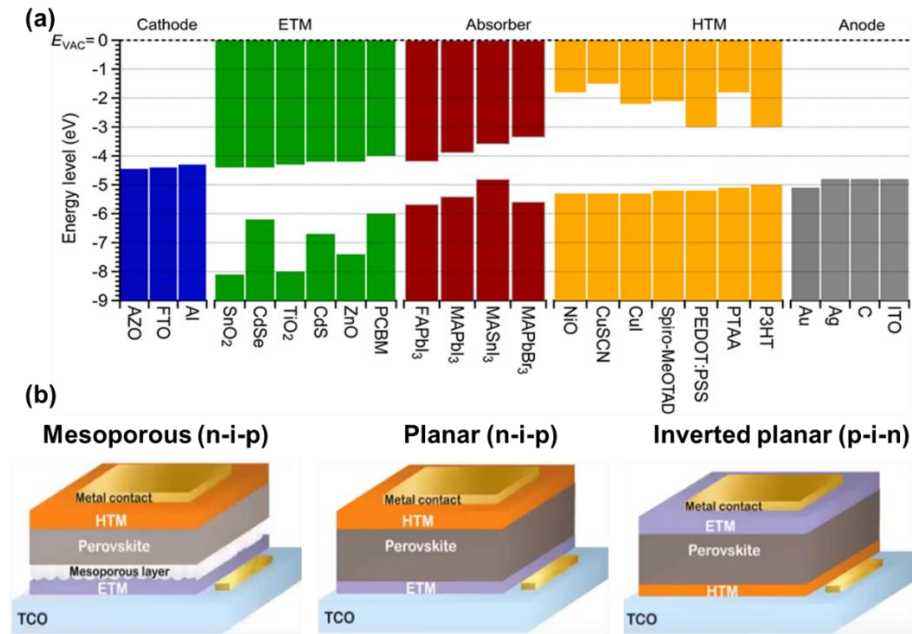


Figure 2. 4 (a) Illustration of chart showing energy levels of materials from left to right for a corresponding cathode, ETMs (n-type), perovskite a light absorber, HTMs (p-type) and anode materials ^[153]. (b) Graphic illustrations of mesoporous, planar and inverted planar PSCs ^[154].

2.3.2 Working Principle of Perovskite Solar Cell

Generally, solar cell is recognized as the key element in solar energy conversion devices because it is made of semiconductors materials ^[140]. When the solar cell device is exposed to solar irradiations, it absorb the solar energy greater than bandgap of semiconductor materials. The absorbed light energy have sufficient potential for excitation of electrons that causes transportation of electrons and holes to their opposite electrodes ^[143]. Due to variation in the binding energy of perovskite and excitons, the former can form free charge carriers (e^- - h^+) to generate current density or again recombination into excitons. The excited e^- - h^+ pairs created in the field region and separated under the field effect of the region ^[166,167]. Subsequently, electron can start moving towards the n-side and holes towards the p-side. However, some of the electrons and holes gather in the boundaries (n-side and p-side) of field region and neutralizing fragment of them using sequent, while the remaining e^- - h^+ move in the outer circuit, to the load ^[45]. The free charge carriers e^- - h^+ are collected or accumulated at the same time by ETL and HTL respectively. These moves by the outer metal electrode and transparent conductive oxide (TCO) sequentially ^[168]. This process on the other hand, not only offset the effect of the potential energy barrier by electrostatic field but also causes the n-region with negative charge and p-region to have positive charge. Thus, the electromotive force is produced between the two regions ^[141]. In the last step, the flow of current starts when circuit loop is closed. This complete process is schematically shown in Figure 2.5. It is found that the lifetime of perovskites and distance of charge carriers' diffusions are longer due to a smaller number of probabilities in charge carriers e^- - h^+ recombination and higher mobility such as in MAPbI₃ perovskite the carrier diffusion distance is at least around 100 nm and higher than 1 micrometer

(MAPbI₃-xCl). As a result, this longer diffusion distance of carrier and higher lifetime are the reasons for excellent performance of PSCs in solar energy conversion ^[143].

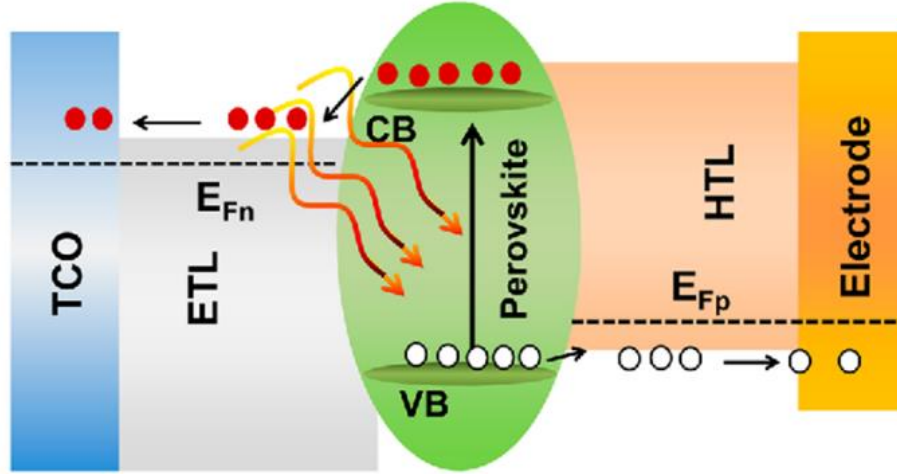


Figure 2. 5: Schematic diagram for charge transport dynamics in the solar cell under solar light illuminations ^[143].

Table 2. 4. Some representative PSC's performance of various HTM and ETM pairs and device structures.

Classification	Charge Transfer Materials	Device type	Device Structure	Stability	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE	Ref
Organic HTL	Spiro-OMeTAD	Mesoscopic/ Planar n-i-p	FTO/ SnO ₂ / FA _{0.83} MA _{0.17} Pb(I _{0.87} Br _{0.17}) ₃ /SW NT/Spiro-OMeTAD /Au	168 h	22.9	1.12	73	18.8 %	[159,169–172]
	PTAA	Planar n-i-p	ITO/PTAA /SSG-(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /	20h	21.86	1.175	0.814	20.9 %	[162,173]

			PCBM/C ₆₀ / BCP/Cu						
	PEDOT:PS S	Mesoscopic/ Planar n-i-p	ITO/ PEDOT:PSS / MAPbI ₃ /PCBM/Ca/Al	8.3 min	23.51	1.0 3	0.8 3	20.1 %	[160,1 74– 176]
Inorganic HTL	NiOx	Planar n-i-p	ITO/Cu-NiO _x /MAPbI ₃ - xCl _x /PCBM/ZrAcac/ Ag	----	23.07	1.1 2	0.7 7	20.5 %	[155,1 56,17 7]
	CuOx	Planar n-i-p/p-i-n	ITO/ CuO_x / MAPbI ₃ - xCl _x /PCBM/C ₆₀ /BCP/ Ag	-----	22.5	1.1 1	0.7 5	19%	[158,1 78]
	CuSCN	Mesoscopic/ Planar n-i-p/p-i-n	ITO/ CuSCN /MAPbI ₃ / PCBM/Bis-C ₆₀ /Ag	300h	19.6	1.0 7	0.7 4	16%	[157,1 79– 181]
	rGO		ITO/ rGO / PTAA/MA PbI ₃ /PCBM/BCP/Ag	500h	20.3	1.0 9	0.7 7	17.2 %	[163,1 82– 184]
Organic ETL	C ₆₀	Planar n-i-p/p-i-n	ITO/PTAA/ SSG-(FAPbI ₃) _{0.8} ₅ (MAPbBr ₃) _{0.15} / PCBM/C ₆₀ / BCP/Cu	20h	21.86	1.1 75	0.8 14	20.9 %	[164]
	PCBM	Planar n-i-p	FTO/NiO _x / SP3 passivated MAPbI ₃ / P	30 days	22.69	1.1 46	0.7 8	20.4 %	[151,1 85– 188]

			CBM/BCP /Ag						
	ICBA		ITO/PTAA /(FA _{0.83} MA 0.17) _{0.95} CS _{0.05} Pb(I _{0.6} Br _{0.4}) 3/ ICBA/C₆₀/ BCP/Cu	720 h	19.7	1.2 0	0.7 7	18.3 %	[152,1 89,19 0]
Inorgani c ETL	TiO ₂	Mesosc opic/ Planar n-i-p	FTO/NiO _x / FA _{1-x} MA _x PbI ₃ /PCB M/ TiO_x /A g	500h	23.09	1.1 0	0.8 1	20.65 %	[149,1 91– 194]
	SnO ₂	Planar n-i-p	ITO/NiO/ MAPbI ₃ /C ₆ 0/ SnO₂ nanopartic les/Ag	30 days	21.8	1.1 2	0.7 7	18.8 %	[150,1 95– 198]
	ZnO		ITO/NiO _x / MAPbI ₃ / Z nO/Al	60 days	21	1.0 1	0.7 6	16.1 %	[148,1 99– 201]

2.4 Conclusion and Future Perspective

The existing demand for more eco-friendly and efficient energy conversion systems or technologies are expanding rapidly, especially in counter to the current global warming situation and depletion of natural resources. As a result, the performance of the renewable, carbon neutral and future sustainable solar conversion research have paramount importance in both the academic institutes and industry. In this regard, in present literature review, we have appraised the basic mechanistic insight of three emerging solar to chemical fuel or electricity technologies: (i) PEC water splitting, (ii) photoreforming, and (iii) organic photovoltaics or perovskite solar cell. These technologies are leading from the front for

renewable energy viewpoint but still there are couple of challenges that should be considered in future research directions. A main challenge in the solar conversion technologies is the insufficient utilization of solar spectrum which results in the loss of more than half of the solar energy as waste heat. The future research should focus on the design and development of cost effective and green photocatalysts capable of harvesting the solar light in the visible portion of solar spectrum. Also, there is still a lot of room to improve the potential efficiency by improving the interfaces through mechanistic insight of the process and photoactive materials energy level. For this purpose, engineering the optical and electronic properties of semiconductor materials used as photocatalyst is required. This can be achieved by manipulating the composition, size, morphology and crystallinity of the photoactive materials.

In some of the technologies used for the solar energy conversion to chemical fuel such as photocatalytic or PEC water splitting and photoreforming, the hole in the VB of photocatalyst mediated oxidation reactions are the rate determining step. Usually, the poor efficiency of the solar to H₂ fuel is related to the mismatch among the sunlight induced hole generation, internal quantum efficiency and the apparent quantum yield of H₂ fuel. In most cases this leftover of photon generated holes are totally unwanted and yet unavoidable. In this regard, enough progress has been made that is well documented in literature. However, we are still far from the expected level of inventiveness to seal with linked issues of hole residue and substantial effects that have placed one of the ultimate bottlenecks in achieving the expected high solar to H₂ fuel efficiency. On the other hand, in the development of solar to electricity technology such as PSCs, the photogenerated holes serves mainly three purposes; firstly, in the conventional PSCs it is deposited prior to the Au electrode to avoid

the direct contact or connection of the metal electrode with the mesoporous layer of perovskite. This increases the selective contact to reduce the recombination which results in the enhanced open circuit voltage and increase in the efficiency of luminescence. Secondly, The HTL enhances the internal quantum efficiency of unbiased applied voltage and increases the wavelength of photon illumination through reducing losses of charges. Thirdly, the HTL increases reflectivity of Au electrode, by smoothing the mesoporous perovskite layer interface and further allowing the second path of incident light through absorption. These combined effects leads to increase in the short circuit current density [202].

Therefore, it is very important to focus on the conceptual and contextual understanding of the kinetics and dynamics of the solar induced generated holes. Also, future research should concentrate on interfaces to improve the redox reactions with better charge separation in these solar energy harvesting technologies. The central motives at the back of this study and concerns of the wasted holes need examination and the investigation of the mechanistic depth for these solar harvesting approaches to enhance the overall efficiencies of the solar fuel conversion.

CHAPTER 3

Bandgap Engineering of Melon using Highly Reduced Graphene Oxide for Enhanced PEC Hydrogen Evolution

3.1 Introduction

Scientists and technologists are constantly exploring renewable energy resources to solve the problems of global energy supply and environmental sustainability.^[203] Among these renewable energy options available, H₂ fuel (green hydrogen) produced from water using solar energy is leading from the front due to its natural abundance and environmentally friendly nature.^[204] Therefore, the development of efficient, environmentally friendly and sustainable technologies for the production of green H₂ fuel is inevitable.^[205] To this end, photocatalytic,^[206] photoelectrochemical^[207] and photoreforming production of green H₂ fuel from water splitting using solar energy is being investigated.^[208] One of the most important research areas for these technologies is the synthesis of photocatalysts that can (i) utilize the maximum solar spectrum (especially in the visible range of sunlight), (ii) be chemically stable, (iii) be inexpensive, and (iv) efficiently separate photoexcited charge carriers.^[209] Conventionally, transition metal oxides/-chalcogenides in combination with noble metals are first-rate photocatalysts.^[28,210] Disadvantages of these photocatalysts, however, are their insufficient chemical stability under the given reaction conditions, their insufficient absorption of sunlight in the optical spectral range, the high demand for precious metals such as platinum and their high cost.^[210] These factors preclude

commercialization. For a practical implementation, metal-free photocatalysts would therefore be much more favorable.

Polymeric carbon nitride based materials have proven successful in various photocatalytic applications.^[211] Their optoelectronic properties can be influenced by "proper" synthesis. Moreover, they are affordable and available in nature in sufficient quantities. In addition, they have excellent chemical stability under different pH conditions.^[212] Graphitic carbon nitride (g-C₃N₄) has been explored for different photocatalytic applications in the past. Melon (an uncondensed form of g-C₃N₄), another carbon nitride-based material attracted attention recently (shown in Figure S.1).^[213] Conventionally, melon has been used as a precursor for the synthesis of graphitic carbon nitride (g-C₃N₄) since its discovery by Berzelius in 1830s.^[214] It also comprises tri-s-triazine subunits linked through a planar tertiary amino group with layered structure,^[209,215] and it is akin to g-C₃N₄ with respect to its composition and basic skeleton.^[216] However, it differs from g-C₃N₄ due the presence of –NH₂ groups on the surface. NH₂ groups on the surface can improve the physicochemical properties such as solubility, stability of hole states, and localization of excitons within each heptazine unit of melon.^[217] Therefore, melon may prove to be a better choice over g-C₃N₄, its structural counterpart, for photocatalytic applications such as water splitting. In addition, the NH₂ groups on the surface could provide reactive centres for the preparation of composites through covalent tailoring or weak intermolecular interactions with other functional molecules.^[217,218]

Often one attempts to overcome shortcomings of metal-free carbon nitride photocatalysts by substitution ("doping") with nonmetals,^[219] copolymerization,^[220,221] or with the help of hybrid heterostructures or nanocomposites.^[222,223] Nanocomposites with a conductive

material are an intriguing option to improve the charge separation efficiency.^[224] Graphene oxide, reduced graphene oxide, or doped graphene-based materials are intuitive choices due to their inherent electronic properties and structural (also 2D) compatibility.^[225,226] As an example, Dai et al. showed that the inclusion of graphene oxide into carbon nitride films resulted in an enhanced photocurrent and photocatalytic efficiency.^[227] They proposed the enhancement to be due to better charge separation. In other reports, the inclusion of graphene oxide with g-C₃N₄ led to better efficiencies for the reduction of carbon dioxide to methane,^[228] in the oxygen evolution reaction (OER)^[229] for hydrogen generation^[230] and pollutant degradation.^[231]

Considering these criteria and the structural and functional characteristics of melon, we explored the use of melon in combination with HRG in photoelectrochemical (PEC) water splitting. We performed experimental PEC studies and verified the mechanism using advanced computational methods to determine whether there is strong electron coupling at the interface between the optically active metal-free organic semiconductor melon and the conductive HRG. We also calculated the role of the remaining oxygen functional groups on HRG. The inclusion of HRG into melon resulted in a decrease of the bandgap of melon and an improvement of its optical properties. This explains the significance of including HRG in melon in the charge redistribution at the interface between melon and HRG sheets. In addition, we tested the role of the HRG amount by preparing different HRG@melon nanocomposites with different HRG/melon ratios and tested the photoelectrochemical water splitting in HER reactions.

3.2 Materials and Methods

3.2.1 Materials

Graphite powder (99.999%,-200 mesh) was purchased from Alfa Aesar, sulfuric acid (H_2SO_4) (98%), potassium permanganate (KMnO_4) (99%), sodium nitrate (NaNO_3) (99%), hydrogen peroxide (H_2O_2) (30 wt%), hydrazine hydrate (28 %), and melamine were purchased from Sigma-Aldrich.

3.2.2 Preparation of Graphene Oxide (GO)

GO was prepared using a modified Hummer's approach.^[232] Briefly, 0.5 g of graphite powder and 0.5 g of sodium nitrate (NaNO_3) were added to a flask containing 20 mL of H_2SO_4 . The mixture was stirred for 15 minutes in an ice bath, followed by addition of 3.0 g of KMnO_4 . This changed the color of the solution to dark green. At this point, the ice bath was replaced by an oil bath to maintain the temperature at 40 °C for 60 minutes. Heating resulted in the formation of a thick paste. To this thick paste was added 30 mL of deionized water. The stirring was continued for another 40 minutes at 95 °C. Finally, 100 mL of deionized water was added to the mixture, followed by a dropwise addition of 3 mL of H_2O_2 . After adding H_2O_2 , the color of the mixture was changed from dark brown to yellow. This yellow-coloured mixture was cooled to room temperature and washed with deionized water using filtration and centrifugation (first round with 1000 rpm for 10 minutes, followed by four rounds with each 8000 rpm for 10 minutes). The final product was dried at 100 °C *in vacuo*.

3.2.3 Preparation of Highly Reduced Graphene Oxide (HRG).

HRG was prepared as earlier reported by us.^[233] Briefly, (shown in figure 3.1) 0.1 g of the synthesized GO were dispersed in 30 mL of deionized water by ultrasonication for 40 minutes. To the resulting suspension was added 3 mL of 55% hydrazine hydrate at 100 °C and stirred at this temperature overnight. The solution was cooled to room temperature and washed with deionized water, separated by filtration followed by centrifugation (first round at 1000 rpm for 10 minutes, followed by four rounds each at 8000 rpm for 10 minutes). Finally, the black powder obtained was dried *in vacuo* and used for characterization and experiments.

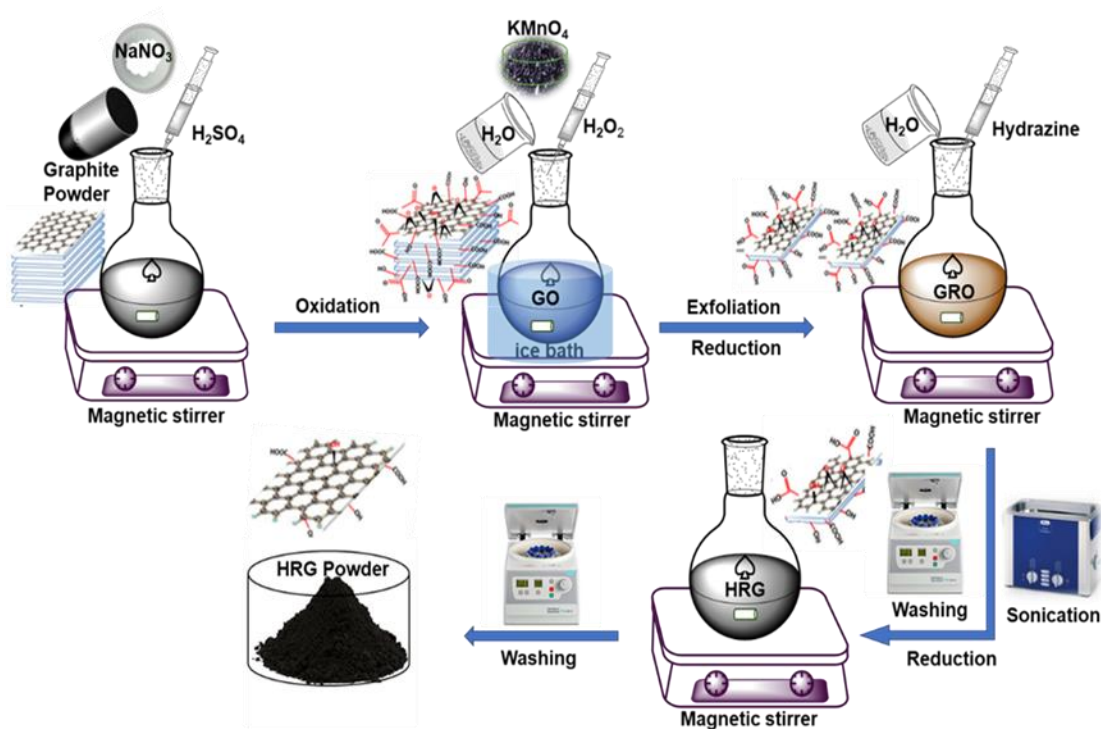


Figure 3. 1. Schematic illustration of the step by step preparation of HRG.

3.2.4 Synthesis of Melon

Melon was synthesized by pyrolysis using a horizontal tube furnace under a continuous flow of nitrogen gas. Melamine powder (2.5 g) was loaded in a ceramic boat and kept inside the quartz tube. It was heated in a horizontal tube furnace at 390 °C for the formation of melem and then at 520 °C to form melon. The temperature was controlled using programmed protocol with a ramp rate of 5 °C per minute under a constant flow of N₂ gas. The temperature was maintained at 520 °C for 4 hours. The synthesized product (melon) was cooled to room temperature under inert conditions. The product was ground to a fine powder with a mortar and a pestle.

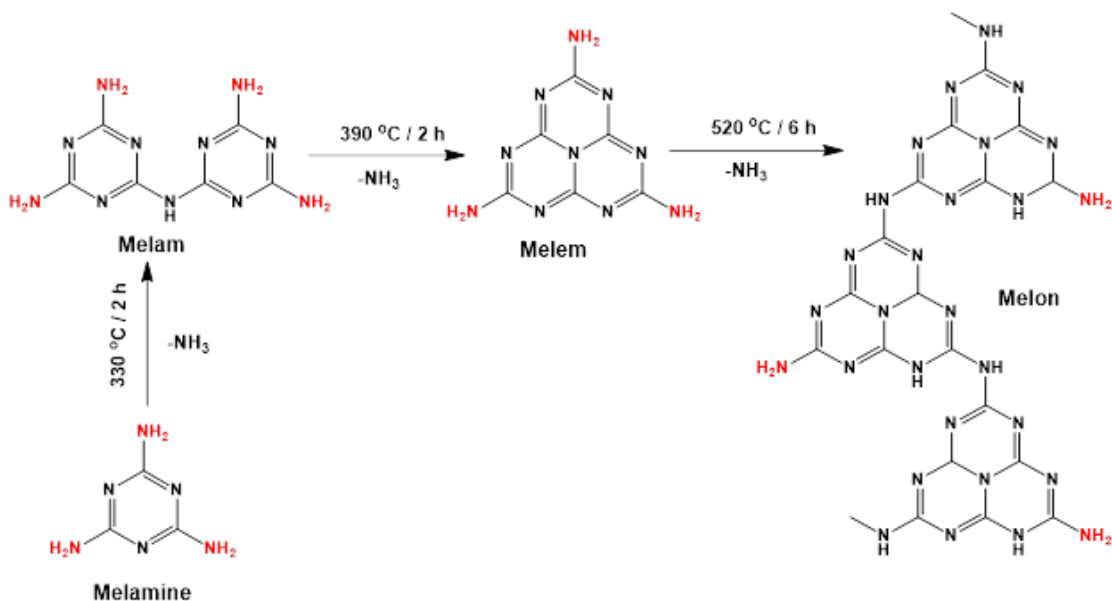


Figure 3. 2. Schematic illustration of the chemical structures of precursor material, intermediates and melon.

3.2.5 Synthesis of HRG@melon Nanocomposites

The HRG@melon nanocomposites were prepared using ultrasonic bath as depicted in Figure 3.3. A refined suspension of 0.5 g of melon in 80 mL of deionized water was

prepared using ultrasonication. Separately, 5 mg of HRG was suspended in 20 ml of water using ultrasonication for one hour. Both suspensions of melon and HRG were mixed. The mixture was further sonicated for two hours. This was named 1% HRG@melon nanocomposite. Finally, the water was removed using a rotary evaporator and the nanocomposite was dried under a vacuum. The other HRG@melon nanocomposites with names, 0.5%, 1%, 2% of HRG@melon were also prepared using the same set of conditions except for the amount of HRG calculated to finally achieve the relevant amount of HRG in nanocomposite.

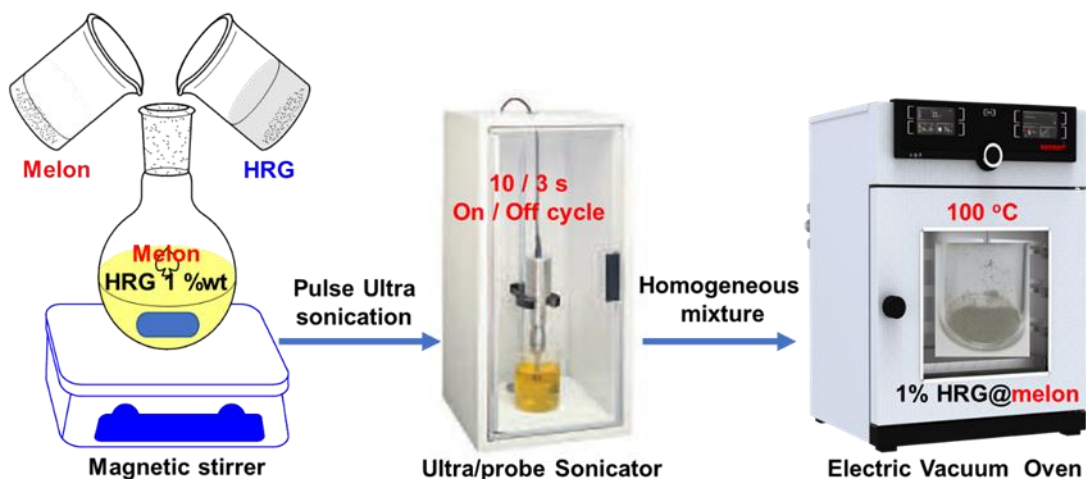


Figure 3. 3. Schematic illustration of the preparation of HRG@melon nanocomposites.

3.2.6 First-Principles Calculations

To support the experimental observation that addition of 1% HRG enhances the HER activity of melon, we used density functional theory as implemented in the Vienna ab-initio simulation package. The generalized gradient approximation of Perdew-Burke-Ernzerhof was used for the exchange-correlation functional and the damped van der Waals correction of Grimme [10] was used to describe the non-bonding interactions. To avoid interaction between the periodic slabs a 15 Å vacuum slab was added in the *c*-direction. A

$2 \times 2 \times 1$ k-mesh was used for the Brillouin zone integrations. The plane wave cutoff energy was set to 500 eV and the force convergence criterion to 0.01 eV Å⁻¹. For calculating the H adsorption and Gibbs free energies, we applied the already established procedure. We considered a HRG nano-flake passivated with H atoms and functionalized with O, OH, and/or COOH groups.

The Gibbs free energy difference of the HER is calculated as

$$\Delta G_{H^*} = E_{\text{melon}+H^*} - E_{\text{melon}} - \frac{1}{2}E_{H_2} + \Delta E_{\text{ZPE}} - T\Delta S_H,$$

where $E_{\text{Melon}+H^*}$ and E_{melon} are the total energies with and without H adsorption at the active site (*) of melon, respectively, and E_{H_2} is the total energy of a H₂ molecule in the gas phase (-6.80 eV). Moreover, ΔE_{ZPE} is the difference in the zero-point energy between a H atom adsorbed on melon and in the gas phase (H₂ molecule),

$$\Delta E_{\text{ZPE}} = E_{\text{ZPE(melon+H)}} - E_{\text{ZPE(melon)}} - \frac{1}{2}E_{\text{ZPE(H}_2)}.$$

We obtain $E_{\text{ZPE(melon+H)}} - E_{\text{ZPE(melon)}} = 0.18$ eV for H adsorption on top of both N and C, and $E_{\text{ZPE(H}_2)} = 0.28$ eV. Thus, $\Delta E_{\text{ZPE}} = 0.04$ eV. The entropy change due to the adsorption of a H atom is

$$\Delta S_H = S_{\text{melon+H}} - S_{\text{melon}} - \frac{1}{2}S_{H_2},$$

where the entropy of the adsorbed H atom is much smaller (negligible) than that of the H₂ molecule in the gas phase (130.68 J K⁻¹ mol⁻¹) at standard conditions (T = 298.15 K) [12], implying

$$\Delta S_H \approx -\frac{1}{2}S_{H_2}.$$

Thus, $T\Delta S_H = -0.20$ eV and

$$\Delta G_{H^*} = E_{\text{melon}+H^*} - E_{\text{melon}} - \frac{1}{2}E_{H_2} + 0.24 \text{ eV}.$$

3.3 Results and Discussion

The oxidation of graphite to graphene oxide (GO) followed by reduction to prepare highly reduced graphene oxide (HRG) was monitored using X-ray diffraction (XRD) and Raman spectroscopy. The diffractogram for GO resulted in a reflection at a lower Bragg angle $2\theta = 12.5^\circ$ that after reduction appeared as a broad reflection between $2\theta = 20^\circ$ and 30° , centred at 25° , indicating the removal of most of the functional oxygen containing groups (Figure S.2, black line).

The X-ray diffractogram (Figure 3.4a, red line) of as-synthesized melon showed two reflections around $2\theta = 12.32^\circ$ and 27.45° , respectively.^[234] The small reflection at $2\theta = 12.32^\circ$ corresponds to the (100) plane related to the structural motif of tri-s-triazine units, whereas the reflection centred at $2\theta = 27.45^\circ$ corresponds to the (002) plane due to the aromatic segments.^[234] The X-ray diffractogram of the 1.0% HRG@melon nanocomposite showed a very similar pattern as that of pristine melon and its reported counterpart because it constitutes the major portion of the composite.^[227]

The Raman spectrum of as-synthesized GO, RGO and HRG (Figure S.2b,) showed two well-defined bands centred at 1345 cm^{-1} (D-band) and 1585 cm^{-1} (G-band). For the D and G bands of HRG (Figure 3.4a,), there were significant variations in the intensity ratio of the D and G bands during the oxidation and reduction steps. The Raman spectra of HRG showed a higher intensity ratio of the D/G bands. This indicates that the reduction process

increases the average size of the sp^2 domains after removal of the O-containing functional groups.^[235] Raman spectra of pristine melon (Figure 3.4b, red line) showed a very broad band between 1100 cm^{-1} to 2200 cm^{-1} due to its strong fluorescent background. In the case of the HRG@melon nanocomposite, (Figure 3.4b, blue line) the broadened D-band at 1345 cm^{-1} originates from multiple overlapping bands such as the D-mode of graphene, the C–N vibration mode at 1285 cm^{-1} , and the C=N vibration mode of melon at 1400 cm^{-1} . The broadened of G-band at 1585 cm^{-1} arises from the overlap of the G-bands of graphene and melon.

The structure of melon was further confirmed by solid-state ^{13}C and ^{15}N NMR spectra.^[236] The ^{13}C cross polarization-magic angle spinning (CP-MAS) spectrum of melon (Figure 3.4c) showed two sharp signals with peak maxima at $\delta = 166$ and 157 ppm . The low field signal at $\delta = 166\text{ ppm}$ was assigned to the carbon atoms adjacent to the amino groups, whereas the high field signal at $\delta = 157\text{ ppm}$ corresponds to the CN_3 moieties present in the heptazine ring. For the assignment the contact time was set to 10 ms (τ_c). The high-resolution ^{15}N CP-MAS spectrum of melon (Figure 3.4d) showed similarities with the spectra of semicrystalline rather than of amorphous materials.^[236] Through a cross-polarization with polarization inversion (CPPI) experiment, a consistent signal was assigned using the time dependence of the polarization inversion dynamics of unequal ^{15}N nuclei. The distinguished signals (Figure 3.4d) detected were a broad intense signal from $\delta = -171$ to -205 ppm , due to a continuous slow reduction in polarization confirming the presence of tertiary nitrogen (N_{tert}) atoms. The resonance at $\delta \sim -224\text{ ppm}$ showing a moderate intensity loss can be ascribed to central nitrogen atom. The signals at $\delta = -245$ and -267 ppm indicate a covalently bonded, proton-induced two-step polarization process.

The intensity between the dipolar and spin diffusion regime cross-over according to $[2/(n + 1)] - 1$ ($n = 0, 1, 2$) approved the variation among the NH (cross-over at 0) and NH_2 (cross-over at $-1/3$) ^{15}N nuclei, respectively. The presence of NH and NH_2 groups in the ^{15}N CP-MAS spectrum of melon proves a partially condensed network structure. The nature of the building blocks can be determined from the isolated intense signal at $\delta = -224$ ppm in the ^{15}N CP-MAS spectrum. The resonance of N_{tert} is frequently suggestive for the central N atom (N_c) of the heptazine core.^[236] The ^{15}N CP-MAS spectrum gives us a strong indication of the heptazine-based nature of melon.

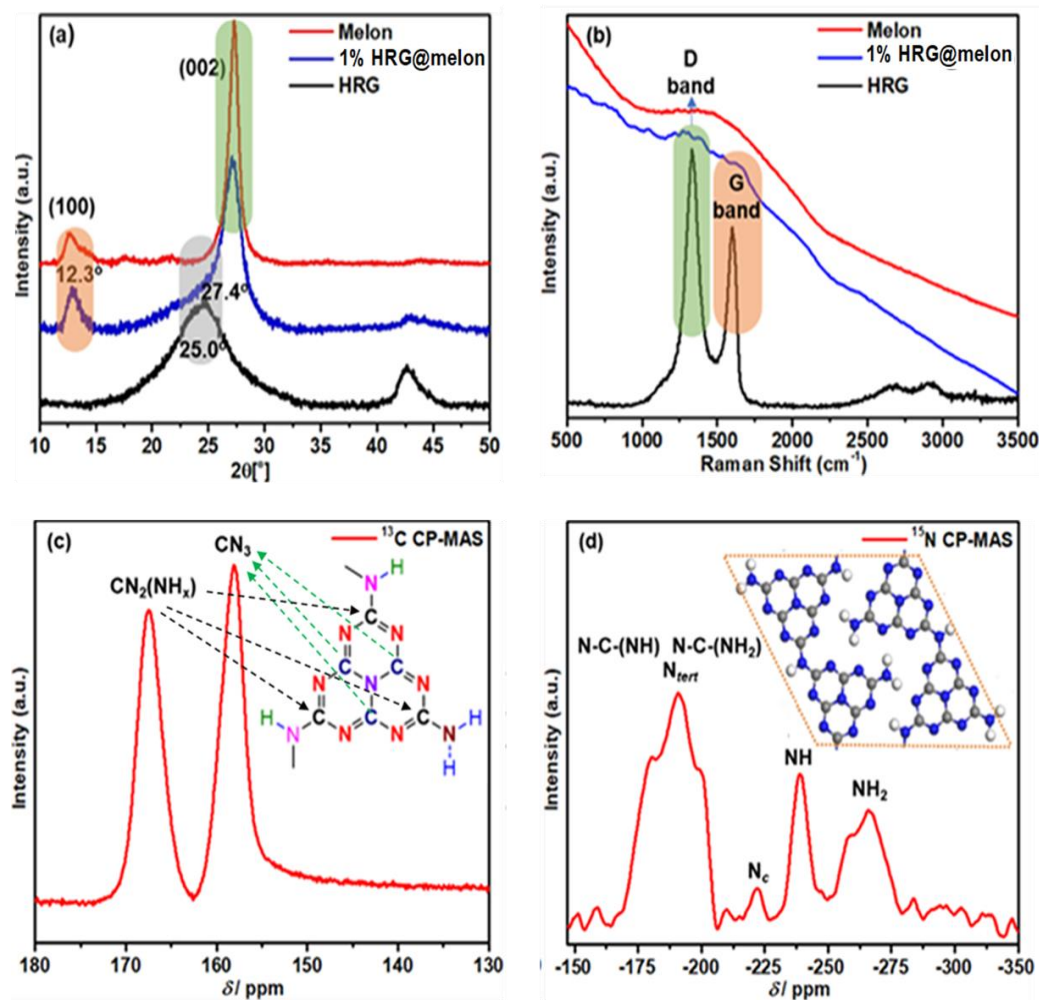


Figure 3. 4 (a) XRD pure HRG, pure melon, and 1 % HRG@melon nanocomposite, (b) Raman of HRG, pure melon and 1 % HRG@melon nanocomposite. (c) ^{13}C CP-MAS spectra and (d) ^{15}N CP-MAS spectra of melon.

The lamellar structure of HRG and 1% HRG@melon was confirmed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM and TEM microscopy images of HRG, melon and HRG@melon nanocomposites are shown in Figure 3.5, respectively. The SEM image of the as-synthesized HRG shows (Figure S.3a) layered structure, which was confirmed by TEM (Figure 3.4a). The TEM micrograph (Figure 3.5a) shows many crumpled and curved layered nanostructures of HRG due to the strong van der Waals interlayer interaction between the sheets. Melon also showed stacked lamellar structures. The TEM image of the 1% HRG@melon nanocomposite (Figure 3.5b) exhibited two-dimensional (2D) sheets with the assembly of well-oriented lamellae of melon stacked with HRG. The thickness of the HRG sheets and the 1% HRG@melon nanocomposite was confirmed by atomic force microscopy (AFM, tapping mode) analysis (Figure 3.5c, and d). The average height profile of HRG (inset Figure 3.5c) was approximately 1.1 nm, which confirmed the atomically thin nature of the HRG layer. The thickness of 1% HRG@melon nanocomposite was confirmed by measuring the height profile on the AFM image, which showed a height range between 16.8 nm and 45 nm (Figure 3.5d). This suggests an assembly of 2D melon sheets and HRG.

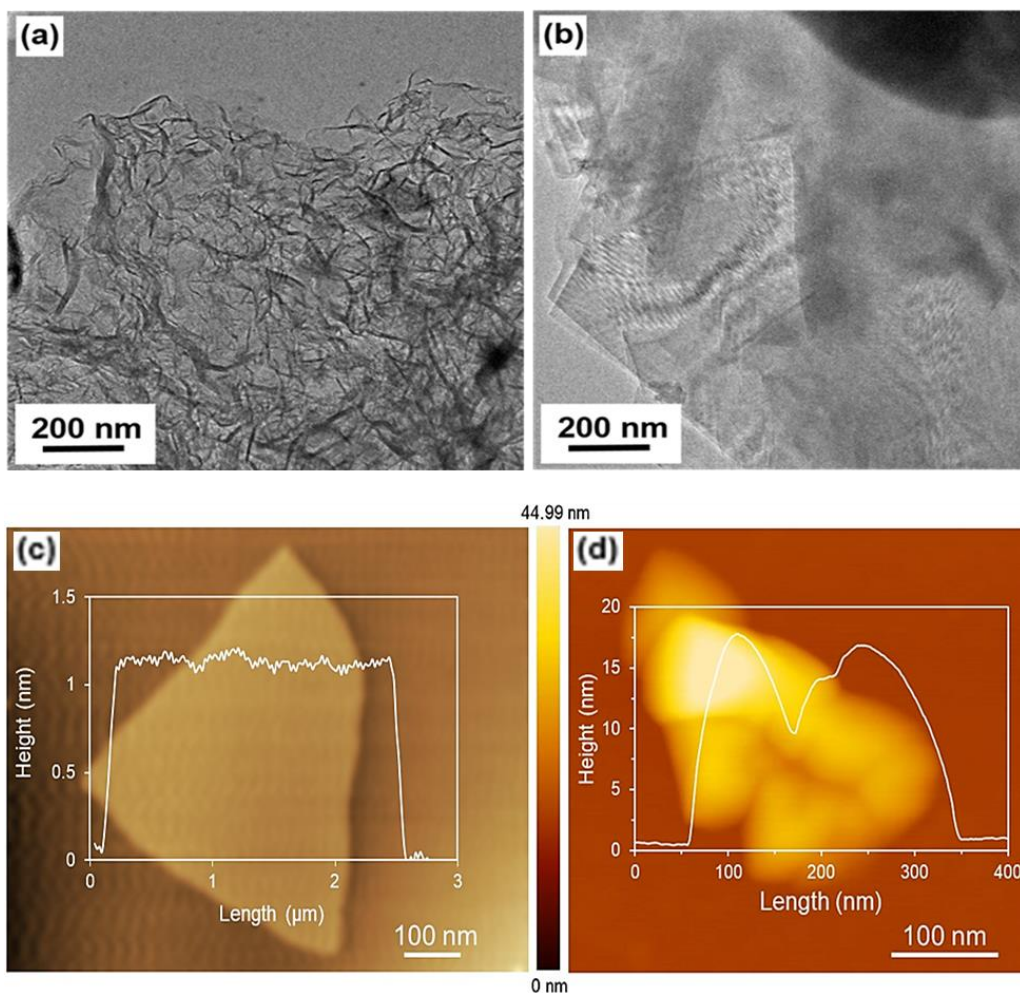


Figure 3. 5 (a,b) TEM images of HRG showing the 2D layers (a) and 1 % HRG@melon nanocomposite (b) and (c,d) AFM images of HRG with height profile (inset) confirming the atomically thick nature of sheets(c) and 1 % HRG@melon nanocomposite, indicating the self-assembly of HRG and melon(d).

The EDX analysis recorded using field emission SEM (FE-SEM) for the 1% HRG@melon nanocomposite (Figure S.3a) confirmed the presence of C and N as the major elements present in the nanocomposites. The empirical formula calculated based on elemental analysis showed relative ratio of $C_{2.98}$: $N_{4.39}$: $H_{3.33}$. The presence of H and little excess of N could be because of the primary amine groups in melon due to its uncondensed nature.

The chemical structure and the chemical environment of different elements in the near range of pristine HRG, melon and 1% HRG@melon nanocomposite were analysed using FT-IR and X-ray photoelectron spectroscopy (XPS). The FT-IR spectrum of the HRG (Figure S.4a, black line) showed no prominent bands except for a tiny peak around 1704 cm^{-1} and 1611 cm^{-1} and broadband signal centered at 700 cm^{-1} . The former bands could be related to the C=O and C=C stretches whereas the latter are due to the out-of-plane deformations of the C–H bonds. This proves the reduction of most of the oxygen-containing functionalities. Pristine melon and the 1% HRG@melon nanocomposite (Figure S.4b, red and blue lines, respectively) showed bands between 1200 cm^{-1} to 1600 cm^{-1} . These could be due to the stretching vibrational modes of carbon-nitrogen bonds (C–N) in heterocycles. A weak broad absorption band between 3100 cm^{-1} and 3350 cm^{-1} (Figure S3a, red line) could be assigned to the $-\text{NH}_2$ groups of melon. A small sharp peak at 810 cm^{-1} could be attributed to the stretching mode of the triazine unit of melon.

Figure S.4b shows the survey spectrum of HRG, melon and 1% HRG@melon nanocomposites. The survey scan indicated the presence of C & N for melon (Figure S.4b, red line), C & O for HRG (Figure S3b, black line) and C, N, & O in case 1%HRG@melon nanocomposite (Figure S.4b, blue line). The high-resolution C 1s spectrum (Figure 3.6a) for HRG indicated the reduction process because the peak centred at 284.5 eV in the C1s spectrum corresponds to the sp^2 carbon, i.e., C=C bonded as the prominent peak. The other signals related to C1s due to the C–O or C=O moieties centred at 285.7 eV and 288.3 eV are very much reduced. This confirms the structure of HRG majorly contains sp^2 carbon skeleton. A signal of deconvolution with curve Gaussian fitting for the O1s spectrum (Figure 3.6b) points out the presence of three chemically different O species, having O1s

binding energies centred at around 530.7 eV, 533 eV and 535 eV. The intense peak at approximately 533 eV was ascribed to C–O, while the peaks at 530.7 and 535 eV are attributed O1s due to the C=O, O–H–, respectively. The high-resolution XPS spectra for the N1s binding energy of melon upon deconvolution showed four different chemical species for N1s (Figure 3.6c). The peaks centred at 401.4 eV, 400.4 eV, 399.6 eV and 398.7 eV correspond to amino –NH₂ or –NH– or pyrrolic (labelled as NH_x) and the quaternary or tertiary nitrogen N–(C)₃, present as central nitrogen of heptazine ring and nitrogen that is present in the ring as pyridinic N, respectively. The presence of –NH₂ groups shows the uncondensed nature of melon. The C1s high-resolution XPS spectra (Figure 3.6e) for melon showed two distinctive peaks with binding energies centred ≈ 288.6 eV and 284.6 eV. The peak at 288.6 eV corresponds to the N–C=N in the heptazine rings, and 284.6 eV is related to the C1s binding energy for the graphitic carbon (C–[C, H]) as also reported earlier by Alwin et al.^[215] The high-resolution XPS spectra of N1s for 1% HRG@melon nanocomposite (Figure 3.6d) showed similar binding energies as described above for pure melon. However, the peak intensities were broadened due to the inclusion of HRG. The high-resolution XPS spectra of C1s for 1% HRG@melon nanocomposite (Figure 3.6f) also showed similar binding energies as that of melon. Again, the peak intensities were changed due to the electronic interaction between HRG sheets and melon in the nanocomposite.

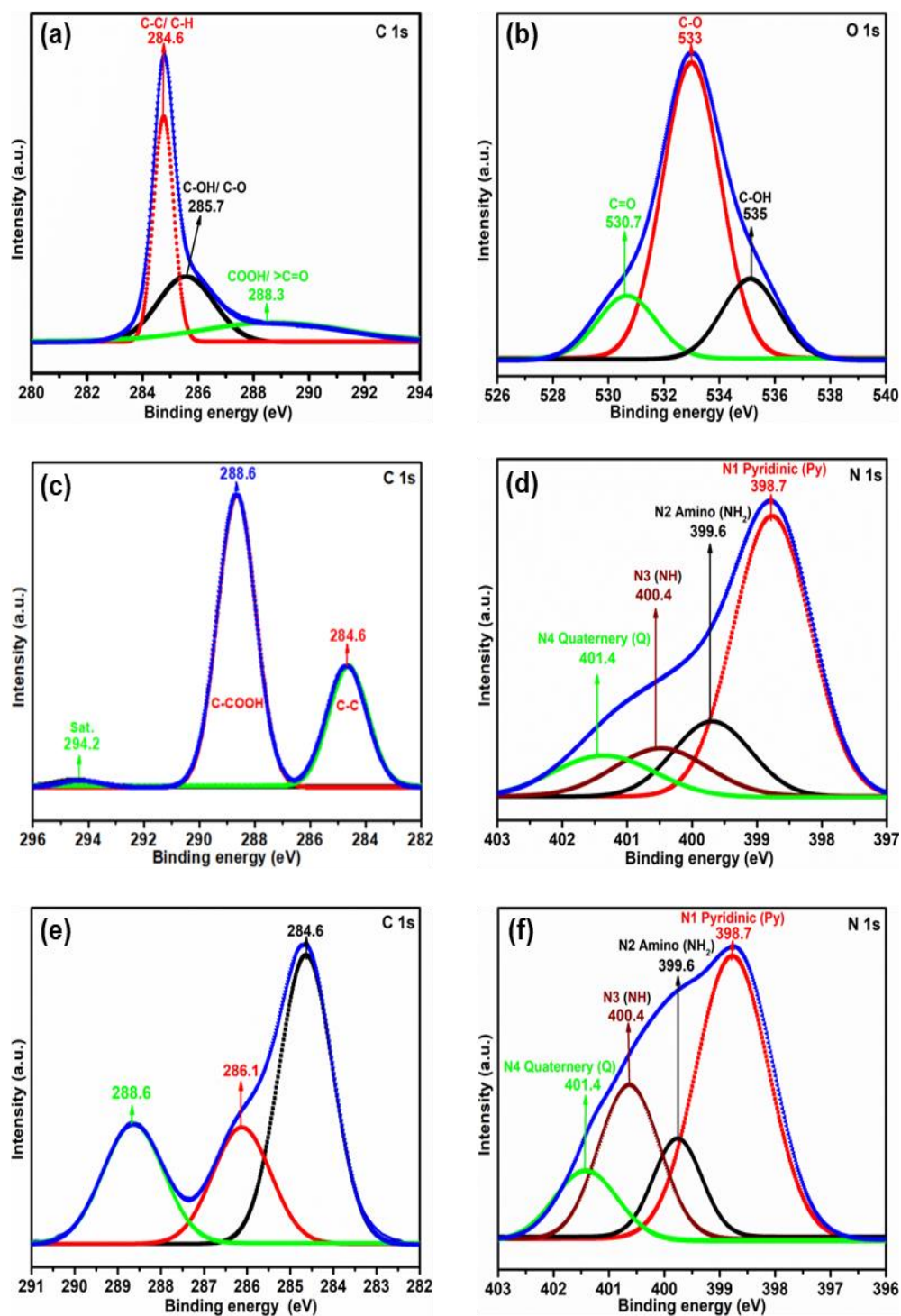


Figure 3. 6. XPS spectra of (a) HRG C 1s, (b) HRG O 1s, (c) melon C 1s, (d) melon N 1s (e) 1 % HRG@melon nanocomposite C 1s, (f) 1 % HRG@melon nanocomposite N 1s.

The optical properties and bandgap of pristine HRG, melon and the 1% HRG@melon nanocomposite were determined using UV-visible (UV-vis) diffuse reflectance

spectroscopy. Figure 3.7a shows the diffuse reflectance absorption spectra of HRG, melon, and the 1% HRG@melon nanocomposite. HRG showed a very weak absorption, mostly in the UV region (Figure 3.7a, black line). Melon showed a broad absorption in the UV-vis region with an absorption edge at ≈ 480 nm (Figure 3.7a, red line). However, with 1% HRG@melon, the absorption edge was red-shifted to the visible region ~ 520 nm (Figure 3.7a, blue line).^[231] The bandgap energies were estimated using Kubelka-Munk functions. The bandgap energies for melon and 1% HRG@melon nanocomposite were 2.6 and 2.4 eV, respectively (Figure 3.4b). The enhancement of the visible light utilization and narrowing of the bandgap in the nanocomposite can be attributed to the contact of the HRG nanosheets with the melon lamella that results in an electronic redistribution at the interface between HRG and melon. The valence band (VB) and conduction band (CB) potentials of pristine melon, HRG and the HRG@melon nanocomposite were calculated using the following empirical equations (i, ii, iii).

$$E_{CB} = X - E_e - \frac{1}{2}E_g \quad (i)$$

$$X = [X(A)^a \times X(B)^b \times X(C)^c]^{1/(a+b+c)} \quad (ii)$$

$$E_{VB} = E_{CB} + E_g \quad (iii)$$

where E_{CB} is the conductive band and E_{VB} is the valence band potential, X stands for the geometric average of the absolute electronegativities of the corresponding atoms of a semiconductor calculated from equation 2 and a, b, c represent the number of the individual elements A, B, C, i.e., carbon, nitrogen, oxygen in the chemical formula of the semiconductor. The E_e is the energy of a free electron using the hydrogen scale (4.5 eV),

and E_g denotes the bandgap of a particular semiconductor. By applying the above formulae, the relative positions of E_{CB} and E_{VB} are presented graphically in Figure 3.7c.

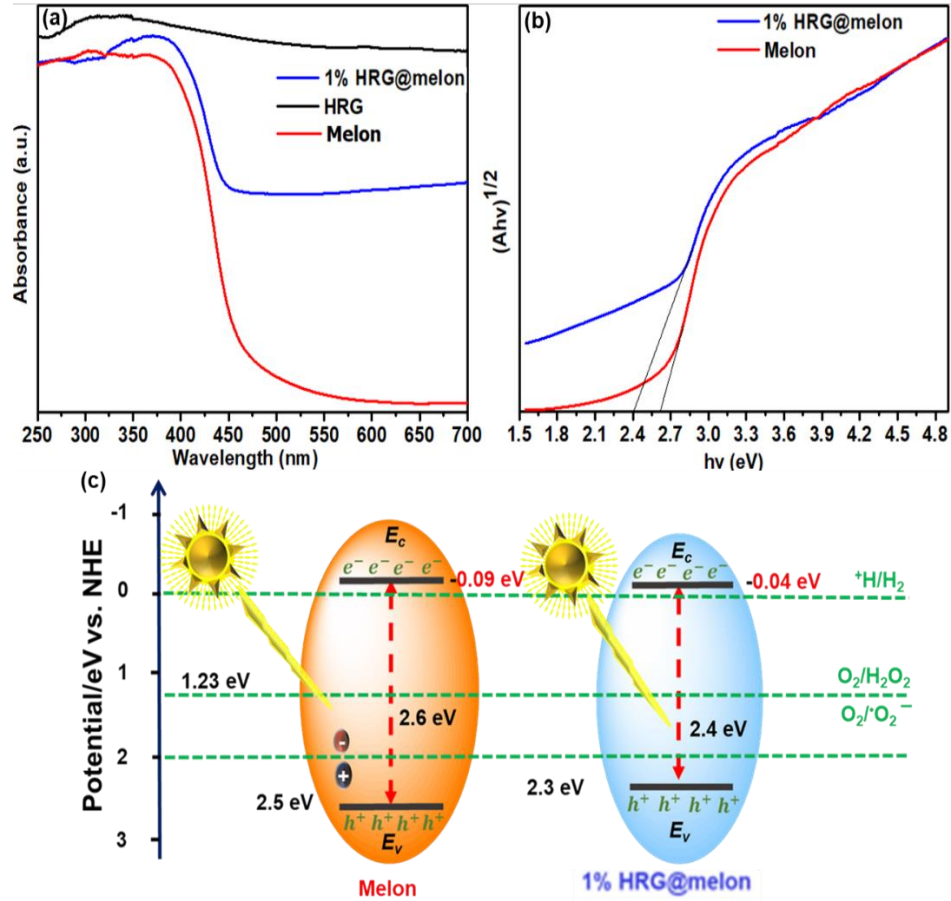


Figure 3. 7 (a) UV-vis diffuse absorption spectra of melon, HRG and a 1% HRG@melon nanocomposite. (b) Plots of converted Kubelka Munk functions vs. light energy. (c) Scheme representing the theoretical optical band positions for melon and the HRG@melon nanocomposite.

As a potential application of this heterostructure (HRG@melon nanocomposite), we explored PEC water splitting. The PEC water splitting performance of the as-fabricated photoelectrodes using melon in combination with different ratios of HRG was carried out in a 3-electrode cell under AM 1.5 G illumination. The results are shown in Figure 3.8a. The conductive character of HRG (a zero bandgap material) facilitates charge transfer in many optoelectronic applications.^[224,237–239] As expected, the inclusion of HRG enhanced

the HER activity by charge redistribution at the interface between HRG and melon (semiconductor nature with bandgap > 2).^[240,241] The *I-V* behavior of the as-fabricated melon and HRG@melon photoelectrodes (Figure 3.8a, Table S.2) under illumination, clearly envisions the effect of solar light on the performance of the samples. Under simulated light exposure, the photoelectrodes showed a significant increase in the current density compared to dark conditions.^[242] We compared the linear sweep voltammograms of the HRG@melon photoelectrodes with different percentages of HRG and melon (Figure 3.8a, shown in Figure S5a&b) under continuous AM 1.5 G illumination and in 0.1 M KOH aqueous electrolyte containing 10% (volume/volume) triethanolamine. The photoelectrode consisting of only melon showed very little photocurrent under light with a significant onset potential, i.e., 0.071 mA/cm² at -0.75 V_{RHE}. In contrast, the photoelectrode prepared from the 1% HRG@melon nanocomposite showed the highest photocurrent density of 0.63 mA/cm² at -0.75 V_{RHE}. The other photoelectrodes containing 0.1% and 2% HRG did not show a better photocurrent in comparison. For the 0.1% composite, it could be due to the insufficient amount of HRG to show an influence whereas 2% HRG showed a conventional conducting behaviour that led to insignificant improvement under the light. Additionally, the higher amount of HRG (2%) contributes more to the electrochemical behaviour of HRG, which dominates the photocatalytic performance at higher concentrations. It provides a feasible pathway for electronic transport from melon.^[243] Furthermore, the potential onset value is shifted significantly towards the lower HER potential with HRG supplement until 1%, i.e., from -0.24 V_{RHE} (in the case of melon) to -0.71 V_{RHE} at 0.05 mA/cm² for 1% HRG@melon nanocomposite. Thus 1% HRG@melon nanocomposite

indicated the best photoelectrochemical behavior among three different HRG@melon photoelectrodes.

The photostability of photoelectrodes in terms of I - t plots was analysed using chronoamperometry. The Chronoamperometric curves (Figure 3.8b) declined slightly initially due to the possible charge recombination behavior.^[244] However, the photocurrent was sustained up to 2000 s with minimal loss in photocurrent. We also carried out transient photocurrent tests to explore the photocurrent stability and recovery (Figure 3.8c). All the samples showed recoverable photocurrent density levels under solar illumination, which is the characteristic of photocatalysts. As expected, the photocurrent density level is sustained after multiple transient cycles, specifically for 1% HRG@melon.

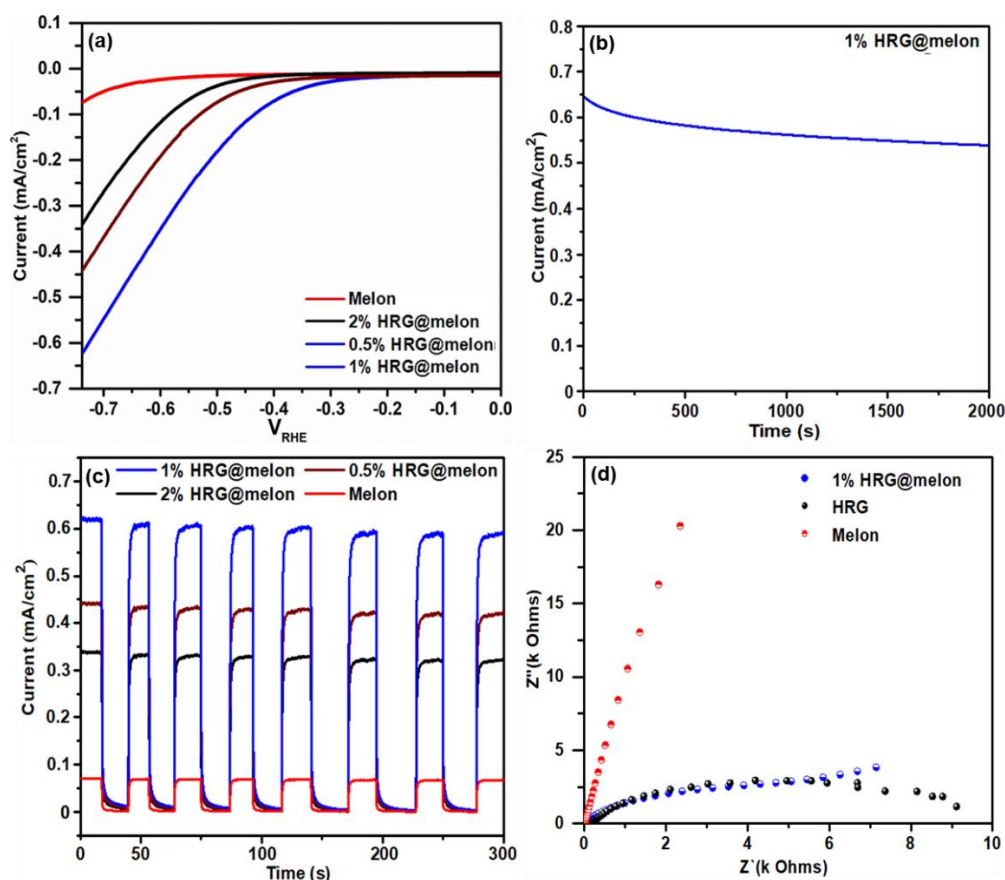


Figure 3. 8. (a) linear sweep voltammograms of pristine melon, and 0.5%, 2%, and 1% HRG@melon nanocomposites in 0.1 M KOH aqueous electrolyte containing 10% (v/v) triethanolamine under visible light irradiation for hydrogen evolution reactions. (b) Chronoamperometric curves of the 1% HRG@melon nanocomposite. (c) Transient photocurrents of melon and 0.5%, 2%, and 1% HRG@melon nanocomposites in 0.1 M KOH aqueous electrolyte containing 10% (volume/volume) triethanolamine under visible light. (d) Photoelectrochemical impedance spectra of melon, HRG, and 1% HRG@melon nanocomposite.

Electrochemical impedance spectroscopy (EIS) analysis was carried out to understand the effect of HRG on the resistances and the separation efficiency of the charge carriers. The EIS analysis was performed using 0.1 M KOH aqueous solution as an electrolyte under visible light. In the EIS Nyquist plot (Figure 3.8d), the pristine samples showed larger radii than the 1% HRG@melon nanocomposite. The order of decreasing semicircle radii is melon > HRG > 1% HRG@melon. Thus, the 1% HRG@melon nanocomposite, upon illumination showed more charge transfer than melon. Exquisite potential of HRG@melon in photocatalytic applications results from the facts that ^[245] (i) the assembly of HRG and melon reduces the bandgap of melon from 2.6 to 2.4 eV and (ii) the peripheral amino groups of melon enhance the wettability of photoanodes and improve the kinetics of the HER.

Further elucidation of the mechanism was possible by Mott-Schottky analysis. Figure 3.9 shows that the incorporation of HRG significantly shifted the band position from $-0.91 \text{ V}_{\text{Ag/AgCl}}$ to $-0.76 \text{ V}_{\text{Ag/AgCl}}$. This distinct behaviour of the 1% HRG@melon photoelectrode leads to an enhanced HER activity at a lower potential than for the melon photoelectrode which is due to the (i) high surface area of HRG, (ii) presence of π -conjugated heptazine moieties of melon, and (iii) charge redistribution at the interface of HRG and melon. The materials are n-type, as the slopes of the Mott-Schottky plots are positive.

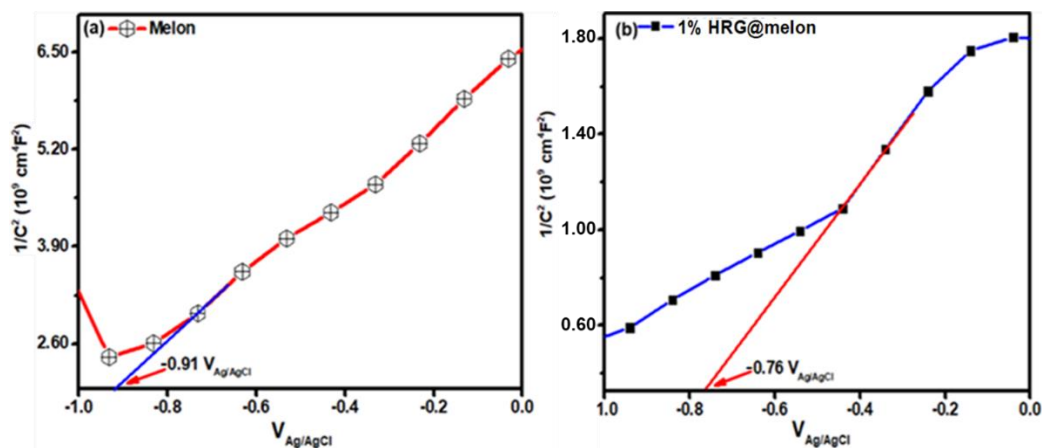


Figure 3. 9. Mott-Schottky plots indicating the band positions for (a) melon and (b) the 1% HRG@melon nanocomposite.

To obtain better mechanistic insights, we performed first-principles calculations (details are given in the supporting information) to study the coupling between HRG and melon. Figure 3.10a shows the crystal structure of melon (unit cell marked) and Figures 10b &c show the obtained band structure and projected densities of states, respectively. We find a direct bandgap of 2.6 eV at the Γ -point, which is consistent with the experimental value of 2.6 eV. The projected densities of states indicate that the valence band edge is dominated by N p states, while the conduction band edge is dominated by hybridized C p and N p states. Melon has a high absorption coefficient in the range of 10^5 cm^{-1} (Figure S.6).

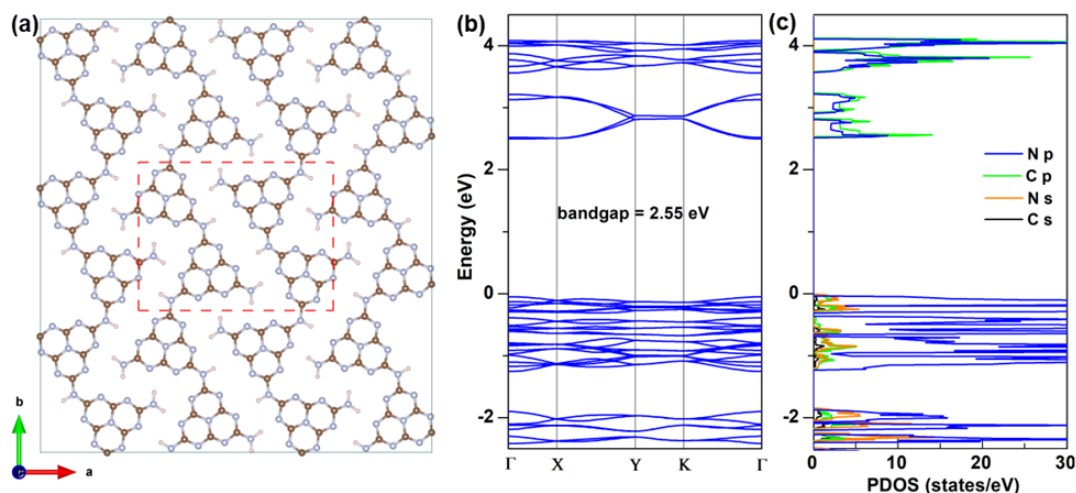


Figure 3. 10. (a) Crystal structure of melon with the unit cell marked. (b) Band structure and (c) projected densities of states of melon obtained by the Perdew-Burke-Ernzerhof functional.

The Gibbs free energy difference (ΔGH^*) can be used to predict the HER activity. The ideal value of zero indicates that H is neither too weakly nor too strongly bound. In the case of melon, we calculate ΔGH^* for 38 N sites and find that the symmetry-equivalent sites 1, 2, 7, 9, 10, 16, 21, 27, 28, 30, 35, and 36 are highly HER active with $\Delta GH^* = 0.39$ eV (Figure S6). As experimentally addition of 1% HRG enhances the HER activity of melon, we add an HRG nano-flake to our simulation model, specifically, we place HRG (i) above the void area of melon and (ii) above the heptazine of melon (Figure S.7). We study again all 38 N sites with an OH functional group attached to the HRG nano-flake at two different positions (red circles in Figure S.8). The same sites as before are found to be highly HER active (red values in Table S.3). Among them, site 9 is favorable for high HER activity. Therefore, we consider for this case additionally O, OH, and/or COOH functional groups attached to the HRG nano-flake Figure 3.11(a&b). Figure 3.11(c& d) and Table S.3 show that the addition of HRG to melon improves ΔGH^* , which confirms our experimental findings. We next study the charge transfer in HRG@melon with attached O, OH, and COOH functional groups when HRG is placed above the void area of melon and when HRG is placed above the heptazine of melon. Figure 3.11(e, f, g, h) demonstrates a significant charge redistribution, which may enhance the conductivity.

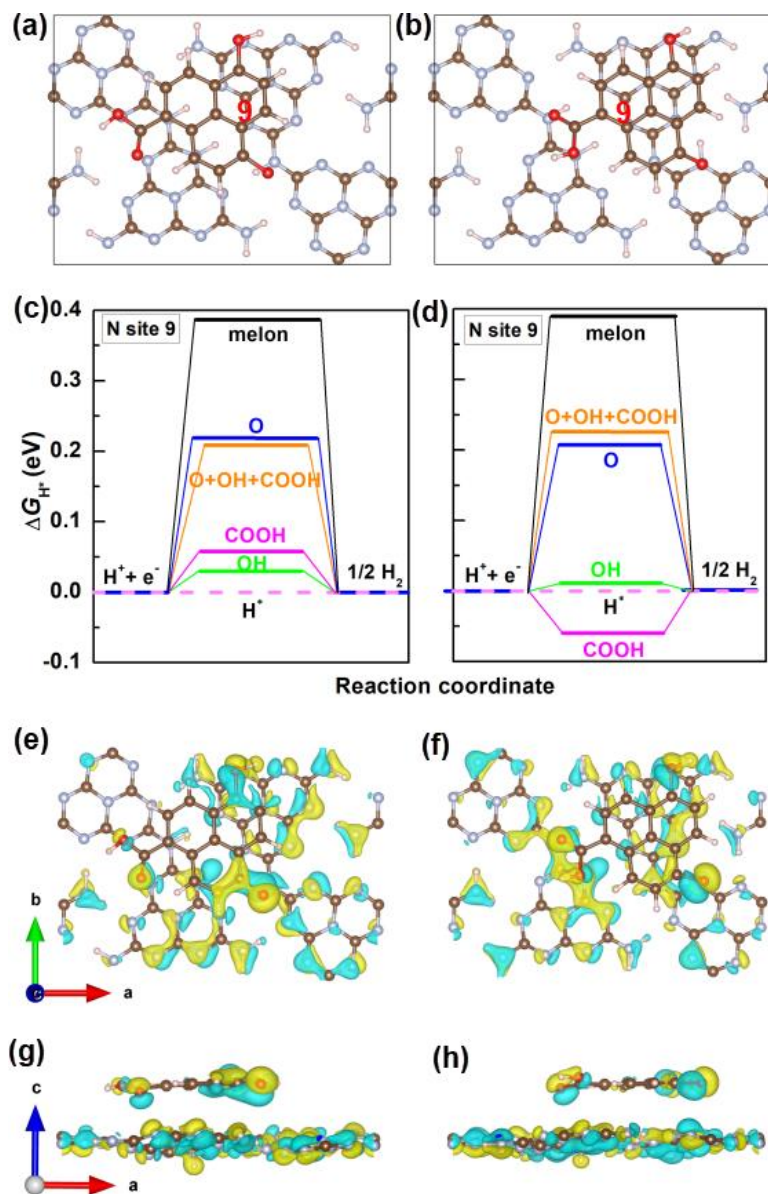


Figure 3. 11. HRG on melon (a) above the void area of melon and (b) above the heptazine of melon. The obtained values of ΔG_{H^+} for H adsorption at site 9 (favorable for high HER activity) are shown in (c) and (d), respectively, for HRG with attached O, OH, and/or COOH functional groups. Charge transfer between HRG and melon in (e) top and (g) side views when HRG is placed above the void area of melon and in (f) top and (h) side views when HRG is placed above the heptazine of melon. The yellow and cyan colours (value of $0.03 \text{ e}\text{\AA}^{-3}$) represent electron accumulation and depletion, respectively.

3.4 Summary

In conclusion, we synthesized highly reduced graphene oxide (HRG), melon, and HRG@melon nanocomposites with different HRG: melon ratios. The nanocomposites

were tested for photoelectrochemical water splitting. Our experimental data show that the inclusion of 1% HRG enhances the HER activity by a factor of ~ 9 . The findings were confirmed and explained by first-principles calculations. Both the experimental and theoretical results indicate that the enhanced HER activity is due to the (i) high surface area of HRG, (ii) presence of π -conjugated heptazine moieties of melon, and (iii) charge redistribution at the interface of HRG and melon. Moreover, the presence of primary amine groups in melon enhances the wettability of the photoanodes. In addition, we studied the effect of the oxygen functional groups (O, OH, and/or COOH) of HRG on the HER activity. The designed photocatalyst (1% HRG@melon nanocomposite) showed excellent potential for efficient HER without using costly metals or metal oxides. The HRG@melon nanocomposites can also be applied as a green, cost-effective, and efficient photocatalysts for related applications such as photoreforming, light-induced organic reactions, and solar energy conversion.

CHAPTER 4

Engineered Carbon Nitride (C_3N_3) with Non-Noble Metal Ni_2P Co-Catalyst based Nanocomposites for PEC Water Splitting

4.1 Introduction

Molecular form of hydrogen (H_2) is an emerging potential among renewable and environmentally benign green chemical fuels to substitute non-renewable conventional fossil fuels. H_2 fuel is carbon neutral in nature with relatively high energy density (120 MJ/kg) and can be stored for long time.^[46,71] Among the available technologies under research, the most ideal route is the production of green H_2 from water using sunlight and suitable photocatalyst. The overall process is also termed as water splitting.^[246] Water and sunlight being abundant in nature, the efficient, cost effective and chemically stable photocatalyst is the key to the progress with this technology. Since the first report in 1972, different semiconductors based photocatalysts have been synthesized and investigated.^[59,247] However, some of these photocatalysts are able to absorb only in the UV portion (wide bandgap) whereas other fails for their chemical stability or charge separation efficiency.^[41,248] In last two decades, carbon nitrides based photocatalyst have emerged due to their tunable electronic and optical properties, economic competitiveness, natural abundance and ease of scalability on industrial scale. However, carbon nitrides based 2D materials also suffers from low efficiency and fast charge recombination that limits its commercial appliance too. It is almost impossible to meet the requirements of an exemplary photocatalytic conditions for water splitting to produce H_2 fuel using single domain

photocatalysts. It is well documented that a suitable co-catalyst with the ability to lower the overpotential for H₂ generation is inevitable and enhances the kinetics of this reaction. This also serves as sink for photo-excited electrons to withdraw it from semiconductor photocatalyst. However, the co-catalyst should be cost competitive to ensure effective economical H₂ generation.^[249–251] Therefore, the coupling of a suitable co-catalyst with the photocatalysts is paramount for the successful production of H₂ fuel.^[249,252] To overcome these issues most of the researchers used noble metals (Au, Pt) as co-catalysts.^[253,254] But the natural dearth, high cost and cyclic reproducibility of noble metals are the big challenges for their use on commercial level.[20] Therefore, earth abundant photocatalysts with non-noble metal based materials as co-catalysts are the most viable option.^[251,255] In this contribution, non-noble metal phosphides such as Ni₂P,^[256–258] FeP_x,^[259,260] CoP_x,^[261,262] Cu_xP^[263,264] and MoP^[265] are investigated as efficient co-catalysts together with various semiconductors based photocatalysts for H₂ production through water splitting. But still the mechanism for H₂ generation of these non-noble metal phosphides as co-catalysts is not yet fully comprehended. Therefore, to understand the coupling of co-catalyst with photocatalysts from mechanistic point of view remains a worthwhile venture.^[266]

Among the non-noble metal phosphides, nickel phosphides nanomaterials as co-catalyst takes the lead because of ease of preparation. Recently, Sun et al. reported three different types of nickel phosphides (Ni₂P, Ni₁₂P₅, and Ni₃P) synthesized onto g-C₃N₄ for the photocatalytic hydrogen generation.^[267] The Ni₂P, with higher amounts of P proved the best among these three phases. In another study, Xu et al. reported the loading of Ni₂P as co-catalyst through two step mechanism during polymerization of urea to form g-C₃N₄.

They grew $\text{Ni}(\text{OH})_2$ by *in-situ* hydrothermal method to obtained $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$.^[268] Xu et al. work validated the role of Ni_2P as substitute co-catalyst for expensive Pt in boosting the efficiency of H_2 generation.^[268] It is also evident that the enhancement in photocatalytic performance of H_2 generation is dependent on the synthetic strategy of photocatalyst, and the loading of co-catalyst in every photocatalytic material.^[269] Thus, in terms of technological point of view, it is necessary to develop benign synthetic methods for the formation of carbon nitride nanocomposites with Ni_2P .^[270] Particularly, it is imperative to explore the other counterparts of 2D $\text{g-C}_3\text{N}_4$ such as recently reported C_3N_3 because it has relatively low bandgap (2.2 eV) in comparison to $\text{g-C}_3\text{N}_4$ and can harvest the light energy in the visible portion of solar spectrum.^[271,272] The chemical formula and structure of C_3N_3 was first time predicted in 1997,^[273] and recently reported by Hao Yin and co-worker in 2017.^[271] Compared with $\text{g-C}_3\text{N}_4$, the chemical structure of C_3N_3 is composed of having delocalized $\text{C}=\text{N}-\text{C}$ more π - conjugated bonds due to its basic skeleton of triazine ring rather than heptazine framework in $\text{g-C}_3\text{N}_4$.^[274] The optical properties of C_3N_3 are also different from $\text{g-C}_3\text{N}_4$ which have the band gap 2.2 eV rather than 2.7 eV respectively.^[272] Also, its structural architect having 6 pyridinic nitrogen per unit cell, favors C_3N_3 over conventional $\text{g-C}_3\text{N}_4$ for its conductivity.^[271,275,276]

Here, we report a facile method to synthesize $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanocomposite by mixing of Ni_2P nanoparticles and C_3N_3 2D polymer using ultrasonication. The as synthesized $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanocomposites offer enhanced H_2 generation efficiency. To the best of our knowledge, the present work is the first report on the synthesis of $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanocomposites and its application in water splitting to generate H_2 . The microstructure, crystal phase and optical properties of the as synthesized Ni_2P , C_3N_3 polymer and $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanocomposites were

characterized using XRD, XPS, Raman spectroscopy, SEM, TEM and UV-visible spectroscopy.

4.2 Materials and Methods

4.2.1 Materials

The chemicals for the synthesis of C_3N_3 , such as sodium metal, $NiCl_2$, cyclohexane, and cyanuric acid were purchased from Sigma-Aldrich. While for the preparation of its nanocomposite with Ni_2P , Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99.999 %), $NaH_2PO_2 \cdot H_2O$ and $NaOH$ were also obtained from Sigma-Aldrich.

4.2.2 Synthesis of C_3N_3

The pure C_3N_3 were synthesis by using modified reported method. Briefly, shown in Figure 4.1 $NiCl_2$ (100 mg) was first gently ground into fine powder and further dispersed in cyclohexane (35 ml) through ultrasonic sonication for half hour. The as prepared $NiCl_2$ -cyclohexane homogenous solution were added to the 100 ml stainless steel autoclave reactor along with 1 gram sodium metal (Na). The stainless steel autoclave reactor was sealed and heated up to 230 °C for 6 hour. After completion of reaction the reactor was cooled down into normal temperature gradually. Then quickly 1.5 g cyanuric acid was added to the reactor, and at the same time the 100 ml were filled with cyclohexane up to 60 ml. The reactor was sealed again sealed and heated up to 230 °C for 10 hour under 1.8 mega pascal pressure. At accomplishment of reaction the reactor was cooled down into normal temperature gradually and treated thrice with absolute ethanol, then diluted acid and deionized water for the removal of residual impurities. At last, the product was dried

under vacuum at 80 °C for 6 hour. The as obtained product was 0.5 g, which correspond to the final yield around 75 %.

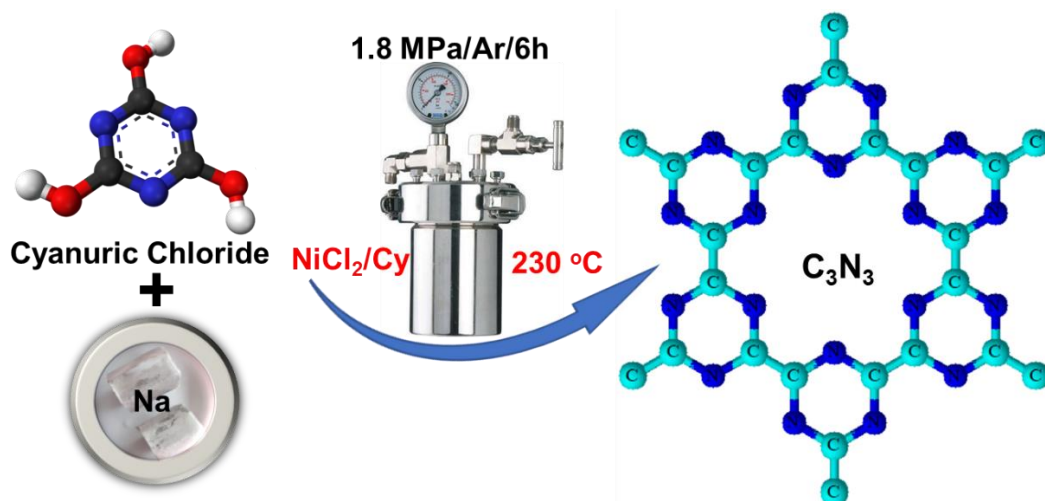


Figure 4. 1: Mechanistic scheme for the preparation of C_3N_3 .

4.2.3 Synthesis of Ni_2P/C_3N_3 Nanocomposite

Analogous to a previously reported procedure. Briefly we combined 300 mg C_3N_3 nanosheets and 2wt% of $NiCl_2 \cdot 6H_2O$ (20 mg) in 2 ml water with continuous stirring and sonication for 1 hour. After proper mixing 2wt% of $NaH_2PO_2 \cdot H_2O$ (100 mg) was accordingly included to the Ni based mixture and then again 1 hour stirred and sonicated for another 1 hour followed by drying under vacuum at 60 °C. The dried solid powder was calcined for 1 hour at 200 °C under argon condition. After cool down to 25 the as obtained solid powder was washed three times with water and ethanol separately and dried under vacuum at 60 °C.

4.3 Results and Discussion

Figure 4.2a shows the structure of C_3N_3 with triazine rings connected to each other. The X-ray diffraction (XRD) patterns of Ni_2P nanoparticles, C_3N_3 polymer and Ni_2P/C_3N_3 nanocomposites are shown in Figure 4.2b. The Ni_2P/C_3N_3 nanocomposites were prepared using different weight ratios of Ni_2P ranging from 1-3wt%, later named (1wt%) Ni_2P/C_3N_3 ,

(2wt%) Ni₂P/C₃N₃ and (3wt%) Ni₂P/C₃N₃ nanocomposites respectively. However, it is worth mentioning that (2wt%) Ni₂P/C₃N₃ nanocomposite showed better results for HER reaction, therefore, we will discuss only (2wt%) Ni₂P/C₃N₃ nanocomposite in this publication. In case of pristine C₃N₃, the X-ray diffractogram showed diffraction reflection centered at $2\theta = 27^\circ$, which is equivalent to the *d*-spacing of 0.326 nm, corresponding to the (002) lattice plane of interlayer packing of C₃N₃ sheets (Figure 4.2b, black line). This indicates the in plane periodic tri-s-triazine motif stacking and the distance among the interlayer aromatic packing of graphitic materials. The X-ray diffraction data of (2wt%) Ni₂P/C₃N₃ (Figure 4.2b, blue line) indicated main reflection at $2\theta = 27^\circ$, due to the interlayer packing of C₃N₃ and though not fully visible but very low intensity reflections of only Ni₂P phase were observed (because of the very small amounts (2wt%) of Ni₂P in the nanocomposite). The X-ray diffractogram of the as synthesized Ni₂P nanoparticles (Figure 4.2b, red line) showed sharp reflections centered at 40.77° , 44.59° , 47.45° and 54.16° that could be indexed to the hexagonal crystal structure of Ni₂P (JCPDS#74-1385). The XRD patterns of C₃N₃, Ni₂P and Ni₂P/C₃N₃ nanocomposite showed no extra reflection that confirm the phase purity of the as synthesized materials. The Raman spectra of as synthesized C₃N₃ (Figure 4.2c, black line) showed the broad bands at around 1578 cm^{-1} due to the formation of C-C bond while the band related to the C-N moiety appeared at 1349 cm^{-1} in the pristine Raman spectrum of C₃N₃. The Raman spectra of Ni₂P/C₃N₃ (Figure 4.2c, blue line) nanocomposite also confirmed that there were no structural changes to the C₃N₃ polymer after nanocomposite formation. The Fourier-transform infrared spectroscopy (FT-IR) analysis (Figure 4.2d, black line) further validates the chemical structure of C₃N₃. The presence of broad band starting from 3100 to 3500 cm^{-1} could be

due to the protonation to form N-H groups and sharp bands in between $700\text{-}1700\text{ cm}^{-1}$ correspond to C=N and stretching vibration of triazine ring. The FT-IR spectrum of $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ (Figure 1d, blue line) nanocomposite confirms that the original C_3N_3 backbones were retained after Ni_2P hybridization.

For the investigation of light absorption properties of the as prepared samples i.e., C_3N_3 and $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanocomposites with different mass ratios of Ni_2P in the nanocomposite, UV-vis and diffuse reflectance spectroscopy (DRS) spectral analysis were performed (Figure 4.2e). Pure C_3N_3 showed typical semiconductor absorption edge at 450 nm, corresponding to the band gap energy of 2.4 eV (Figure 4.2f, black line), which originates from charge transfer mechanistic response of C_3N_3 from valence band populated by N 2p orbital to the conductive band formed by C 2p orbitals. Trailing light absorption behavior is revealed that its surface defects and leading to the inter band absorption. The absorption edge of $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanocomposites (Figure 4.2f, blue line), becomes more broaden towards the visible region of solar spectrum due to the presence of Ni_2P nanoparticles. Because it is known that the Ni_2P has its own band gap of around 1.0 eV, which corresponding to up to 1240 nm wavelength of solar spectrum. With the addition of Ni_2P up to 3 % there were no such change in absorption intensity, but the absorption edge was red shifted to the visible region. From the DRS spectra of both C_3N_3 and $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ (Figure 4.2f), it is evident that the bandgap of $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanocomposite was reduced from 2.4 eV (C_3N_3) to 2.1 eV ($\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanocomposite).

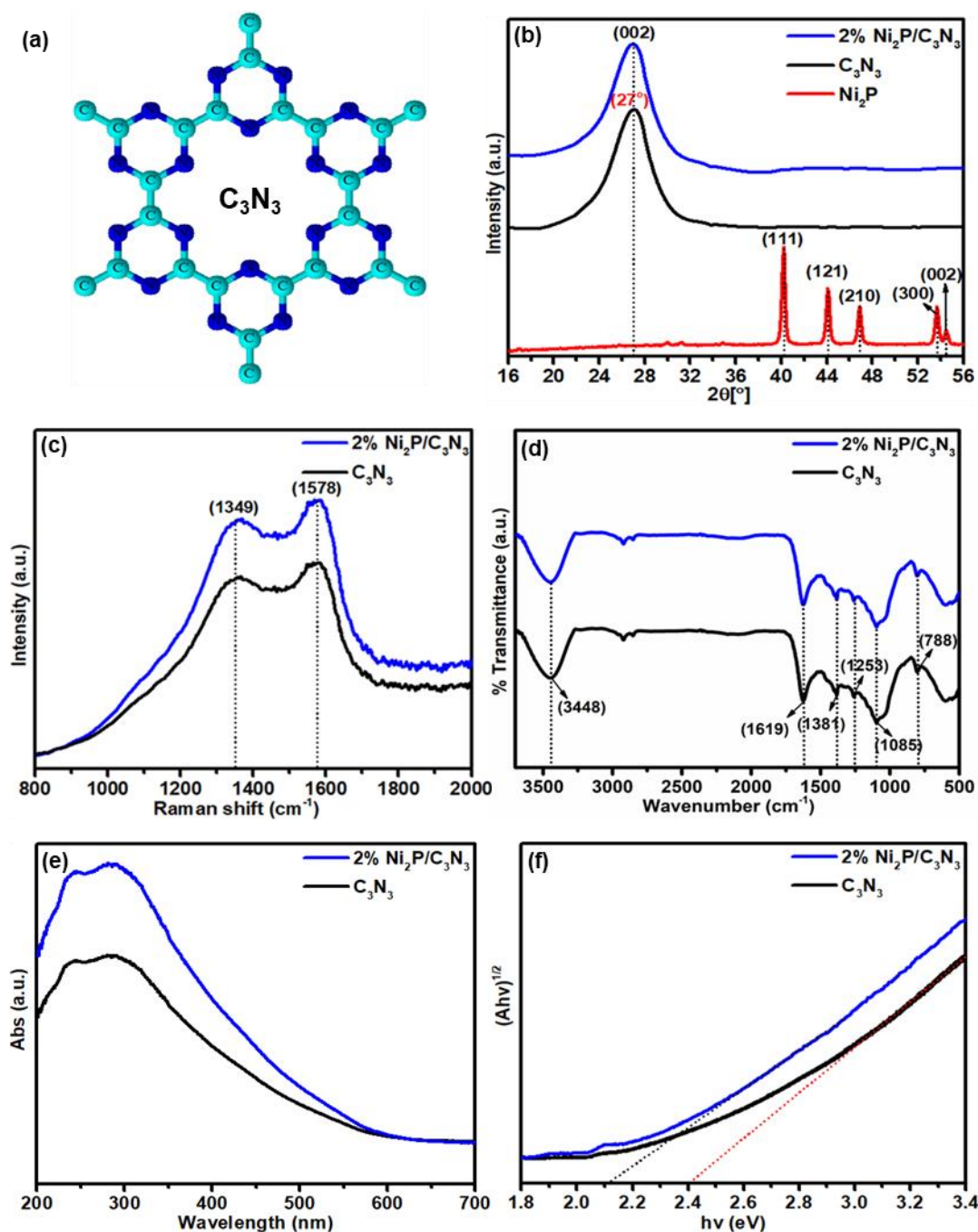


Figure 4. 2: (a) Structural illustration of C_3N_3 (b) (a) XRD pattern of pure C_3N_3 and 2% Ni_2P/C_3N_3 nanocomposite, (b) Raman spectra of pure C_3N_3 and 2% Ni_2P/C_3N_3 nanocomposite (c) FT-IR spectrum of pure C_3N_3 and 2% Ni_2P/C_3N_3 (e) Absorption spectra of the pure C_3N_3 and 2% Ni_2P/C_3N_3 nanocomposite and (f) DRS band gap calculation spectra of the pure C_3N_3 and 2% Ni_2P/C_3N_3 nanocomposite.

The structural morphologies of the as synthesized Ni_2P (Figure 4.1) and 2% Ni_2P/C_3N_3 nanocomposite were investigated using high resolution transmission electron microscopy

(HR-TEM) analysis as shown in Figure 4.3. The as synthesized Ni_2P nanoparticles consist of very small crystallite domains sheathed with each other as shown by TEM image displayed as Figure S.9. These domains are well crystallized as indicated by well define lattices fringes (Figure S.10). The inter spacing distance between the fringes is ≈ 0.22 nm corresponding to the d-spacing for (111) plane of the hexagonal phase of Ni_2P . The 2% $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanocomposite displaying a lamellar multilayer structure of C_3N_3 nanosheets decorated with small Ni_2P dots and sheathed/flakes nanocrystals (Figure 4.3a & 4.3c). The C_3N_3 consist of layered structure (2D morphology), while Ni_2P shows dark contrast as compared to C_3N_3 . The high resolution TEM image for the 2% $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanocomposite (Figure 2d) showed the lattice d-spacing ≈ 0.32 nm, consistent with the XRD data for C_3N_3 . The HRTEM images recorded on the dark spot (Figure 4.3c) marked with circle showed fringes with d-spacing ≈ 0.22 nm. This confirms the presence of Ni_2P onto the C_3N_3 sheets as this lattice spacing matches well with the (111) plane of the hexagonal structure of Ni_2P . In conclusion, TEM and HRTEM images confirmed the formation of layered 2D morphology of C_3N_3 decorated with Ni_2P nanodomains. It is also investigated that the loading of higher amount of Ni_2P on the surface of C_3N_3 result in the deterioration of its nanosheets exfoliation efficiency, leading to the formation of $\text{Ni}_2\text{P}/\text{C}_3\text{N}_3$ nanosheets unexfoliated aggregates. This behavior is mostly not favorable for photocatalytic reactions.

[277]

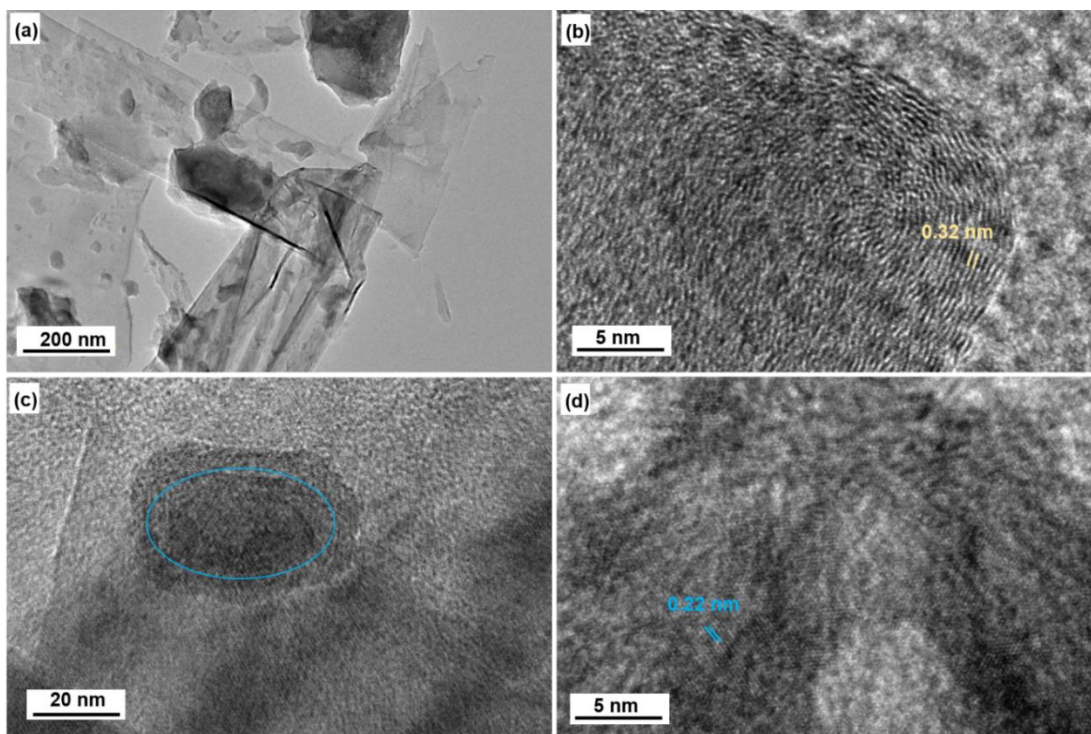


Figure 4. 3: (a) overview TEM image of the 2% Ni₂P/C₃N₃ nanocomposite and (b) HR-TEM image of the 2% Ni₂P/C₃N₃ nanocomposite taken at the rim of C₃N₃ sheet indicating the interlayer *d*-spacings related to C₃N₃ and (c & d) confirming the presence of Ni₂P onto the surface of C₃N₃ sheets.

X-ray photoelectron spectra (XPS) of the pure C₃N₃, Ni₂P and 2% Ni₂P/C₃N₃ nanocomposite confirmed the composition and chemical environment (hybridization) of different elements present in the as synthesized materials. The only prominent peaks observed in the survey spectra of (Figure S.12, black line) correspond to the C, N and O for C₃N₃, whereas we see addition peaks for Ni and P in case of Ni₂P/C₃N₃ nanocomposite. (Note: the atomic ratio of O is basically coming from the substrate used during the XPS analysis). The XPS spectrum of C₃N₃ shows the presence of C and N with atomic ratio after background correlation around 2.8:3 which roughly correspond to the chemical formula C₃N₃. The deconvoluted XPS spectrum of C 1s for pure C₃N₃, (Figure 4.4a) exhibits a more intense peak at 284.8 eV, the broader peak at 286.2 eV and the smallest broader peak at 289.4 eV. These could be assigned to the C-C, C=N and C-N₃ respectively.

The XPS spectrum of N 1s in pure C₃N₃ (Figure 4.4b) showed a deconvolution bigger peak at 398.1 eV and a broader peak at 399.3 eV corresponding to the N=C and H-N=C respectively. The deconvoluted XPS spectrum of C 1s for the Ni₂P/C₃N₃ nanocomposite, (Figure 4.4c) exhibited more intense peak at 284.3 eV and a broader peak at 286.8 eV. These could again be assigned to the C-C and C=N respectively. Whereas XPS spectrum of N 1s in Ni₂P/C₃N₃ (Figure 4.4d) showed a deconvolution of main intense peak at 400.1 eV and a less intense peak at 402.1 eV ascribed to the N=C and H-N=C respectively. The Figure 3e shows the Ni 2p XPS spectrum with six type fitted peaks, which were related to the two intense Ni 2p peak such as Ni 2p_{1/2} and Ni 2p_{3/2} at the binding energy levels of 857 eV and 875 eV respectively. The two peaks at the binding energy levels of 853 eV and 871 eV were assigned to Ni^{δ+} (0 < δ < 2) in Ni₂P, Whereas the two broad peaks at the binding energy levels of 861.8 eV and 880 eV appeared due to the shake-up satellite related multi electron excitation of Ni. On the other hand, the P 2p XPS spectrum (Figure 4.4f) shows the binding energy levels at signals 129 eV and 132 eV. These were attributed to the P^{δ-} of metal phosphides, followed by the two satellite signals at 130.6 eV and 133.9 eV. These results suggest the formation of Ni₂P in close proximity of the surface of C₃N₃ nanosheets. The deconvoluted Ni 2p and P 2p spectra for the pristine Ni₂P are similar to as described above, in case of nanocomposites.

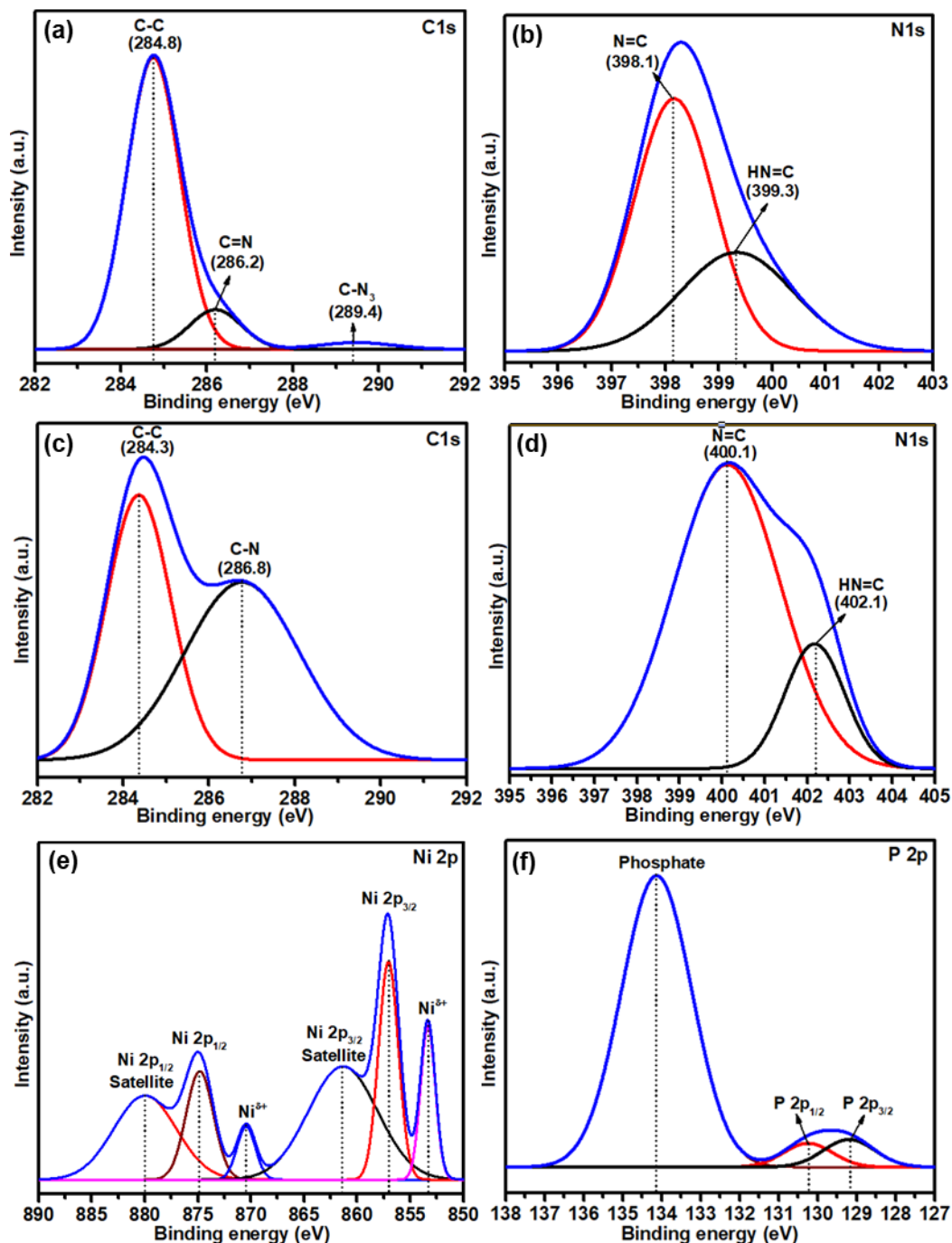


Figure 4. 4: XPS spectra of the pure C_3N_3 and 2% Ni_2P/C_3N_3 nanocomposite and pure Ni_2P (a) C 1s of pure C_3N_3 (b) C 1s of 2% Ni_2P/C_3N_3 (c) N 1s of pure C_3N_3 (d) N 1s of 2% Ni_2P/C_3N_3 (e) Ni 2p spectra of Ni_2P (f) P 2p spectra of Ni_2P .

Based on the elemental analysis, the formula of the product can be calculated as C_3N_3 . The C/N atomic ratio in the product was approximately 1:1 (Total wt% 72.38, wt% of C 36.50,

wt% of N 35.88, which agrees with the (CN)_n stoichiometry (Extracted empirical formula CN_{0.88}). Quantitative contents of the bulk Ni and P present in Ni₂P/C₃N₃ were investigated by using inductively coupled plasma optical emission spectrometry (ICP-OES) shown in Figure S.13.

The as fabricated electrodes were tested for the photoelectrochemical performance to split water into hydrogen and oxygen. For this purpose, we used a three-electrode system under AM 1.5 G illumination. The obtained PEC results are presented in Figure 4.5. The data was collected using 1 M Na₂SO₄ solution as a neutral electrolyte. In Figure 4.5a PEC linear sweep voltammetry (LSV) shows the photocurrent density versus voltage in reversible hydrogen electrode (RHE). There is pronounced effect on the photocurrent upon the inclusion of Ni₂P for the as-prepared Ni₂P/C₃N₃ photo-electrodes (Figure 4.5a) under light irradiation as compared to pristine C₃N₃ (23 $\mu\text{A}/\text{cm}^2$ to 43 $\mu\text{A}/\text{cm}^2$). The photoelectrode prepared from pristine C₃N₃ resulted in very small photocurrent under light whereas the inclusion of Ni₂P increased the photocurrent. Among the different Ni₂P/C₃N₃ nanocomposites prepared, the maximum photocurrent (43 $\mu\text{A}/\text{cm}^2$) was detected.

Eventually, the stability of the as prepared photoelectrodes were confirmed by measuring transient state current density through chronoamperometric technique as shown in Figure 4.5b & 4.5c. The photostability curve declined slightly initially due to the possible charge recombination behaviour. However, the photocurrent was sustained afterwards up to 2000 s with minimal loss in photocurrent. We have also carried out the transient photocurrent tests to explore photocurrent stability and recyclability. All the samples showed reproducible photocurrent density level upon 1 sun illumination. The transient photocurrent with Ni₂P/C₃N₃ is also much higher than pristine C₃N₃. These results indicate

that C_3N_3 interfaces with Ni_2P effectively to achieve great charge separation and transportation due to the suitable Fermi level and excellent band alignment with Ni_2P as co-catalyst. The measured PEC and impedance spectroscopy (EIS) shown in Figure 4.5d indicated that the impedance spectra for the samples optimized (2% Ni_2P/C_3N_3) is much smaller than the impedance value of C_3N_3 that confirms its fast-catalytic kinetics.

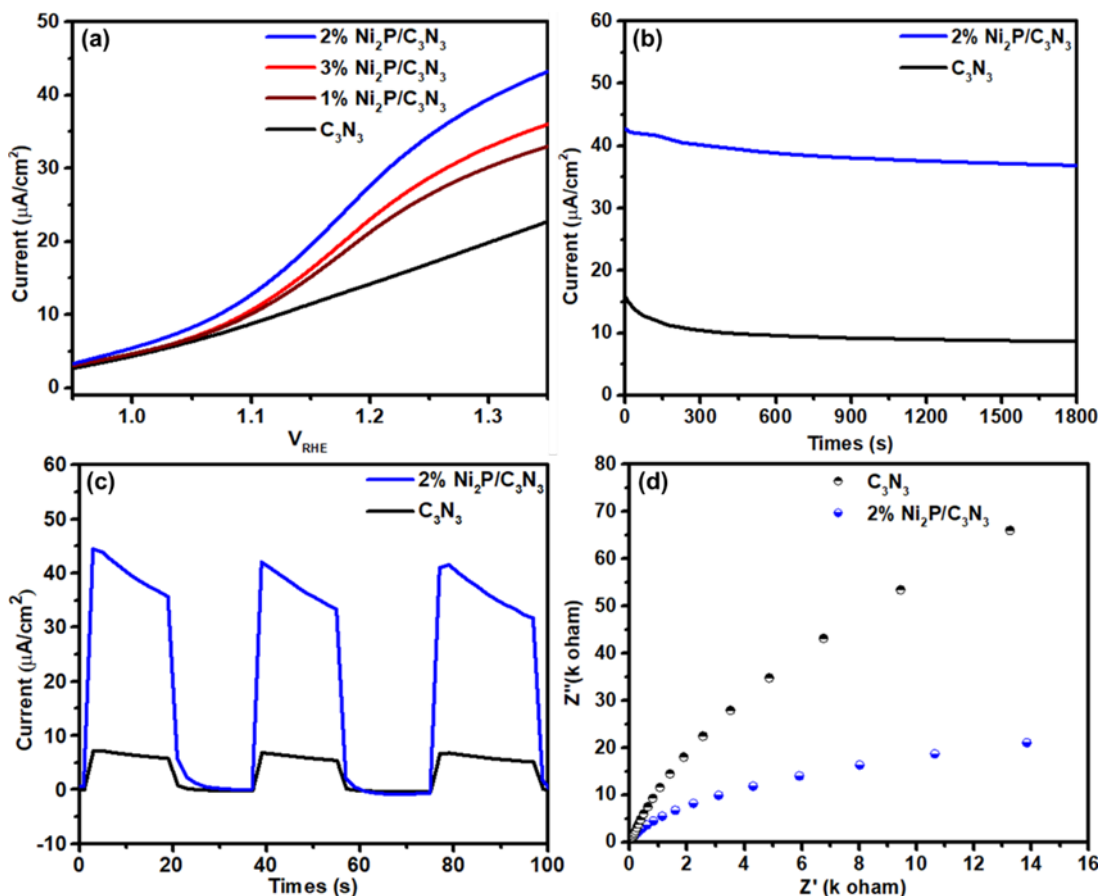


Figure 4. 5: (a) LSV polarization curves of pure C_3N_3 , and 1%, 2%, and 3% Ni_2P/C_3N_3 nanocomposite in 1 M Na_2SO_4 aqueous electrolyte under visible light irradiation for hydrogen evolution reactions (b) Photocurrents of pure C_3N_3 , and 2% Ni_2P/C_3N_3 nanocomposite (c) Chrono potentiometric curves of pure C_3N_3 , and 2% Ni_2P/C_3N_3 nanocomposite (d) photoelectrochemical impedance spectral data of pure C_3N_3 , and 2% Ni_2P/C_3N_3 nanocomposite.

Mechanistically, it has been proposed that the enhanced photocatalytic activity is due to the effective transfer of photoexcited interfacial charge (electron) from C_3N_3 to the surface of Ni_2P nanoparticles used as cocatalyst. It has been reported that photoexcited interfacial

charge can efficiently move from the conduction band (CB) edge of g-C₃N₄ to Ni₂P.^[278] Thus, as a counterpart C₃N₃ also shows the transfer of photoexcited interfacial electrons from the CB edge of C₃N₃ to Ni₂P cocatalyst using the interface of Ni₂P/C₃N₃ nanocomposite created through annealing process. It reveals that the accumulated electron on the surface of Ni₂P particles can efficiently reduce H⁺ to H₂ fuel while the holes in the valence band of C₃N₃ can easily oxidize water molecule to molecular O₂. This effective separation of the photogenerated electrons and holes in Ni₂P/C₃N₃ nanocomposite enhanced its photocatalytic activities.

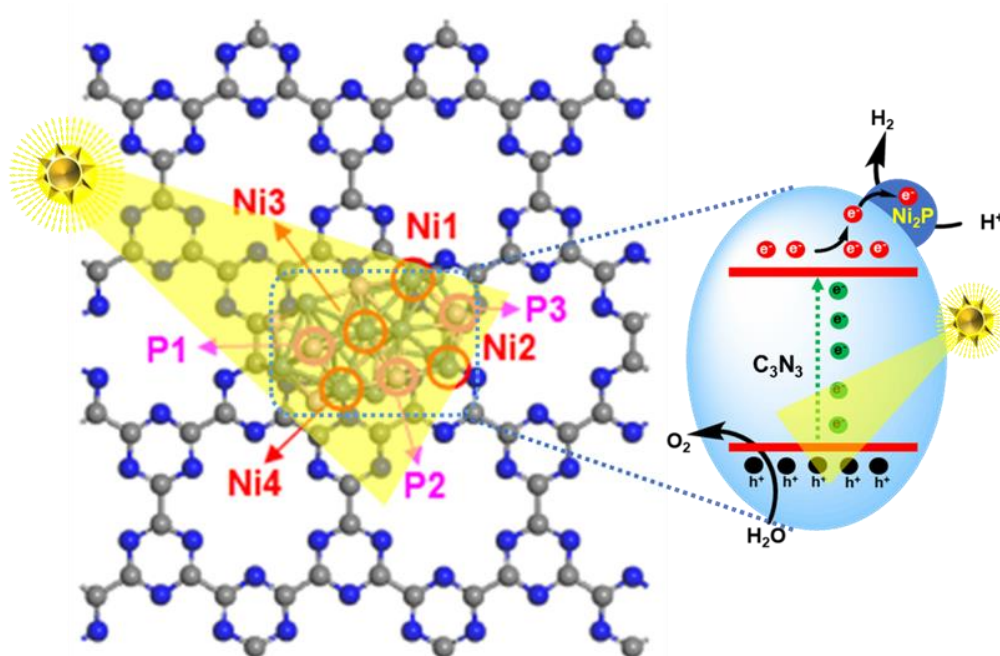


Figure 4. 6: Schematic illustration of the proposed mechanism showing enhanced photocatalytic activity is due to the effective transfer of photoexcited interfacial charge (electron) from C₃N₃ to the surface of Ni₂P nanoparticles used as cocatalyst.

4.4 Summary

In conclusion, the facilely synthesized Ni₂P/C₃N₃ nanocomposite served as efficient photocatalysts for PEC water splitting. Experimental data revealed that Ni₂P nanoparticles is an active site and highly stable noble metal free co-catalyst for the evolution of H₂ over

Ni₂P/C₃N₃ nanocomposite. The enhanced photocatalytic activity was attributed to the effective electron transfer from photoexcited C₃N₃ to Ni₂P as a result suppressed the electron hole pair recombination in C₃N₃. This contribution revealed that Ni₂P/C₃N₃ nanocomposite have a great potential for the enhanced PEC water splitting activity due to the use of low-cost noble metal free Ni₂P nanoparticles as cocatalyst. In addition, the facile synthesized economically feasible polymeric C₃N₃ as photocatalyst provide a new insight for efficient and cost effective water splitting.

CHAPTER 5

Hole Transport Layer/Perovskite Interface Engineering with Low Bandgap 2D Carbon Nitrides (C₃N₅,C₃N₃) in PSC Fabrication

5.1 Introduction

Solution-processed photovoltaics (PVs) employing halide perovskite as a light harvester in solar cells are the future renewable energy source due to their remarkable optoelectronic features, cost competitiveness with crystalline silicon-based PVs, and a potential for high PCE ^[279]. However, the low device reproducibility and long-term stability, mostly induced by irradiation of light source, moisture corrosion, ionic migration, and oxygen infiltration under operational conditions obstruct its commercial applicability ^[280–284]. The further enhancement in PCE of PSCs has been restricted by charge recombination at different interfaces between the interlayers in perovskite thin films ^[285] and their chemical stability. According to state-of-the-art structural features of PSCs, planar and mesoscopic architectures are two representative cell structures ^[286]. Especially the planar configuration of the perovskite has attracted considerable attention because of its facile fabrication methodology, ambient working conditions, and the light-harvesting layer sandwiched between hole transport layer (HTL) & electron transport layer (ETL) ^[146,287].

The interface between perovskite film and HTL remains insecure in the PSCs device in terms of stability because it traps the charge carriers at the interface within the perovskite and charge extraction layer. This is prone to instigate the irreversible degradation

mechanism caused by moisture ^[288]. Particularly, most organic HTMs materials such as Spiro-OMeTAD or PTAA in their pristine form show lower charge carrier mobility, and therefore, doping is required. Here, mostly organic hygroscopic materials are used as a dopant to achieve higher PV properties ^[289]. However, the dopants accelerate the degradation process in HTL in the perovskite layer, which affects the stability and reproducibility of PSCs ^[290]. Alternatively, couple of inorganic materials such as VO_x, ^[291,292] WO₃, ^[293,294] CuI ^[295] and NiO_x ^[296,297] have been used as HTL in PSCs. Particularly, NiO_x has been explored considerably more in comparison to other inorganic materials due to its ease of preparation, suitable work function and relatively higher optical transmission ^[298,299]. However, a redox reaction between Ni³⁺ in NiO_x and organic cation in the A-site of perovskite compromises the chemical stability of perovskite ^[300]. Therefore, in order to enhance the efficiency and stability of PSCs using NiO_x as HTL, the development of new strategies to improve the interface through modification and engineering of HTL materials are inevitable. Recently, 2D materials have emerged as an effective remedies in many different photoconversion applications due to their distinctive properties such as high surface area, short diffusion path length for photoexcited charge carriers, and mechanical, electronic, and optoelectronic properties ^[301]. Particularly, metal-free carbon nitride-based polymeric 2D materials as passivation or as an additive in the PSCs have attracted more attention due to their chemical, mechanical and optoelectronic properties ^[302–304]. In 2016, Chen *et al.*, introduced *g*-C₃N₄ quantum dots as an active layer in the PSCs to enhance the conductivity and charge transfer carriers ^[305]. Later in 2018, Liao and coworkers developed a convenient strategy to improve the crystallization process by introducing the *g*-C₃N₄ in the perovskite layer. The incorporation of *g*-C₃N₄ in the

perovskite films improved the crystalline quality with large grain size through its kinetic control and lower intrinsic defects density by passivating the charge recombination centers in the grain boundaries ^[303]. They also showed that the blending of g-C₃N₄ with perovskite precursors material without activating subdued light absorption improved the charge transfer ability in PSCs. ^[306]

The polymeric carbon nitride based 2D materials such as C₃N₃, C₃N₅, C₂N, etc. having a carbon-nitrogen ratio different from conventional g-C₃N₄ have shown enhanced optoelectronic properties ^[307]. The first principle calculations reported by Qi et al., showed that due to the intrinsic electric field band alignments in C₃N₅ suppresses the recombination of photoexcited charge carriers and improve the photocatalytic overall water splitting efficiency ^[308,309]. As an example, P. Kumar et al., reported that blending of C₃N₅ with perovskite active layer MA_xFA_{1-x}Pb(I_{0.85}Br_{0.15}) achieved PCE up to 16.7 % and outperformed the g-C₃N₄ without passive light absorption. ^[310] Li et al., incorporated 0.075 mg/ml of C₃N₃ into the precursor solution for the synthesis of perovskite resulting in improved stability of the perovskite layer as well as the efficiency of the device as compared to control ^[272]. Hence, there is a great potential for exploring 2D carbon nitrides-based materials in solar conversion applications.

In this contribution, we report the synthesis and characterization of polymeric C₃N₃ and C₃N₅ based 2D materials with tailored optical, electronic, and chemical properties. The structure and composition of the as synthesized 2D polymers were characterized using FT-IR spectroscopy, Raman spectroscopy, XRD, XPS and microstructure using SEM and TEM. These 2D polymeric materials are applied as an interfacial layer between the HTL and perovskite to tweak the alignment of the energy levels. This allowed us to obtain an

upgraded open-circuit voltage (V_{oc}) and fill factor (FF), which can be attributed to the suppressed non-radiative recombination and enhanced photo-induced charge transfer dynamics at the perovskite/HTL interface. The interlayer probably suppressed the interfacial charge accumulation at the grain boundaries of perovskites, and hence lowered the non-radiative recombination. Both factors improved the photovoltaic performances. Notably, with the usage of a dopant-free inorganic HTM, a PCE of >17% with significantly upgraded V_{oc} and FF was recorded. Due to the inherent mechanical properties of these 2D polymer materials, the mechanical stability will be increased significantly as well.

5.2 Materials and Methods

5.2.1 Materials

The chemicals for perovskite were purchased from either Dyesol or Tokyo Chemical Industry (TCI) and were used without further purification. [60]PCBM >99.5 % and Bathocuproine (BCP) were purchased from Solenne BV and TCI, respectively. Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99.999 %) and NaOH were obtained from Sigma-Aldrich. Chlorobenzene (CB, 99 %), isopropanol (IPA, 99.9 %), ethanol (EtOH, 99 %), anhydrous dimethyl sulfoxide (DMSO, 99.8 %), and N, N-dimethylformamide (DMF, 99.8 %) were purchased from Acros Organics. Cu foil was purchased from Nimrod Copper Co. (>99.9%, thickness of 0.0254 cm) and $Ni(NO_3)_2 \cdot 6H_2O$, melamine, hydrazine, cyanuric chloride and NaOH were obtained from Sigma-Aldrich.

5.2.2 Synthesis of C_3N_3 2D Materials

In a typical procedure, we used stainless steel lined reactor system for the synthesis of polymeric C_3N_3 2D material (Figure S1) through solid state chemistry. Briefly, 2 g of

cyanuric chloride and a roll of fresh copper foil (0.05mm thick copper foil cleaned with acetone in ultra-sonicator for 2 hour and dried using stream of N₂ gas) were added to the steel reactor in argon atmosphere. The sealed reactor was heated up to 250 °C for 20 hours under argon atmosphere at pressure 20 mega pascal. After the specified time the reactor were cooled down to room temperature. The copper foil having deposited 2D polymeric film were removed and washed with deionized (DI) water. Afterwards, the 2D polymeric films were scratched off from the copper foil using spatula and again washed with ethanol and DI water in an ultra-sonicator using centrifugations for three to four cycles (Figure S2). After centrifugations the obtained solid was dried in vacuum oven at 80 °C. The obtained yield was ~75%.

Removal of copper impurities: The obtained dried samples were ground to powder in mortal and pestle and transfer to a 100 ml centrifuge vials. The already prepared 80 ml of 10 % HNO₃ aqueous solution was added to that centrifuge vial and ultrasonicated for one hour and then centrifuged to remove the copper impurities. The above step was repeated for three to four times and assured that there were bubbles generated and the aqueous solution turn to deep green blueish color.



Later the sample were washed with 10 % HCl using ultrasonic bath for 2 hour and then centrifuge (4000 rpm) with ethanol and DI water for three cycles. After centrifugations the obtained solid was dried in vacuum oven at 80 °C.

5.2.3 Synthesis of C_3N_5

Synthesis of 2,5,8-triamino-s-heptazine (Melem): Melem was synthesized according to the reported procedures elsewhere with slight modifications. Briefly, in the first method shown in (Figure 5.1). 5 g of melamine was heated in tube furnace at 400 °C at 5 °C /minutes for 6 hours in alumina crucible under inert conditions. For the second method ,5 g of melamine was first heated in tube furnace at 330 °C at 5 °C /minutes for 2 hours in alumina crucible under inert condition to obtain melam and then 4 g of melam was heated in tube furnace at 400 °C at 5 °C /minutes for 6 hours in alumina crucible under inert condition to obtained melem. After cooling to room temperature, the obtained off-white yellowish color powder was suspended in DI water and refluxed for 2 hours for the removal of unreacted melamine and some other impurities. The resulting off-white powder (2.5g) melem was collected after centrifugations and drying at 50 °C in oven. It is worth mentioning, that both methods resulted in the successful synthesis of melem.

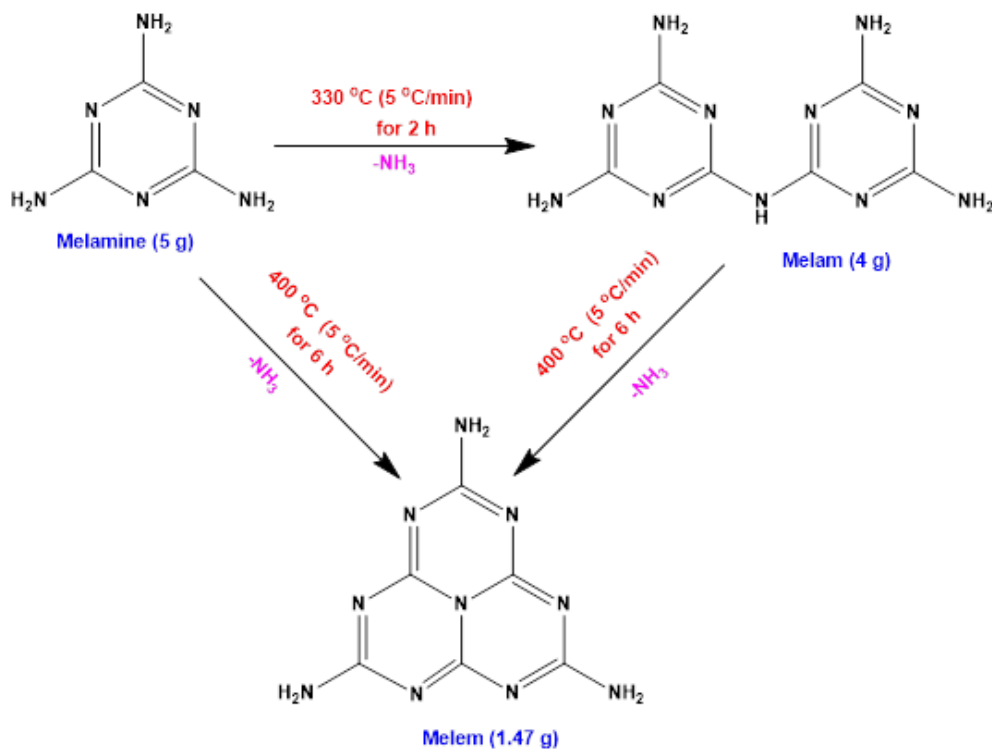


Figure 5. 1: Two steps chemical reaction and structural presentation for the synthesis of melem.

Synthesis of Melem or 2,5,8-trihydrazino-s-heptazine hydrazine (MH): Melem hydrazine hydrate were synthesized by slightly modified established procedure through a hydrothermal reaction of hydrazine hydrate with melem shown in Figure 5.2. Briefly, 2 g of melem was dispersed in 20 ml of 80 % aqueous solution of hydrazine hydrate and sealed in 50 ml Teflon-lined autoclave. This Teflon-lined autoclave was taken in the drying oven at 140 °C for 20 hours. After 20 hours, the autoclave was cooled to room temperature and subsequently the prepared yellowish suspension was transferred to 200 ml beaker and 10% of aqueous HCl solution was slowly added with shaking to control pH up to 2. The suspended white unreacted melem solid residue was removed through filtration. The filtrate was further precipitated with the addition of 10% aqueous solution of NaOH by adjusting pH around 8. This process was repeated by further three cycles. Lastly, the obtained solid product 2,5,8-trihydrazino-s-heptazine (melem hydrazine hydrate) was

washed three times with DI water, then with ethanol and dried in electric oven. The basic analytical and spectroscopic analysis of product were well matched with already reported literature.

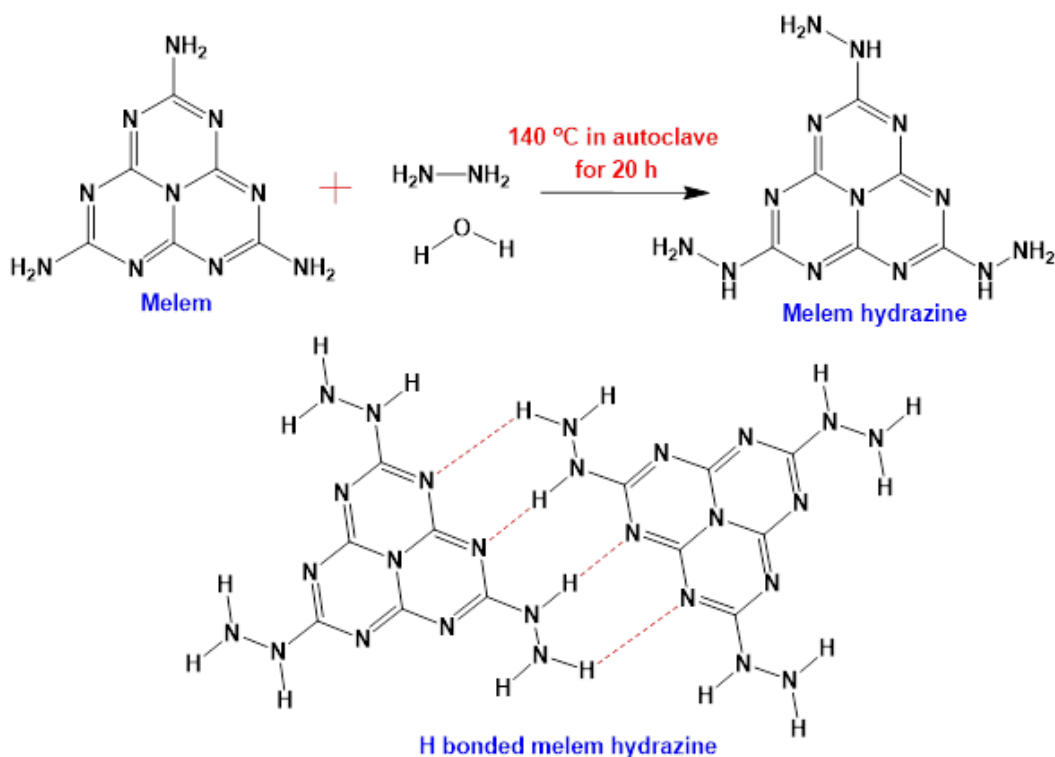


Figure 5. 2: Chemical reaction and structural presentation of melem, melem hydrazine, H-bonded melem hydrazine.

Synthesis of C_3N_5 polymer: The obtained 2,5,8-trihydrazino-sheptazine (melem hydrazine) was heated in tube furnace at 450°C at ramping of $2^\circ\text{C}/\text{minutes}$ and holding the temperature for 120 minutes under inert conditions. After cooling to room temperature, the final product bright orange color powder were obtained and further used in PSCs (Figure 5.3).

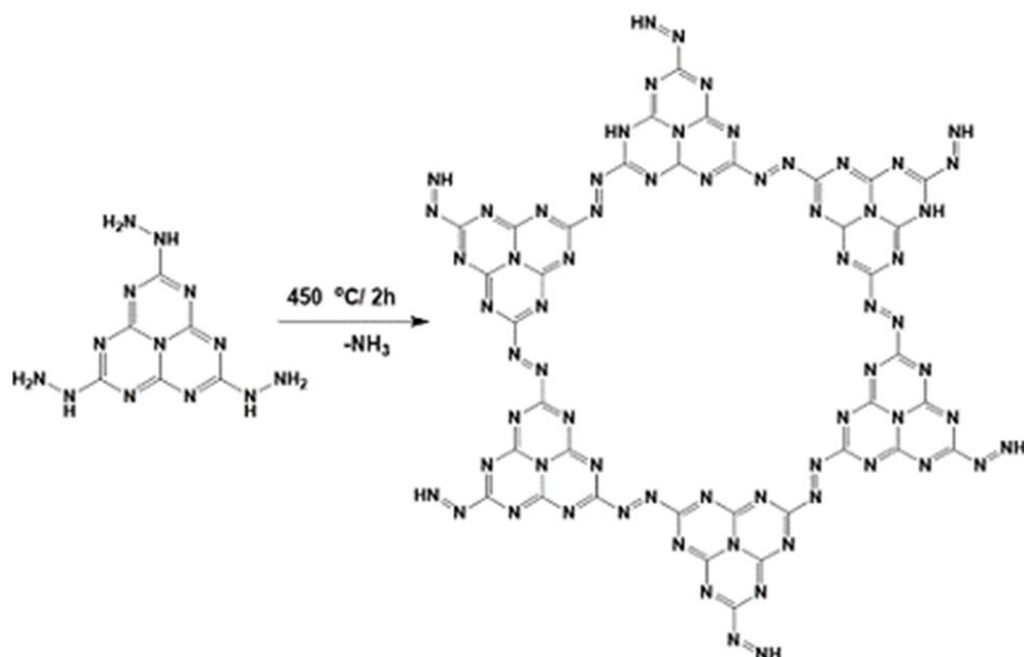


Figure 5. 3: Synthetic scheme for the preparation of C_3N_5 polymer started from melem hydrazine.

5.2.4 Synthesis of Perovskite Solar Cell

NiO_x nanocrystals (NCs) synthesis: NiO_x NCs were prepared according to the reported procedures elsewhere, with modifications noted herein below^[311]. Briefly, 25 mmol Ni(NO₃)₂·6H₂O was dissolved in 50 mL of deionized (DI) water to obtain a dark green solution. The pH at 10 was maintained with dropwise addition of NaOH (10 mol/L) while stirring for 30 min. The obtained colloidal precipitation was thoroughly washed with DI water five times via ultracentrifugation and dried at 90 °C overnight under vacuum. The obtained green powder was calcined for 2 h at 275 °C to obtain a dark-black powder. 15 mg/ml NiO_x NCs ink was prepared by dispersing the as synthesised NiO_x NCs in DI water. The above solution was ultrasonicated at 45 °C for 1 h and filtered using 0.22 μm nylon filter.

HTM solution preparation: solution preparation of CN-based materials was carried out by stirring 5 mg of materials in 1 ml of isopropanol/absolute ethanol (70/30, V/V) mixture

for 8 h at 45 °C and rest for 30 min. The obtained solution part was collected and subjected to ultracentrifugation for 30 min at 2000 rpm. 80 % of the supernatant was carefully collected and precipitation was discarded. The final concentration was adjusted to 1 mg/ml by adding the mixture of isopropanol/absolute ethanol (70/30, V/V).

Device fabrication: The laser-etched FTO-coated glasses (TEC15) were thoroughly cleaned by sequential sonication with Hellmanex II (2 vol.%) solution, deionized water, ethanol, acetone, and isopropanol for 20 min each step. After being dried by compressed airflow, the substrates were further treated by UV-ozone for 30 min prior to use. NiO_x films were formed atop of FTO substrates by spin coating at 4000 rpm for 35 s with 2000 rpm/s acceleration, followed by annealing at 150 °C for 30 min. The 1 mg/ml solution of CN-based material was spin-coated on the NiO_x layer and annealed at 60 °C for 5 min to achieve the desired interfacial layer. The samples were transferred immediately (to avoid moisture absorption to the samples) to the argon-filled glovebox under controlled moisture and oxygen conditions (H₂O level: <1 ppm and O₂ level: <10 ppm) and annealed another 5 min at 60 °C. Triple-cation-perovskite precursor solution was prepared according to the previous reports containing CsI (0.10M), FAI (1.05 M), PbI₂ (1.24 M), MABr (0.12 M), and PbBr₂ (0.12 M) in an anhydrous solvent mixture of N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) with 4:1 vol ratio ^[279,312]. The perovskite precursor solution was then spin-coated in a two-step spin-coating program set at 1000 rpm and 6000 rpm for 10 and 30 s, respectively. During the second spin step, 112 µL of chlorobenzene was dripped at 10 s prior to the ending of the program followed by annealing at 100 °C for 1 h. The PCBM solution of 15 mg/ml in chlorobenzene was spin-coated at room temperature on perovskite film at 1000 rpm (500 rpm/s) for 20 s and vacuum dried for 5

min. Then thin bathocuproine (BCP) was deposited atop of PCBM layer by spin-coating at 5000 rpm for 40 s followed by evaporating Ag (100 nm, $<1 \text{ \AA/s}$) in a thermal evaporator under low vacuum conditions (10^{-7} Torr). The control device was fabricated according to the above procure without the interfacial layer.

Device characterization: Current density–voltage (J – V) curves shown in Figure S8 were performed using an Oriel solar simulator (Newport) producing 1 sun AM1.5G (100 mW cm^{-2}) 3A sunlight and were recorded by applying an external potential bias to the devices. The generated photocurrent was recorded at a scan rate of 100 mV/s (pre-sweep delay: 10s) with the help of Keithley 2604 source meter and 0.09 cm^2 black metal mask as the active area. IPCE measurements were carried out using a 150 W xenon lamp attached to a Bentham PVE300 motorized 1/4 m monochromator as the light source.

5.3 Results and Discussion

C_3N_5 was synthesized using two steps as also reported earlier by Kumar et al., (Kumar et al., 2019). The first step involves the synthesis of 2,5,8-triamino-s-heptazine (melem) using melamine as precursor using solid state synthesis under inert conditions followed by its derivatization with hydrazine using hydrothermal. In the second step, the 2,5,8-triamino-s-heptazine hydrazine hydrate was converted to polymerized carbon nitride (C_3N_5) in the tube furnace under inert condition at 450 °C. C_3N_3 was synthesized using Ullman reaction employing cyanuric chloride as precursor and copper sheet as catalyst and support. The product was deposited onto copper sheet (Figure s2) which was carefully scratched from the copper sheet. The coordinated copper inside the triazine rings was removed by repeated washing with 10% HNO_3 and 10% HCl and MilliQ water. The synthesis details for both 2D carbon nitrides based polymers are mentioned in the experimental section provided as

supplementary information. The chemical structures and reaction schemes along with reaction conditions are provided in the (Figure 5.4). The structure and crystalline nature of the as-synthesized low band gap 2D carbon nitrides C_3N_3 and C_3N_5 were investigated using an X-ray diffraction pattern (XRD) which exhibited a distinctive broad reflection at 2θ value 27.2° and 27.6° respectively. These reflections correspond to the (002) plane which is related to the inter-layer reflection of graphite-like stacking in conjugated aromatic segments (C-N). However, the slight increase in the 2θ value for C_3N_5 as compared to g- C_3N_4 could be due to the presence of higher π electron density as already reported in the literature^[310]. Fourier transform infrared (FTIR) spectroscopy spectra were employed to determine the functional groups present in C_3N_5 and C_3N_3 . FTIR spectra for both C_3N_3 and C_3N_5 show a series of distinct bands in the region from 1200 to 1700 cm^{-1} . These could be indexed to C-N stretching of heptazine rings in the aromatic nucleus. There is a prominent peak centered around 775 cm^{-1} which corresponds to the molecular vibrational modes of triazine rings. The broadband in the high-frequency region at around 3400 cm^{-1} could be indexed to symmetric and antisymmetric $-NH_2$ stretching modes. In the case of C_3N_5 , two new peaks emerged at 1073 and 1025 cm^{-1} corresponding to the N-N stretch of azo linkage and $-NH_2$ rocking vibration respectively.^[310] The chemical structure, phase crystallinity, and molecular structure of the as-synthesized conjugated polymers were further characterized using Raman spectroscopy. The Raman spectra for the C_3N_5 sample displayed a sharper G band that could be due to the contribution of the C=N stretching mode. There were also two small peaks observed centered at 1025 and 1160 cm^{-1} . These can be assigned to the mixed vibration of heptazine moiety and azo stretch. Whereas the Raman spectra of C_3N_3 showed a very condensed structure with two peaks

centered at 1320 and 1596 cm^{-1} related to the D and G bands.^[310] The UV-visible spectroscopy was measured to monitor the optical properties. Although the C_3N_5 almost absorbs in the full visible region. The C_3N_3 also showed an extended absorption edge in the visible region with a prominent broad absorption band in the near-visible region around 400 nm. The energy bandgap calculated using DRS spectra showed 2.5 eV to 1.7 eV for C_3N_3 and C_3N_5 respectively.

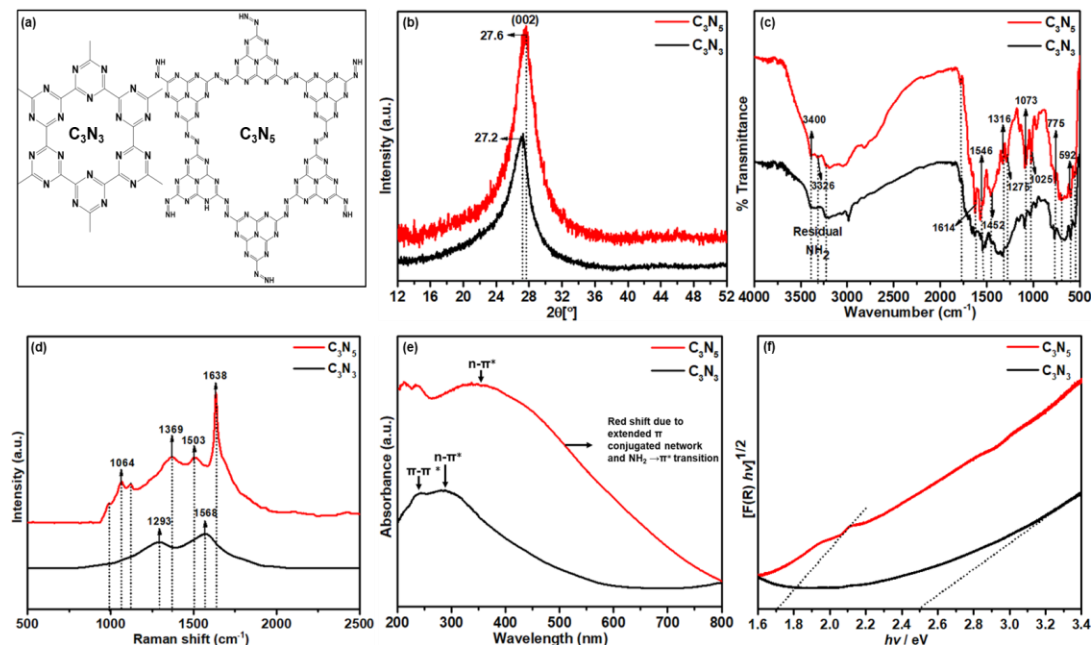


Figure 5. 4 (a) Chemical structure of tri-*s*-triazine-based C_3N_3 and azo linked low band gap C_3N_5 . XRD pattern (b), FTIR spectra (c), Raman spectra (d), DR-UV-Vis spectra (e), and $[F(R)h\nu]^{1/2}$ vs. $h\nu$ plot (f) for C_3N_3 and C_3N_5 .

The microstructural morphology of the samples C_3N_3 and C_3N_5 were investigated by scanning electron microscopy (SEM) as shown in Figure S6. The SEM image (Figure S6a) of the C_3N_3 reveals its layered structure. These layers appear with wrinkled structure as marked by the arrow inside the SEM image (Figure S.14a). The C_3N_5 also clearly indicated the 2D layered structure (Figure S.14b). The 2D layered morphology was further confirmed using high-resolution transmission microscopy (Figure 5.5). The representative TEM

images of C_3N_5 are shown in Figure 5.5 a & b. The zoomed-in TEM image (Figure 5.5b) showed layers stacked onto each other as indicated by steps (marked by arrows). The TEM images for C_3N_3 (Figure 5.5 c & d) also revealed the 2D morphology. The HRTEM data for both C_3N_5 and C_3N_3 do not reflect any lattice fringes. However, it is worth mentioning that as-synthesized C_3N_3 (before washing with mineral acids to remove copper) showed clear lattice fringes (Figure S.15).

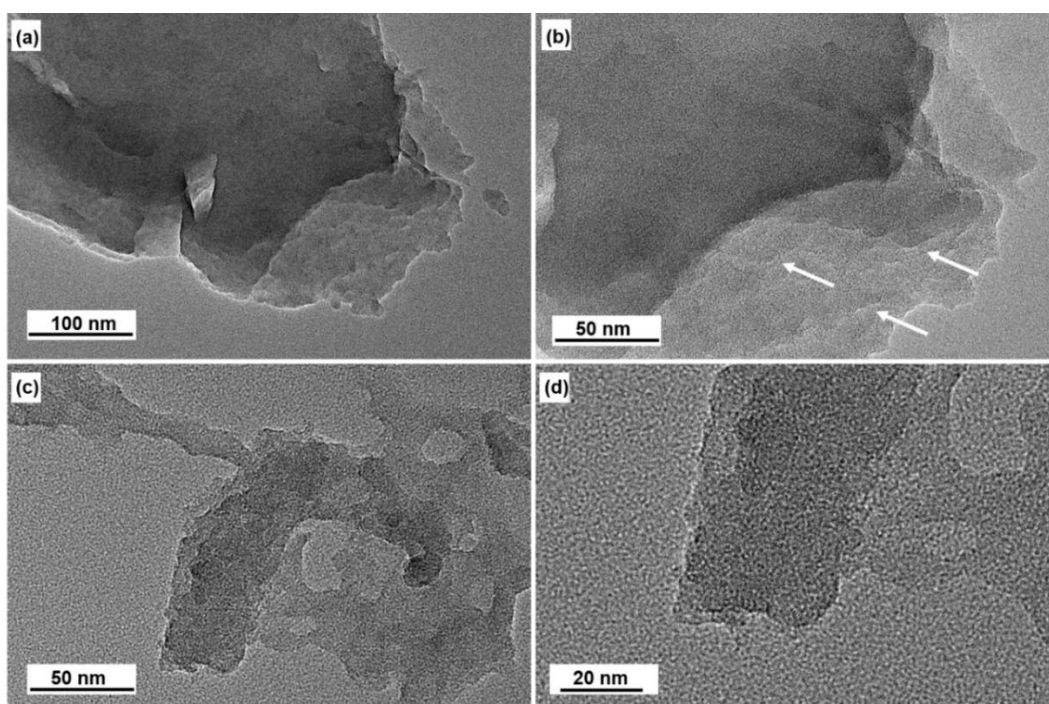


Figure 5. 5. Transmission electron microscopy (TEM) images for the photocatalyst. (a) overview TEM image of C_3N_5 showing the layered structure and (b) high-resolution TEM image indicating the layers stacked as marked by arrows. (c) overview TEM image showing the 2D structure of C_3N_3 and (d) high-resolution TEM image indicating the amorphous nature of C_3N_3 .

The chemical composition and chemical states of different elements in the as-synthesized samples C_3N_3 and C_3N_5 were determined using X-ray photoelectron spectroscopy (XPS) (Figure 5.6 a, b, c & d.). The high-resolution C1s XPS spectrum of C_3N_3 (Figure 5.6a) shows three deconvoluted peak components, in which the peak at 284.8 eV originated

from the sp^3 C-C group which bridge the two triazine ring while the deconvoluted peak observed at 284.6 eV attached to N in aromatic structure (N-C=N). The peaks observed at 289.4 eV were assigned to sp^2 aromatic C attached to C-N₃ or NH₂ group (C-NH₂).³² Similarly, C₃N₅ shows deconvoluted three peaks centered at 283.5, 287.1, and 289.1 eV, corresponding to the graphitic carbon, sp^2 aromatic carbon N-(C)₃ and (N-C=N) or C-NH₂, respectively. The high-resolution XPS of N 1s of C₃N₃ shows two peaks after deconvolution where the predominant peak at ca. 398.12 eV is assigned to sp^2 N percent in triazine rings as C=N-C, while the medium peak at 399.3 eV corresponding to bridging N atoms in N-(C)₃.²⁷ The N 1s spectrum of C₃N₅ shows the three deconvolution peaks at 397.1, 398.8, and 400.5 eV, respectively. The two peaks with a binding energy of 397.1 eV and 398.8 eV were assigned to secondary and tertiary nitrogen present in the aromatic ring structure while 400.5 eV was exhibited to the presence of bridging C-N=N-C type nitrogen and some of the residual primary -NH₂ groups.

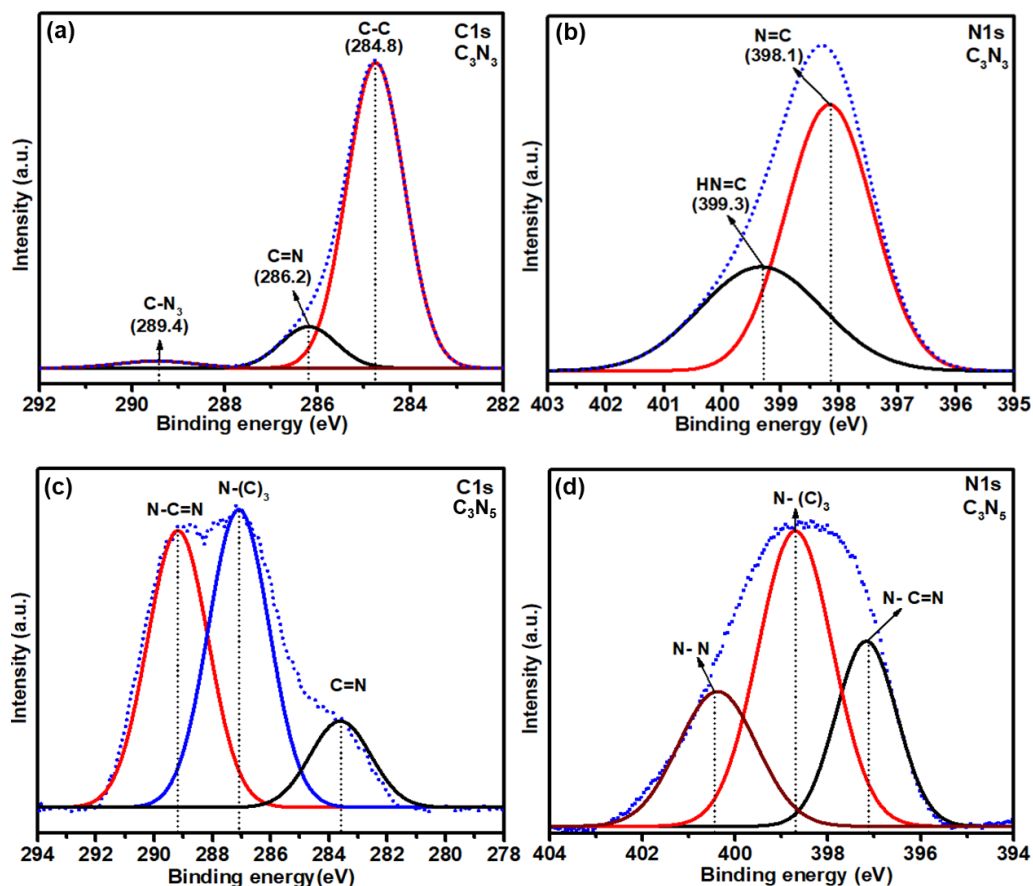


Figure 5. 6. High-resolution XPS spectra of; (a) C 1s and (b) N 1s for C_3N_3 and (c) C 1s and (d) N 1s for C_3N_5 .

We examined the capability of low dimensional carbon nitrides to serve as an interfacial layer in inverted PSCs in a configuration of FTO/ NiO_x/C_3N_x ($x=3, 5$)/CsFAMA/PCBM/BCP/Ag, where CsFAMA denotes triple-cation-based perovskite $[Cs_{0.1}(FA_{0.9}MA_{0.1})_{0.9}Pb(I_{0.9}Br_{0.1})_3]$. The employed device architecture is illustrated (Figure 5.7a) and device fabrication steps are detailed in the experimental section. The control device without an interfacial layer shows a PCE of 16.69% with an open-circuit voltage (V_{oc}) of 1001.89 mV, short-circuit current density (J_{sc}) of 22.79 $mAcm^{-2}$, and fill factor (FF) of 73.07%, (Figure 5.7b and Table 5.1). The PCE of the C_3N_5 incorporated device increased to 17.17%, with a V_{oc} of 1003.48 mV, J_{sc} of 22.52 $mAcm^{-2}$, and noticeably

enhanced FF of 75.95%. Upon C_3N_5 interface layer, a relatively reduced series resistance (R_s) and higher shunt resistance (R_{sh}) were observed (Table S.4). The high R_{sh} can be correlated to synergistically suppressed charge build up and defeated recombination losses at perovskite/ NiO_x interface, which result in high FF detected from the device incorporating C_3N_5 . In contrast, the device with C_3N_3 showed a significantly lower PCE of 10.99%. We hypothesize that the poor interfacial compatibility of C_3N_3 at the NiO_x /CsFAMA interface, leading an undesirable photo-charge transfer at the interface as observed by higher R_s and lower R_{sh} , which results in reduced FF, J_{sc} , and V_{oc} . Undesirable device properties also originated from lower solubility/ complete miscibility of C_3N_3 in the solvent. We further, calculated the hysteresis factor following the equation; $HF = [PCE_{RS} - PCE_{FS}]/PCE_{RS}$, where PCE_{RS} and PCE_{FS} represent the PCE from reverse and forward scans, respectively (Figure S.17 and Table S.5). The HF for the control and C_3N_5 -based devices is 1.4 and 0.82%, respectively, which indicates that the C_3N_5 -based device exhibits a narrow hysteresis. The integrated current densities from incident photon-to-current efficiency (IPCE) spectrum were 21.46, 16.52, and 21.23 $mAcm^{-2}$ for control, with C_3N_3 , and with C_3N_5 devices, respectively (Figure 5.7c), which are in well agreement with J_{sc} values detected from J - V characteristics. Expectedly, the C_3N_3 shows lower performance which is corroborated with the PV properties.

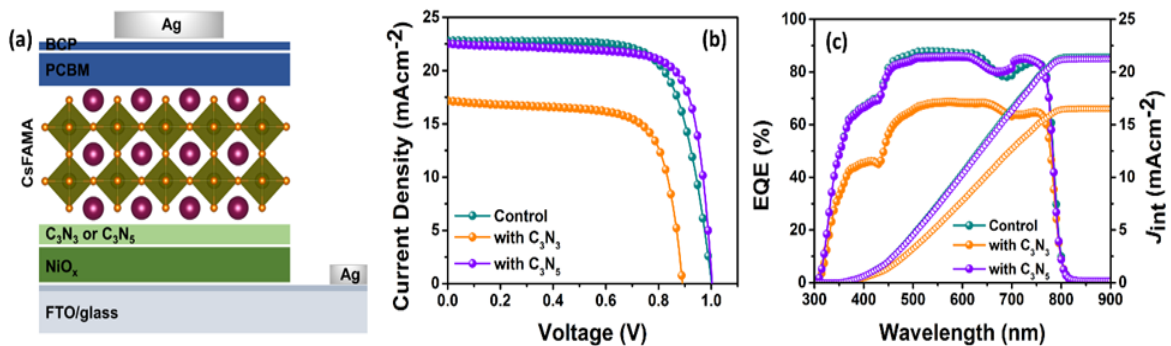


Figure 5. 7 (a) Schematic configuration of PSCs, (b) J-V curves of the champion PSCs employing different interfacial layers, and (c) the corresponding EQE and integrated current densities of the devices.

Table 5. 1. Photovoltaic parameters of the champion devices without and with interfacial layers.

Device	Scan direction	V_{oc} (mV)	J_{sc} (mAcm ⁻²)	FF (%)	PCE (%)
Control	RS	1001.89	22.79	73.07	16.69
	FS	1001.72	22.79	72.04	16.45
with C₃N₃	RS	890.16	17.21	71.74	10.99
	FS	893.74	16.98	69.66	10.57
with C₃N₅	RS	1003.48	22.52	75.95	17.17
	FS	1001.67	22.56	76.62	17.31

5.4 Summary

In conclusion, we have reported the synthesis and characterization of carbon nitride-based 2D materials with compositions C₃N₃ and C₃N₅. The as-synthesized materials are characterized using X-ray diffraction (XRD), SEM, HRTEM, FT-IR, and Raman spectroscopy. The UV-visible and diffused reflectance spectroscopy showed improved optical properties. These metal-free 2D materials are used to engineer the interface between hole transport material and the perovskite layer. Particularly, the device fabricated using low band gap metal free 2D material (C₃N₅), resulted in improving the fill factor and power conversion efficiency (PCE) and open-circuit voltage (V_{oc}) by minimizing the non-radiated recombination of photoexcited charge carriers.

CHAPTER 6

Photoreforming of Biomass Intermediates Integrated with H₂ Fuel Catalyzed by Fabricated C₃N₃ Thin Films on Cu Foil

6.1 Introduction

Lignocellulosic biomass is an easily available and non-fossil fuel based renewable carbon source which can offer the most sustainable alternative source to existing fossil fuel.^[313–315] Amongst, most of the available technologies, photoreforming of lignocellulosic biomass is an emerging as a prominent option due to ease of operation and dual function of its conversion into value added chemicals and green H₂ fuel.^[316–319] However, among the obtained value added chemicals from biomass sources, FDCA have a near future market due to its potential to replace terephthalic acid used in the production of polyethylene terephthalate (PET) plastics.^[320,321] FDCA is also mostly served as an intermediate in the synthesis of other fine chemicals used in pharmaceuticals and agrochemicals industries.^[315,322] In the photoreforming process, FDCA can be obtained from oxidation of 5-Hydroxymethylfurfural (HMF) (intermediate derived from lignocellulosic biomass using isomerization and dehydration of lignocellulosic hexoses sugars).^[317,318,323] The oxidation of HMF taking place using both aldehyde and alcohol group forming FDCA.^[315,320,322] Generally, there are two possible pathways to form FDCA from HMF;^[324] (i) by the oxidation of alcoholic group of HMF forms diformylfuran (DFF) as the initial intermediate, (ii) the oxidation of aldehydic group of HMF can form 5-hydroxymethyl-2-furancarboxylic acid (HMFA) as the initial intermediate.^[325–327] The

both intermediates (DFF and HMFCA) are further oxidized to 5-formyl 2-furancarboxylic acid (FFCA) and the final product FDCA.^[324,327] In electrochemical oxidation of HMF in aqueous electrolyte can offer several significant pros over other conventional oxidation strategies.^[328] Principally, this electrochemical oxidation is driven by the electrochemical applied potential of electrode instead of environmentally harmful chemical oxidants.^[328] Also, the water used in the electrolytic media serves as an oxygen donor to form carboxylic acid from aldehyde and alcohol group of HMF. This is more environmentally friendly because no other chemicals than HMF and water are needed for the formation of FDCA.^[324] In addition, electrochemical oxidation taking place at ambient pressure and temperature can be coupled with the electrochemical reduction, electrons obtained at the anode during HMF oxidation can be concurrently used for the reduction of proton at the cathode leading to the formation of green H₂ fuel, which importantly increases the worth of this approach.^[329,330] The concept of photoelectrochemical reforming of lignocellulosic biomass derived intermediate, HMF into value added product FDCA integrated with H₂ fuel was carried out by Hyun Gil Cha and Kyoung Shin Choi in 2015.^[326] They investigated the possibility of utilizing sun light energy for the oxidation of HMF into FDCA at the n-type BiVO₄ as an photoanode of PEC and 2, 2, 6, 6-tetra methyl-piperidine 1-oxyl (TEMPO) using as an electron mediator achieved > 99% yield of the product (FDCA) with up to 94% Faradic efficiency.^[326,331,332] However, the recyclability of TEMPO and other homogeneous catalysts is not easier. Therefore, the development of photoanode that itself is used as a photocatalyst for the oxidation of HMF can be advantageous.^[326,331] Until now, there are few studies reported using catalytic anode for the electrochemical oxidation of HMF. Among reported catalyst, initially they used noble metals or noble metals alloy such

as Pt, Pd/C, Au/C, PdAu₂/C (highest yield 83% at pH 13) and Pd₂Au/C as anode materials.^[327,328,333–335] Later Sun and coworkers reported various non-noble metals based heterogeneous catalysts ((Ni, Ni₂P, Ni₃S₂, and Co-P) as electrodes that can achieve around 90% yield to form FDCA under pH 14 condition.^[336–339] Although, increase in the pH enhanced the kinetic of HMF oxidation which boosted the rate and yield of FDCA but highly basic environment resulted in the induction of polymerization of HMF into insoluble humins. This substantially decreases the HMF stability under reaction conditions.^[340] Thus, the development of non-noble metal catalysts which can operate well at lower pH because pH 14 may not be a feasible option for industrial scale processes.^[341] More importantly, also required to develop a non-noble metal catalysts that can operate under aqueous conditions and the active species on the anode surface layer is most likely be made of metal oxide or hydroxide are highly appreciated.^[323,341] This needs the deep insight into the catalyst engineering or design of material that is not only stable under the high pH conditions and careful investigation of the active surface layer of the anodic materials is necessary.^[326,330,341] Therefore, in the present study, we report on the excellent performance of photoelectrochemical oxidation of HMF under alkaline conditions into FDCA with concomitant production of H₂. This is achieved using *in-Situ* fabricated artificial leaf from environmentally benign and cheap materials carbon nitride with composition C₃N₃ on the Cu foil. According to the literature reports, during the chemical reactions of water splitting Cu based oxides or hydroxides are not involved in the water oxidation, which is the main reaction that compete with the oxidation of HMF under aqueous conditions. Thus, the use of Cu based oxide or hydroxides may achieve the HMF

oxidation into FDCA with high yield and Faradic efficiency (FE), therefore, the active photocatalyst was in-situ grown onto the copper foil.

6.2 Materials and Methods

6.2.1 Materials

The chemicals HMF (97%, Alfa Aesar), DFF (98%, TCI America), HMFCFA (95%, Oxchem), FFCA (98%, TCI America), FDCA (97%, AstaTech Inc.), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (98%, Sigma-Aldrich), H_2SO_4 (95–98%, Sigma-Aldrich), and KOH (85%, Sigma-Aldrich) were used without further purification. Cu foil used as support for the active catalyst and Cu electrode preparation was purchased from Nimrod Copper Co. (>99.9%, thickness of 0.0254 cm) and Cu woven mesh sheet used for control experiments was purchased from Small Parts (ASTM E2016-06, 41% open area, wire diameter of 0.03048 cm). Deionized water (Barnstead E-pure water purification system, resistivity >18 M Ω cm) was used to prepare the HMF solutions and electrolytes.

6.2.2 Synthesis of C_3N_3

In a typical procedure, we used stainless steel lined reactor system for the synthesis of C_3N_3 2D polymeric material through solid state chemistry (Figure 6.1). Briefly, 2 g of cyanuric chloride and a roll of fresh copper foil (0.05mm thick copper foil cleaned with acetone using ultrasonication for 2 hour) were added to the steel reactor under inert argon atmosphere. The sealed reactor was heated up to 250 °C for 20 hours under Ar atmosphere at a pressure of 20 mega pascals. After the specified time the reactor was cooled down to room temperature and the copper foil having deposited 2D polymeric film was removed and washed with deionized (DI) water. Afterward, the 2D polymeric films were scratched

off from the copper foil using sharp spatula and again washed with ethanol and DI water using ultra-sonication and with subsequent centrifugations for three to four cycles. After centrifugations the obtained solid was dried in and vacuum oven at 80 °C. The obtained yield was ~ 75%. To prepare the C₃N₃ based photoanodes, the similar procedure was adopted except time was 24 hrs to get thin films deposition.

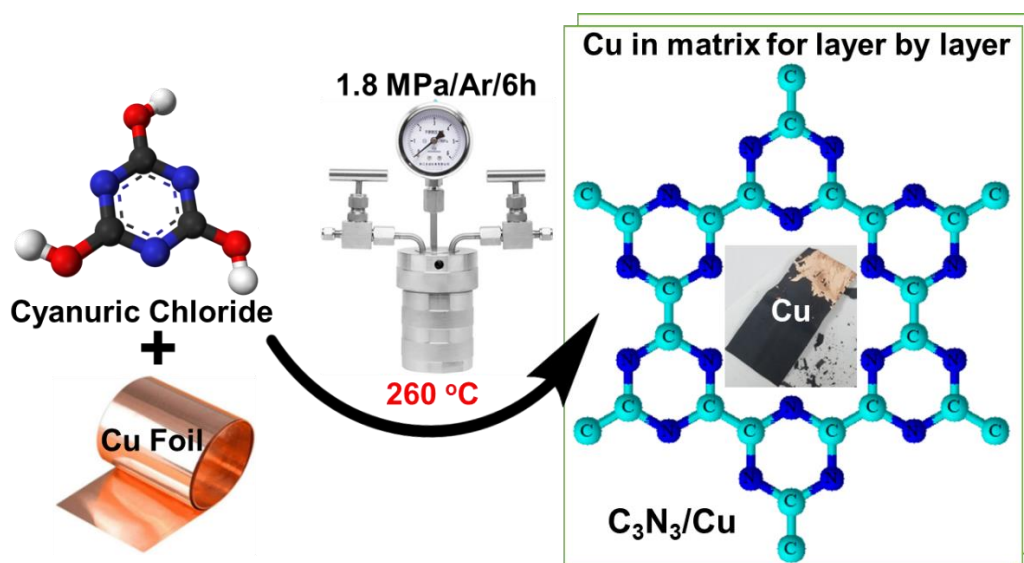
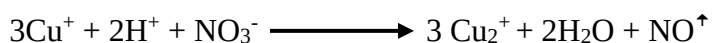


Figure 6. 1. (a) Chemical structure of tri-*s*-triazine-based C₃N₃ and azo linked low band gap C₃N₅. XRD pattern (b), FTIR spectra (c), Raman spectra (d), DR-UV-Vis spectra (e), and [F(R)hν]^{1/2} vs. hν plot (f) for C₃N₃ and C₃N₅.

Removal of copper impurities:

The obtained dried samples were ground to powder using mortar and pestle and transferred to a 100 ml centrifuge vials. The already prepared 80 ml of 10 % HNO₃ aqueous solution was added to the centrifuge vials and ultrasonicated for one hour, followed by centrifugation to wash the copper impurities. The above step was repeated three to four times to ensure that there were no bubbles generated. The aqueous solution turns from deep green to bluish color.



Afterwards, product was washed with 10 % HCl using ultrasonic bath for 2 hours, followed by centrifugation (4000) using ethanol and DI water for three cycles. After centrifugation, the obtained solid product was dried in vacuum oven at 80 °C. The o yield was ~47%. The overall, procedure for the work-up is shown in Figure 6.2.

It is worth mentioning that the cleaned solid powder was used as reference material for the *in-situ* synthesized C_3N_3 photoanodes. These anodes were tested further without any washing treatment with acids. These may contain Cu atoms cleated in the C_3N_3 . Therefore, these were represented as $\text{C}_3\text{N}_3/\text{Cu}$.

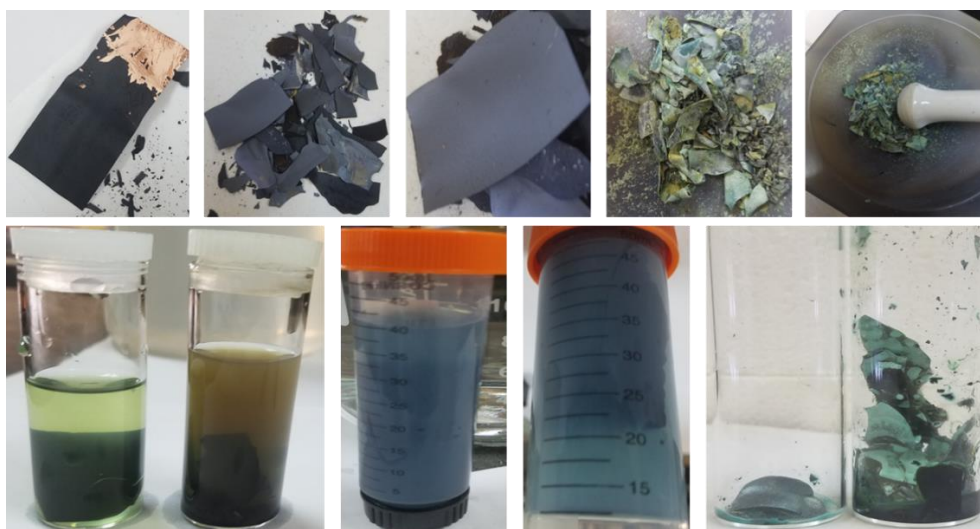


Figure 6. 2: Various steps for the washing of the as prepared C_3N_3 .

6.3 Results and Discussion

The structure and crystalline nature of as the synthesized 2D carbon nitride C_3N_3 and $\text{C}_3\text{N}_3/\text{Cu}$ were investigated by X-ray diffraction pattern (XRD) which exhibited a distinctive broad reflection at the 2θ value 27.2° corresponding to the (002) reflection of

C_3N_3 , whereas reflection at $2\theta = 45.3^\circ$ (111) and 52.4° (200) represent the presence of Cu in the crystal structure (Figure 6.3a). The broad reflection at 2θ value 27.2° C_3N_3 correspond to the (002) typical inter layer reflection of graphite like stacking in conjugated aromatic segments (C-N). The chemical structure, phase crystallinity and molecular structure of the as synthesized conjugated polymers were also characterized using Raman spectroscopy. The Raman spectra of C_3N_3 and C_3N_3/Cu showed very condensed structure with two peaks centered at 1320 cm^{-1} , 1600 cm^{-1} , 1410 cm^{-1} and 1573 cm^{-1} related to the D and G bands respectively (Figure 6.3b).^[310] Fourier transform infrared (FTIR) spectroscopy spectra was employed to determine its change in the functional moiety in C_3N_3 (Figure 6.3c). FTIR spectra shows a series of distinct bands in the region from 1200 to 1700 cm^{-1} . These could be indexed to C-N stretching of heptazine rings and a prominent peak of typical triazine rings with molecular vibrational modes at approximately around 775 cm^{-1} . The broad band at high frequency region around 3400 cm^{-1} indexed to symmetric and antisymmetric $-NH_2$ stretching modes. The UV-visible spectroscopy was employed to monitor the optical properties. Although the C_3N_3 showed only absorption in the near visible region with broad absorption band around 500 nm . The energy bandgap calculated for C_3N_3 using DRS spectra was 2.3 eV (Figure 6.3d).

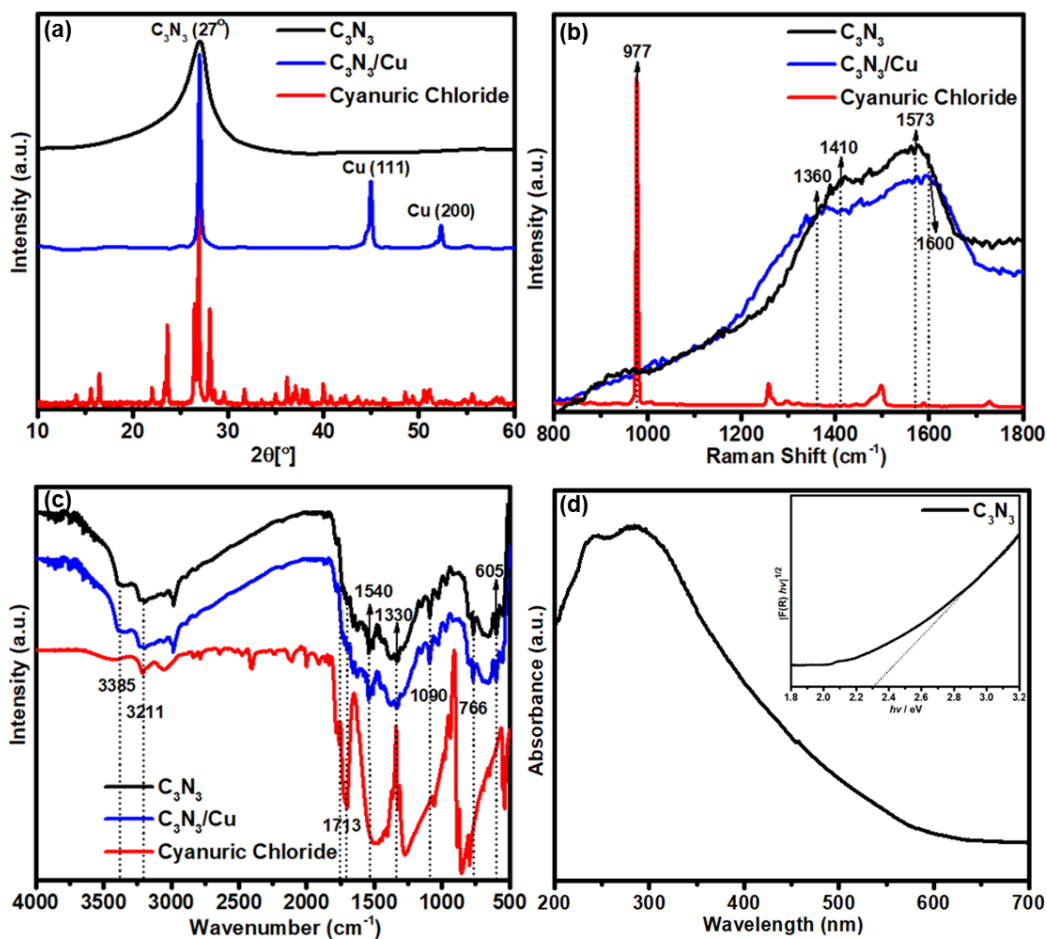


Figure 6. 3. (a) XRD pattern (b), Raman spectra (c), FTIR spectra (d), DR-UV-Vis spectra and $[F(R)h\nu]^{1/2}$ vs. $h\nu$ plot for C_3N_3 .

Chemical composition and chemical states of the as synthesized samples C_3N_3 and C_3N_5 were determined by using XPS (Figure 6.4). The XPS spectra depicts its chemical composition in the collected survey spectra. The only prominent peaks observed in the survey spectra of (Figure 6.4, black line) correspond to the C, N and O for C_3N_3 (Note: the atomic ratio of O is basically coming from the substrate used during the XPS analysis). The XPS spectrum of C_3N_3 shows the presence of C and N with atomic ratio after background correlation around 2.8:3 which roughly correspond to the chemical formula C_3N_3 .

The high-resolution C1s XPS spectrum of C₃N₃ (Figure 6.4a) shows three deconvoluted peak components, in which the peak at 284.8 eV originated from sp³ C-C group which bridge the two triazine ring while deconvoluted peak observed at 284.6 eV attached to N in aromatic structure (N-C=N). The peaks observed at 289.4 eV were assigned to sp² aromatic C attached to C-N₃ or NH₂ group (C-NH₂).³² The XPS spectrum of N 1s in pure C₃N₃ (Figure 6.4b) showed a deconvolution bigger peak at 398.1 eV and a broader peak at 399.3 eV corresponding to the N=C and H-N=C respectively.

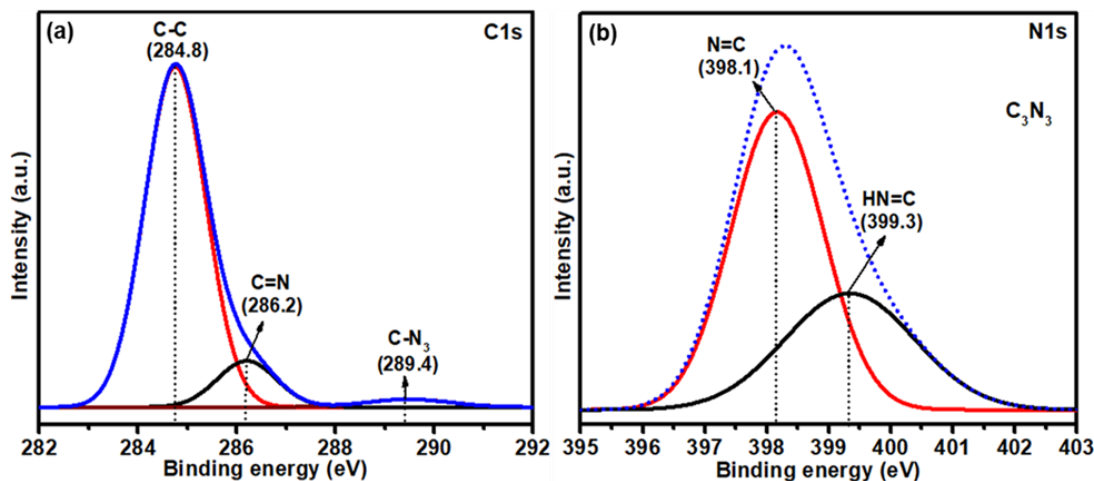


Figure 6. 4. High-resolution XPS spectra's of C1s and N1s of C₃N₃

The microstructural morphology of the as synthesized samples C₃N₃ were investigated using transmission electron microscopy (TEM). The TEM images of C₃N₃ reveals its layered and agglomerated structure (Figure 6.5a). After washing and long term ultrasonication, one can see exfoliated 2D sheets in the micrometer size range (Figure 6.5b). The High-resolution transmission electron microscopy image (Figure 6.5c) confirms the crystallinity and *d*-spacing 0.31 nm corresponding to (001) reflection can be indexed. The fast fourier transform (FFT) also confirms the structure of C₃N₃.

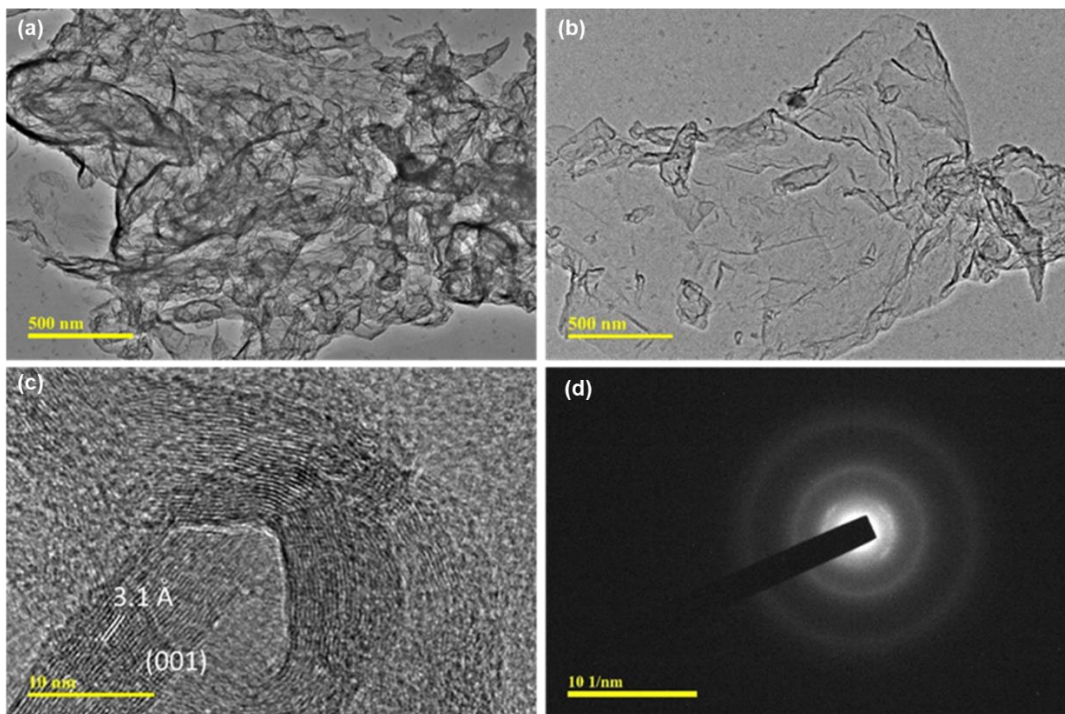


Figure 6. 5 The TEM images of the Cu containing C_3N_3 (a) overview, (b) TEM image showing very thin layers, (c) HRTEM image showing the d-spacing and (d) FFT showing the (001) plane.

Based on the elemental analysis, the empirical formula of the product can be calculated as CN. The C/N atomic ratio in the product was approximately 1:1 (wt% of C 37, wt% of N 36, which agrees with the $(CN)_n$ stoichiometry (Extracted empirical formula $CN_{0.98}$).

The as fabricated electrodes were tested for the photoelectrochemical reforming performance to selectively convert intermediate of biomass HMF into value added product FDCA and green H_2 fuel. For this purpose, we used a three-electrode system under AM 1.5 G illumination. The obtained PEC reforming results are presented in Figure 6.6. The data was collected using 1 M KOH solution using basic electrolyte. In Figure 6.6a & b linear sweep voltammetry (LSV) PEC reforming of 10 mM HMF solution shows the boosted photocurrent density verses voltage against reversible hydrogen electrode (RHE).

There is pronounced effect on the photocurrent upon the inclusion of HMF solution for the as-prepared *in-situ* fabricated photo-electrodes of C₃N₃/Cu foil (Figure 6.6b) under light illumination as compared to without HMF inclusion (0.55 A/cm²) and with addition of HMF the current density boosted into 0.82 A/cm² at voltage 1.9 vs RHE but in onset to low potential to 1.22 V vs. RHE show that there is oxidation of HMF taking place which was further confirmed by HPLC. The photoelectrode prepared from pristine C₃N₃ resulted in very small photocurrent under light (Figure 6.6b, blue line). It is worth mentioning that pristine C₃N₃ electrodes were fabricated on to FTO glass using drop casting from ink formed in ethanolic solution. The Nafion was used as binder. The catalytic current shown in LSV confirmed the occurrence of the oxygen evolution reaction. The addition of 20 mM of HMF shifts the current catalytic onset to low potential to 1.22 V vs. RHE., which indicates that photo-electrodes of C₃N₃/Cu foil could preferably catalyze the oxidation of HMF at a lower potential compared to the one required for OER in the basic medium. The catalytic current density improved dramatically after 1.22 V. It reached a 20 mA/cm² current density at 1.22 V vs. RHE, less than water oxidation. It ought to be noticed that the photo-electrodes of C₃N₃/FTO was less active compared to the HMF oxidation using photo-electrodes of C₃N₃/Cu foil shown in (Figure S. 19).

There are two-potential pathway for HMF PEC oxidation to FDCA. The first path is via the initial oxidation of the aldehyde to yield HMFCFA as an intermediate product, while the second path proceeds by the initial oxidation of alcohol to obtain DFF. The latter is unfavorable. The two pathways converge at the formation of FFCA before the final FDCA product. To recognize and evaluate the final product and oxidation intermediates of HMF oxidation and decide the Faradaic efficiencies. The photo-electrodes of C₃N₃/Cu foil -

catalyzed HMF oxidation was performed at an applied potential of 1.22 V vs. RHE in 20.0 mL of 1.0 M KOH as the supporting electrolyte and with 20 mM of HMF substrate. The transformation of all the HMF to FDCA needs around 40.53 Coulomb charges in 22 hours, if 100% Faradaic efficiency is to be accomplished. High performance liquid chromatography (HPLC) with a UV detector was used to monitor the reaction after PEC reforming. The Figure 6.6b shows the oxidation of HMF to the final main product FDCA during PEC reforming. The HPLC spectra shows that increase in the final formation product FDCA and the decline of the HMF over time. After passing the charge of approximately 40.53 Coulomb, the HPLC trace of HMF disappeared even though FDCA increased to the highest value, which indicated the total transformation of HMF.

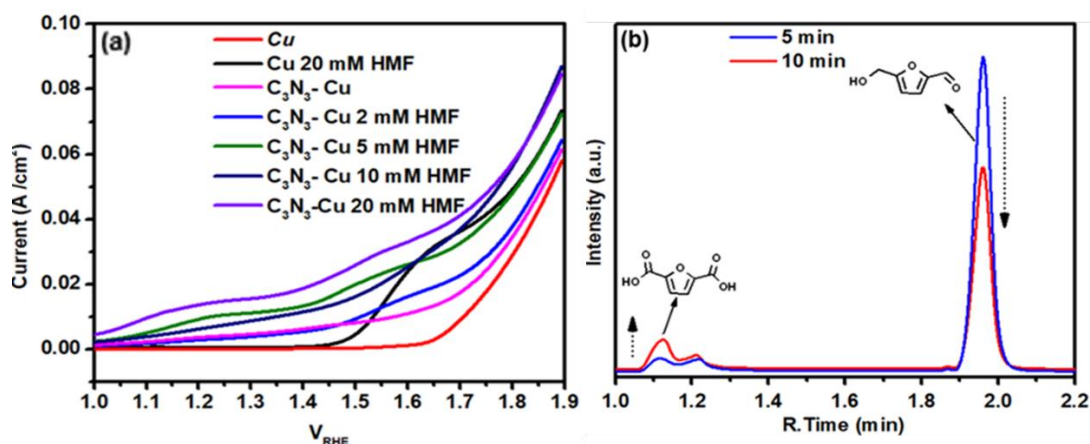


Figure 6. 6: (a) LSV polarization curves of in-situ electrode of C₃N₃, in 1 M KOH aqueous electrolyte under visible light irradiation for hydrogen evolution reactions with HMF on different ratio (b) HPLC data of in-situ electrode of C₃N₃ with HMF selective conversion in to FDCA.

A possible mechanism is illustrated in Figure 6.7 which radical species are first produced by the oxidation and deprotonation of the formyl group in intermediate of biomass as HMF. The carbon atom is then further oxidized, and the O atom in H₂O attacks it to form carboxylate. The photo-electrodes of C₃N₃/Cu foil plays a vital role in the reaction

mechanism through a surface phase change and surface structure with a high surface-area-to-volume ratio, making photo-electrodes of C_3N_3/Cu foil an efficient catalyst in basic conditions. It is worth mentioning that the active site in the photo-electrode C_3N_3/Cu foil offered a high surface area for both the substrate and the product. The Figure 6.7 demonstrates the proposed mechanistic pathway to produce FDCA from HMF. The hydroxide ions attach the carbonyl group to the HMF side by a nucleophilic addition reaction. The formation of geminal diol took place via hydration after a proton departed from the aldehydic group of HMF molecules. Due to large hydroxyl groups adsorbed on the surface of photo-electrodes of C_3N_3/Cu foil, as a result dehydrogenation of diol occurs to form the carboxylic group. From that point, the other alcohol part was dehydrogenated due to the deprotonated reaction by the base. The C-H bond activation occurred due to the hydroxide ion and the aldehyde group formation over photoanode. On the other hand, the formed protons is reduced into H_2 fuel over cathode. Thus, in overall reaction photoreforming of biomass intermediates taking place integrated with H_2 fuel catalyzed by fabricated C_3N_3 thin films on Cu foil.

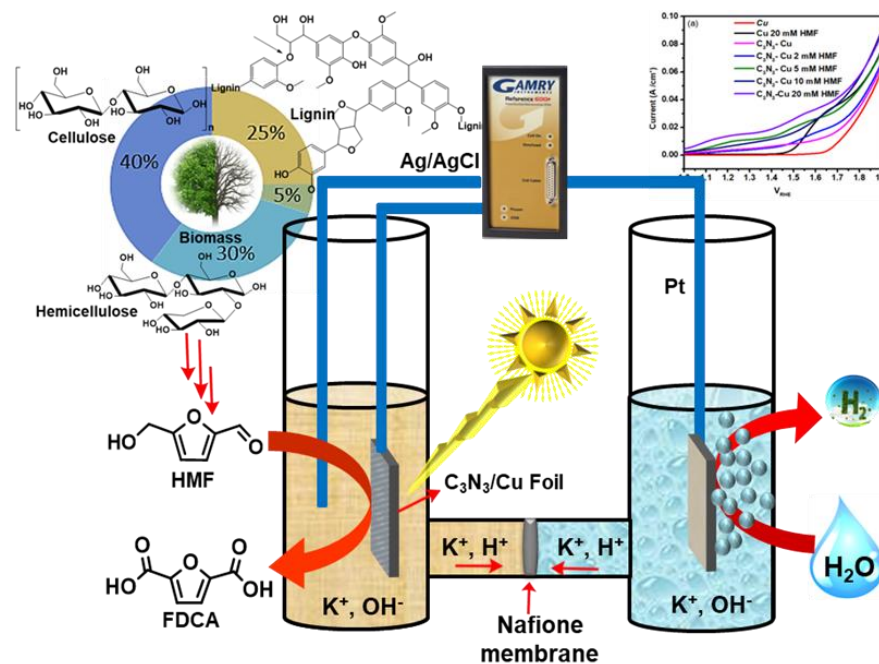


Figure 6. 7: Schematic illustration of the proposed mechanism showing enhanced photocatalytic activity is due to the effective transfer of photoexcited interfacial charge (electron) from C_3N_3 to the surface for HMF into FDCA.

6.4 Summary

In conclusion, the facilely synthesized C_3N_3 on Cu foil nanocomposite served as efficient photocatalysts for photoelectrochemical oxidation of HMF under alkaline conditions into FDCA with concomitant production of H_2 is demonstrated by using in-Situ fabricated artificial leaf of environmentally benign and cheap materials carbon nitride C_3N_3 on Cu foil. According to literature, during the chemical reactions of water splitting Cu based oxides or hydroxides are not involves in water oxidation, which is the main reaction that compete with oxidation of HMF in aqueous solutions. Thus, the use of Cu based oxide or hydroxides may achieve the HMF oxidation into FDCA with high yield and Faradic efficiency (FE).

CHAPTER 7

Conclusions and Future Recommendations

We have reported various bandgap engineered 2D C_3N_x (where $x = 3,4,5$) based nanocomposites with 2D materials such as highly reduced graphene oxide (HRG) and non-noble metal-based co-catalysts for efficient solar energy harvesting applications. The synthesis was optimized, and characterizations were carried out at all length scales using different microscopic, spectroscopic and X-ray based techniques. Some of the main conclusions are provided as follow:

Firstly, the uncondensed form of polymeric carbon nitrides (PCN), which is a stacked two-dimensional poly(aminoimino)heptazine, and generally known as melon $[C_6N_7(NH_2)(NH)]_n$ was synthesized. The PCN has sparked the interest of researchers since 2009 as photocatalysts due to its earth-abundant metal-free and environmentally friendly nature. But its low photoconversion efficiency due to fast charge recombination, high activation energy and low separation of photoexcited charge carriers are the significant limitations. Here we report the experimental as well as theoretical studies of melon (PCN), and its nanocomposite with highly reduced graphene (HRG) to enhance the lifetime of photoexcited charge carriers by lowering the activation energy. HRG@melon displays an around 20 times enhancement of photocurrent density over pure melon in alkaline conditions as well as improved stability over a wide pH range. The addition of hole scavenger jumped photocurrent density from $71 \mu A cm^{-2}$ to $630 \mu A cm^{-2}$ at 1.23V versus reversible hydrogen electrode (RHE). The structure and morphology of the individual

components (HRG & HRG@melon) are confirmed using microscopic (write names of techniques) and spectroscopic analytical techniques (names of techniques). The photocurrent generation of the fabricated photoelectrodes and first density functional calculations revealed that the addition of HRG produce an intrinsic chemical and electronic coupling, which synergistically promotes the separation of photogenerated electrons and averts the electron-hole pairs of melon from recombination due to more proton adsorption and reduction kinetics.

Secondly, carbon nitrides based 2D materials with composition C_3N_3 are synthesized. These materials have been recently explored as photocatalysts due to their unique optoelectronic properties. However, these materials require strategies to improve their photoconversion efficiencies by improving the separation of photoexcited charge carriers and minimizing the charges recombination. Therefore, it requires strategies to improve the efficiencies. Here in this publication, we report on the synthesis of 2D carbon nitride with formula C_3N_3 decorated with non-noble metal nickel phosphide (Ni_2P) co-catalyst-based nanocomposites (C_3N_3/Ni_2P) for the enhanced photoelectrochemical water splitting. There is significant enhancement in the photocurrent ($43 \mu A/cm^2$) measured from the photoelectrodes prepared from Ni_2P/C_3N_3 in comparison to the photo-electrodes fabricated from pristine C_3N_3 ($23 \mu A/cm^2$) under 1 sun light irradiation. Experimental investigations demonstrated that Ni_2P co-catalyst made suitable band alignments to improve the intimate interface of electric field to accelerate the charge transfer of the excited electrons from C_3N_3 to Ni_2P and enhanced the separation of the photoexcited charge carriers effectively. Moreover, C_3N_3/Ni_2P nanocomposites are low cost, naturally abundant, and environmentally friendly.

Thirdly, we have performed the interfacial engineering that could effectively improve the perovskite device performance by suppressing the non-radiative recombination. The inherited ionic and hydrophilic nature of most of the semiconducting materials used for the hole transport layer (HTL) in perovskite solar cells (PSCs) makes it susceptible to moisture. This is one of the factors that compromises the long term durability of PSCs. Therefore, interfacial engineering of HTL in the PSCs ensures enhanced efficiency and long-term stability. In this contribution, here we report the synthesis and characterization of polymeric carbon nitride based 2D materials with composition C_3N_x (where $x = 3$ or 5) and their application as an interfacial layer between HTL and perovskite layer in the inverted PSCs. We introduced these 2D polymeric materials to align the energy levels between the HTL and perovskite by applying them as an interfacial layer in PSCs. This minimizes the voltage deficit that ultimately improved the power conversion efficiency (PCE). The interlayer suppressed the interfacial charge accumulation at the grain boundaries of perovskites and lowered the non-radiative recombination, which results in amplified fill factor (FF). Upon using the C_3N_5 at the inorganic NiO_x HTL interface an increased PCE of >17% is recorded.

Finally, photoelectrochemical reforming of lignocellulosic biomass derived intermediate, 5-hydroxymethylfurfural (HMF) was converted into the value added product 2,5 furandicarboxylic acid (FDCA) integrated with H_2 fuel that was carried out over *in-situ* fabricated artificial leaf of carbon nitride C_3N_3 on Cu foil. Notably, the concurrent production of H_2 fuel was realized upon irradiation of one sunlight under ambient conditions utilizing these lignocellulosic biomass intermediates (HMF) as a source of proton. This used up the waste hole during water splitting through oxidation of HMF into

FDCA. In fact, FDCA is a key near-market chemical platform that can potentially replace terephthalic acid used in the synthesis of non-degradable plastic or polyesters polyethylene terephthalate (PET). In the present study, the photoelectrochemical oxidation of HMF under alkaline conditions into FDCA with concomitant production of H_2 is demonstrated by using in-Situ fabricated artificial leaf of carbon nitride C_3N_3 on Cu foil.

References

- [1] P. E. Brockway, A. Owen, L. I. Brand-Correa, L. Hardt, *Nat. Energy* **2019**, 4, 612.
- [2] T. Ahmad, D. Zhang, *Energy Reports* **2020**, 6, 1973.
- [3] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.* **2006**, 103, 15729.
- [4] K. T. Møller, T. R. Jensen, E. Akiba, H. wen Li, *Prog. Nat. Sci. Mater. Int.* **2017**, 27, 34.
- [5] Y. Tachibana, L. Vayssieres, J. R. Durrant, *Nat. Photonics* **2012**, 6, 511.
- [6] R. de Richter, T. Ming, P. Davies, W. Liu, S. Caillol, *Prog. Energy Combust. Sci.* **2017**, 60, 68.
- [7] J. G. J. Olivier, J. A. H. W. Peters, *Trends in Global CO₂ and Total Greenhouse Gas Emissions 2019 Report*, **2020**.
- [8] Global Energy & CO₂ Status Report 2019 – Analysis - IEA, <https://www.iea.org/reports/global-energy-co2-status-report-2019/emissions>,
- [9] D. M. Sigman, M. P. Hain, G. H. Haug, *Nature* **2010**, 466, 47.
- [10] J. R. Petit, J. Jouzel, D. Raynaud, N. I. Barkov, J. M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V. M. Kotiyakov, M. Legrand, V. Y. Lipenkov, C. Lorius, L. Pépin, C. Ritz, E. Saltzman, M. Stievenard, *Nature* **1999**, 399, 429.
- [11] U. Siegenthaler, T. F. Stocker, E. Monnin, D. Lüthi, J. Schwander, B. Stauffer, D. Raynaud, J. M. Barnola, H. Fischer, V. Masson-Delmotte, J. Jouzel, *Science (80-.)*. **2005**, 310, 1313.
- [12] N. Norouzi, S. Talebi, A. Shahbazi, *Chem Rev Lett* **2020**, 3, 7.
- [13] Y. J. Sa, C. W. Lee, S. Y. Lee, J. Na, U. Lee, Y. J. Hwang, *Chem. Soc. Rev.* **2020**, 49, 6632.
- [14] A. R. Shaikh, M. Ashraf, T. AlMayef, M. Chawla, A. Poater, L. Cavallo, *Chem. Phys. Lett.* **2020**, 745, 137239.
- [15] T. M. L. Wigley, R. Richels, J. A. Edmonds, *Nature* **1996**, 379, 240.
- [16] R. Yuan, P. Behrens, A. Tukker, J. F. D. Rodrigues, *Energy Policy* **2018**, 119, 97.
- [17] N. Norouzi, M. Fani, Z. K. Ziarani, *J. Pet. Sci. Eng.* **2020**, 188, 106827.
- [18] B. Lin, M. Y. Raza, *Energy* **2020**, 200, 117575.

- [19] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15729.
- [20] S. Shafiee, E. Topal, *Energy Policy* **2009**, *37*, 181.
- [21] M. S. Dresselhaus, I. L. Thomas, *Nature* **2001**, *414*, 332.
- [22] J. Murray, D. King, *Nature* **2012**, *481*, 433.
- [23] N. A. Owen, O. R. Inderwildi, D. A. King, *Energy Policy* **2010**, *38*, 4743.
- [24] D. Rutledge, *Int. J. Coal Geol.* **2011**, *85*, 23.
- [25] X. Jiao, K. Zheng, L. Liang, X. Li, Y. Sun, Y. Xie, *Chem. Soc. Rev.* **2020**, *49*, 6592.
- [26] N. Pariona, A. I. Martinez, H. M. Hdz-García, L. A. Cruz, A. Hernandez-Valdes, *Saudi J. Biol. Sci.* **2017**, *24*, 1547.
- [27] T. Kong, Y. Jiang, Y. Xiong, *Chem. Soc. Rev.* **2020**, *49*, 6579.
- [28] M. Ashraf, I. Khan, M. Usman, A. Khan, S. S. Shah, A. Z. Khan, K. Saeed, M. Yaseen, M. F. Ehsan, M. N. Tahir, N. Ullah, *Chem. Res. Toxicol.* **2020**, *33*, 1292.
- [29] F. Dellano-Paz, A. Calvo-Silvosa, S. Iglesias Antelo, I. Soares, *Renew. Sustain. Energy Rev.* **2015**, *48*, 49.
- [30] O. Edenhofer, K. Seyboth, F. Creutzig, S. Schlömer, *Annu. Rev. Environ. Resour.* **2013**, *38*, 169.
- [31] A. G. Olabi, M. A. Abdelkareem, *Renew. Sustain. Energy Rev.* **2022**, *158*, 112111.
- [32] F. Cherubini, *Energy Convers. Manag.* **2010**, *51*, 1412.
- [33] M. Singh, G. Leena, in *Sustain. Waste Manag. Policies Case Stud.*, Springer Singapore, **2020**, pp. 267–278.
- [34] N. Armaroli, V. Balzani, *Angew. Chemie Int. Ed.* **2007**, *46*, 52.
- [35] N. Armaroli, V. Balzani, *Angew. Chemie Int. Ed.* **2007**, *46*, 52.
- [36] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* **2010**, *110*, 6446.
- [37] Y. Sang, H. Liu, A. Umar, *ChemCatChem* **2015**, *7*, 559.
- [38] B. Cocilovo, A. Hashimura, D. J. Tweet, T. Voutsas, R. A. Norwood, *Appl. Opt.* **2015**, *54*, 8990.
- [39] “Climate Science Investigations South Florida - Energy: The Driver of Climate,”

can be found under <http://www.ces.fau.edu/nasa/module-2/radiation-sun.php>, **n.d.**

- [40] M. Ashraf, I. Khan, M. Usman, A. Khan, S. S. Shah, A. Z. Khan, K. Saeed, M. Yaseen, M. F. Ehsan, M. N. Tahir, N. Ullah, *Chem. Res. Toxicol.* **2020**, acs.chemrestox.9b00308.
- [41] M. Ashraf, I. Khan, N. Baig, A. H. Hendi, M. F. Ehsan, N. Sarfraz, *Energy Technol.* **2021**, 2100034.
- [42] D. G. Nocera, *Acc. Chem. Res.* **2017**, 50, 616.
- [43] H. B. Gray, *Nat. Chem.* **2009**, 1, 7.
- [44] E. Kabir, P. Kumar, S. Kumar, A. A. Adelodun, K. H. Kim, *Renew. Sustain. Energy Rev.* **2018**, 82, 894.
- [45] M. A. Green, A. Ho-Baillie, H. J. Snaith, *Nat. Photonics* 2014 87 **2014**, 8, 506.
- [46] A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2008**, 38, 253.
- [47] Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, M. Zhong, C. Wang, Z. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. Li, I. D. Sharp, A. Kudo, T. Yamada, K. Domen, *Nat. Mater.* 2016 156 **2016**, 15, 611.
- [48] C. Sharma, P. D., A. Thakur, Y. S. Negi, *ECS Adv.* **2022**, 1, 030501.
- [49] X. B. Li, C. H. Tung, L. Z. Wu, *Nat. Rev. Chem.* 2018 28 **2018**, 2, 160.
- [50] A. Fujishima, K. Honda, *Nature* **1972**, 238, 37.
- [51] Y. Yamada, T. Miyahigashi, H. Kotani, K. Ohkubo, S. Fukuzumi, *J. Am. Chem. Soc.* **2011**, 133, 16136.
- [52] S. Min, G. Lu, *J. Phys. Chem. C* **2012**, 116, 19644.
- [53] C. Wang, S. Cao, W. F. Fu, *Chem. Commun.* **2013**, 49, 11251.
- [54] R. Abe, K. Sayama, K. Domen, H. Arakawa, *Chem. Phys. Lett.* **2001**, 344, 339.
- [55] G. Zhang, Z. A. Lan, L. Lin, S. Lin, X. Wang, *Chem. Sci.* **2016**, 7, 3062.
- [56] H. Lyu, T. Hisatomi, Y. Goto, M. Yoshida, T. Higashi, M. Katayama, T. Takata, T. Minegishi, H. Nishiyama, T. Yamada, Y. Sakata, K. Asakura, K. Domen, *Chem. Sci.* **2019**, 10, 3196.
- [57] D. Gömpel, M. N. Tahir, M. Panthöfer, E. Mugnaioli, R. Brandscheid, U. Kolb, W. Tremel, *J. Mater. Chem. A* **2014**, 2, 8033.
- [58] S. Chen, Y. Qi, T. Hisatomi, Q. Ding, T. Omohiro Asai, Z. Li, S. Su, K. Ma, F.

- Zhang, K. Domen, C. Li, *Angew. Chemie* **2015**, *127*, 8618.
- [59] M. A. Lange, I. Khan, P. Opitz, J. Hartmann, M. Ashraf, A. Qurashi, L. Prädell, M. Panthöfer, A. Cossmer, J. Pfeifer, F. Simon, M. von der Au, B. Meermann, M. Mondeshki, M. N. Tahir, W. Tremel, *Adv. Mater.* **2021**, *33*, 2007434.
- [60] M. A. Lange, I. Khan, R. Dören, M. Ashraf, A. Qurashi, L. Prädell, M. Panthöfer, M. von der Au, A. Cossmer, J. Pfeifer, B. Meermann, M. Mondeshki, M. N. Tahir, W. Tremel, *Dalt. Trans.* **2021**, *50*, 6528.
- [61] S. Chandrasekaran, L. Yao, L. Deng, C. Bowen, Y. Zhang, S. Chen, Z. Lin, F. Peng, P. Zhang, *Chem. Soc. Rev.* **2019**, *48*, 4178.
- [62] H. Xu, J. Yi, X. She, Q. Liu, L. Song, S. Chen, Y. Yang, Y. Song, R. Vajtai, J. Lou, H. Li, S. Yuan, J. Wu, P. M. Ajayan, *Appl. Catal. B Environ.* **2018**, *220*, 379.
- [63] J. G. Cai, Z. T. Yu, Y. J. Yuan, F. Li, Z. G. Zou, *ACS Catal.* **2014**, *4*, 1953.
- [64] E. D. Cline, S. E. Adamson, S. Bernhard, *Inorg. Chem.* **2008**, *47*, 10378.
- [65] Q. Wang, C. Pornrungrroj, S. Linley, E. Reisner, *Nat. Energy* **2021**, *71*, 13.
- [66] X. Tao, Y. Zhao, S. Wang, C. Li, R. Li, *Chem. Soc. Rev.* **2022**, *51*, 3561.
- [67] D. Spetter, M. N. Tahir, J. Hilgert, I. Khan, A. Qurashi, H. Lu, T. Weidner, W. Tremel, *ACS Sustain. Chem. Eng.* **2018**, *6*, 12641.
- [68] E. I. Epelle, K. S. Desongu, W. Obande, A. A. Adeleke, P. P. Ikubanni, J. A. Okolie, B. Gunes, *Int. J. Hydrogen Energy* **2022**, *47*, 20398.
- [69] M. R. Shaner, H. A. Atwater, N. S. Lewis, E. W. McFarland, *Energy Environ. Sci.* **2016**, *9*, 2354.
- [70] M. Mansha, T. Ahmad, N. Ullah, S. Akram Khan, M. Ashraf, S. Ali, B. Tan, I. Khan, *Chem. Rec.* **2022**, e202100336.
- [71] X. B. Li, C. H. Tung, L. Z. Wu, *Nat. Rev. Chem.* **2018**, *2*, 160.
- [72] H. Bin Yang, J. Miao, S. F. Hung, F. Huo, H. M. Chen, B. Liu, *ACS Nano* **2014**, *8*, 10403.
- [73] H. Ou, P. Yang, L. Lin, M. Anpo, X. Wang, *Angew. Chemie* **2017**, *129*, 11045.
- [74] K. Sivula, R. Van De Krol, *Nat. Rev. Mater.* **2016**, *1*, 1.
- [75] D. V. Esposito, J. B. Baxter, J. John, N. S. Lewis, T. P. Moffat, T. Ogitsu, G. D. O'Neil, T. A. Pham, A. A. Talin, J. M. Velazquez, B. C. Wood, *Energy Environ. Sci.* **2015**, *8*, 2863.

- [76] G. Ma, T. Hisatomi, K. Domen, in *From Mol. to Mater. Pathways to Artif. Photosynth.*, Springer International Publishing, **2015**, 1–56.
- [77] M. S. Wrighton, A. B. Ellis, P. T. Wolczanski, D. L. Morse, H. B. Abrahamson, D. S. Ginley, *J. Am. Chem. Soc.* **1976**, *98*, 2774.
- [78] C. W. Huang, C. H. Liao, J. C. S. Wu, Y. C. Liu, C. L. Chang, C. H. Wu, M. Anpo, M. Matsuoka, M. Takeuchi, *Int. J. Hydrogen Energy* **2010**, *35*, 12005.
- [79] S. U. M. Khan, M. Al-Shahry, W. B. Ingler, *Science* . **2002**, *297*, 2243.
- [80] S. Licht, B. Wang, S. Mukerji, T. Soga, M. Umeno, H. Tributsch, *J. Phys. Chem. B* **2000**, *104*, 8920.
- [81] C. W. Huang, C. H. Liao, C. H. Wu, J. C. S. Wu, *Sol. Energy Mater. Sol. Cells* **2012**, *107*, 322.
- [82] W. Yang, R. R. Prabhakar, J. Tan, S. D. Tilley, J. Moon, *Chem. Soc. Rev.* **2019**, *48*, 4979.
- [83] Y. Qiu, W. Liu, W. Chen, G. Zhou, P. C. Hsu, R. Zhang, Z. Liang, S. Fan, Y. Zhang, Y. Cui, *Sci. Adv.* **2016**, *2*, 1126
- [84] K. P. Sokol, W. E. Robinson, J. Warnan, N. Kornienko, M. M. Nowaczyk, A. Ruff, J. Z. Zhang, E. Reisner, *Nat. Energy* **2018**, *3*, 944.
- [85] C. H. Liao, C. W. Huang, J. C. S. Wu, *Int. J. Hydrogen Energy* **2012**, *37*, 11632.
- [86] J. Brillet, J. H. Yum, M. Cornuz, T. Hisatomi, R. Solarzka, J. Augustynski, M. Graetzel, K. Sivula, *Nat. Photonics* **2012**, *6*, 824.
- [87] X. Shi, K. Zhang, K. Shin, M. Ma, J. Kwon, I. T. Choi, J. K. Kim, H. K. Kim, D. H. Wang, J. H. Park, *Nano Energy* **2015**, *13*, 182.
- [88] V. González-Pedro, I. Zarazua, E. M. Barea, F. Fabregat-Santiago, E. De La Rosa, I. Mora-Seró, S. Giménez, *J. Phys. Chem. C* **2014**, *118*, 891.
- [89] W. Wang, M. O. Tadé, Z. Shao, *Chem. Soc. Rev.* **2015**, *44*, 5371.
- [90] K. Maeda, K. Domen, *J. Phys. Chem. C* **2007**, *111*, 7851.
- [91] D. J. Martin, P. J. T. Reardon, S. J. A. Moniz, J. Tang, *J. Am. Chem. Soc.* **2014**, *136*, 12568.
- [92] K. Sayama, K. Mukasa, R. Abe, Y. Abe, H. Arakawa, *Chem. Commun.* **2001**, *1*, 2416.
- [93] K. Maeda, M. Higashi, D. Lu, R. Abe, K. Domen, *J. Am. Chem. Soc.* **2010**, *132*, 5858.

- [94] Y. Sasaki, H. Kato, A. Kudo, *J. Am. Chem. Soc.* **2013**, *135*, 5441.
- [95] K. Tsuji, O. Tomita, M. Higashi, R. Abe, *ChemSusChem* **2016**, *9*, 2201.
- [96] Y. Sasaki, H. Nemoto, K. Saito, A. Kudo, *J. Phys. Chem. C* **2009**, *113*, 17536.
- [97] H. Kato, Y. Sasaki, N. Shirakura, A. Kudo, *J. Mater. Chem. A* **2013**, *1*, 12327.
- [98] H. Fujito, H. Kunioku, D. Kato, H. Suzuki, M. Higashi, H. Kageyama, R. Abe, *J. Am. Chem. Soc.* **2016**, *138*, 2082.
- [99] X. Li, L. Zhao, J. Yu, X. Liu, X. Zhang, H. Liu, W. Zhou, *Nano-Micro Lett.* **2020**, *121* **2020**, *12*, 1.
- [100] G. Siqueira, A. Várnai, A. Ferraz, A. M. F. Milagres, *Appl. Energy* **2013**, *102*, 399.
- [101] Ki Hyun Yoon, Tae Heui Kim, *J. Solid State Chem.* **1987**, *67*, 359.
- [102] O. Khaselev, A. Bansal, J. A. Turner, *Int. J. Hydrogen Energy* **2001**, *26*, 127.
- [103] T. Kawai, T. Sakata, *Nature* **1980**, *286*, 474.
- [104] T. Kawai, T. Sakata, *J. Chem. Soc. Chem. Commun.* **1980**, 694.
- [105] R. M. Navarro, M. C. Sánchez-Sánchez, M. C. Alvarez-Galvan, F. Del Valle, J. L. G. Fierro, *Energy Environ. Sci.* **2009**, *2*, 35.
- [106] T. Uekert, C. M. Pichler, T. Schubert, E. Reisner, *Nat. Sustain.* **2020**, *1*.
- [107] E. Reisner, *Angew. Chemie Int. Ed.* **2019**, *58*, 3656.
- [108] S. Chen, T. Takata, K. Domen, *Nat. Rev. Mater.* **2017**, *2*, 1.
- [109] Q. Wang, K. Domen, *Chem. Rev.* **2020**, *120*, 919.
- [110] T. Takata, K. Domen, *ACS Energy Lett.* **2019**, *4*, 542.
- [111] L. I. Granone, F. Sieland, N. Zheng, R. Dillert, D. W. Bahnemann, *Green Chem.* **2018**, *20*, 1169.
- [112] A. V. Puga, *Coord. Chem. Rev.* **2016**, *315*, 1.
- [113] M. F. Kuehnel, E. Reisner, *Angew. Chemie Int. Ed.* **2018**, *57*, 3290.
- [114] D. W. Wakerley, M. F. Kuehnel, K. L. Orchard, K. H. Ly, T. E. Rosser, E. Reisner, *Nat. Energy* **2017**, *2*, 17021.
- [115] T. Uekert, M. F. Kuehnel, D. W. Wakerley, E. Reisner, *Energy Environ. Sci.* **2018**, *11*, 2853.

- [116] L. Zhang, W. Wang, S. Zeng, Y. Su, H. Hao, *Green Chem.* **2018**, *20*, 3008.
- [117] T. Uekert, H. Kasap, E. Reisner, *J. Am. Chem. Soc.* **2019**, *141*, 15201.
- [118] R. Geiger, T. Zabel, H. Sigg, *Front. Mater.* **2015**, *2*, 52.
- [119] M. Califano, R. Lu, Y. Zhou, *ACS Nano* **2021**, *15*, 20181.
- [120] D. Liu, W. Zha, R. Yuan, B. Lou, R. Sa, *RSC Adv.* **2020**, *10*, 36734.
- [121] T. Uekert, F. Dorchies, C. Pichler, E. Reisner, *Green Chem.* **2020**, *10*, 1039.
- [122] R. Dong, Z. Zheng, D. C. Tranca, J. Zhang, N. Chandrasekhar, S. Liu, X. Zhuang, G. Seifert, X. Feng, *Chem. – A Eur. J.* **2017**, *23*, 2255.
- [123] R. Marschall, *Adv. Funct. Mater.* **2014**, *24*, 2421.
- [124] A. A. Ismail, S. A. Al-Sayari, D. W. Bahnemann, *Catal. Today* **2013**, *209*, 2.
- [125] O. Merka, D. W. Bahnemann, M. Wark, *ChemCatChem* **2012**, *4*, 1819.
- [126] V. Artero, M. Chavarot-Kerlidou, M. Fontecave, V. Artero, M. Fontecave, M. Chavarot-Kerlidou, *Angew. Chemie Int. Ed.* **2011**, *50*, 7238.
- [127] M. Wang, L. Chen, L. Sun, *Energy Environ. Sci.* **2012**, *5*, 6763.
- [128] X. Zong, H. Yan, G. Wu, G. Ma, F. Wen, L. Wang, C. Li, *J. Am. Chem. Soc.* **2008**, *130*, 7176.
- [129] P. V. Kamat, *J. Phys. Chem. Lett.* **2011**, *2*, 242.
- [130] Q. Xiang, J. Yu, *J. Phys. Chem. Lett.* **2013**, *4*, 753.
- [131] C. O. Tuck, E. Perez, I. T. Horvath, R. A. Sheldon, M. Poliakoff, *Science (80-.)*. **2012**, *337*, 695.
- [132] T. Uekert, M. F. Kuehnelt, D. W. Wakerley, E. Reisner, *Energy Environ. Sci.* **2018**, *11*, 2853.
- [133] SAKATA, T., *Nouv. J. Chim.* **1981**, *5*, 279.
- [134] A. Caravaca, W. Jones, C. Hardacre, M. Bowker, in *Proc. R. Soc. A*, **2016**, p. 472: 20160054.
- [135] A. Speltini, M. Sturini, D. Dondi, E. Annovazzi, F. Maraschi, V. Caratto, A. Profumo, A. Buttafava, *Photochem. Photobiol. Sci.* **2014**, *13*, 1410.
- [136] T. Kawai, T. Sakata, *Chem. Lett.* **1981**, *10*, 81.

- [137] D. M. Smith, J. K. Simon, J. R. Baker, *Nat. Rev. Immunol.* **2013**, *13*, 592.
- [138] L. D. Claxton, *Mutat. Res. Mutat. Res.* **2015**, *763*, 86.
- [139] A. Jain, I. E. Castelli, G. Hautier, D. H. Bailey, K. W. Jacobsen, *J. Mater. Sci.* **2013**, *48*, 6519.
- [140] D. Zhou, T. Zhou, Y. Tian, X. Zhu, Y. Tu, *J. Nanomater.* **2018**, *20*, 155
- [141] B. A. Osman, T. M. Abdolkader, I. S. Ahmed, *Int. J. Mater. Technol. Innov.* **2021**, *1*, 48.
- [142] N. G. Park, *Mater. Today* **2015**, *18*, 65.
- [143] S. Panigrahi, S. Jana, T. Calmeiro, D. Nunes, R. Martins, E. Fortunato, *ACS Nano* **2017**, *11*, 10214.
- [144] M. A. Haque, J. Troughton, D. Baran, *Adv. Energy Mater.* **2020**, *10*, 1902762.
- [145] S. Kazim, M. K. Nazeeruddin, M. Grätzel, S. Ahmad, *Angew. Chemie Int. Ed.* **2014**, *53*, 2812.
- [146] H. Zhou, Q. Chen, G. Li, S. Luo, T. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, Y. Yang, *Science (80-.)*. **2014**, *345*, 542.
- [147] N. Marinova, S. Valero, J. L. Delgado, *J. Colloid Interface Sci.* **2017**, *488*, 373.
- [148] J. You, L. Meng, T. Bin Song, T. F. Guo, W. H. Chang, Z. Hong, H. Chen, H. Zhou, Q. Chen, Y. Liu, N. De Marco, Y. Yang, *Nat. Nanotechnol.* **2015**, *11*, 75.
- [149] H. Il Kim, M. J. Kim, K. Choi, C. Lim, Y. H. Kim, S. K. Kwon, T. Park, *Adv. Energy Mater.* **2018**, *8*, 1702872.
- [150] F. Li, M. Xu, X. Ma, L. Shen, L. Zhu, Y. Weng, G. Yue, F. Tan, C. Chen, *Nanoscale Res. Lett.* **2018**, *13*, 1186
- [151] C. Y. Chang, W. K. Huang, Y. C. Chang, K. T. Lee, C. T. Chen, *J. Mater. Chem. A* **2015**, *4*, 640.
- [152] Y. Lin, B. Chen, F. Zhao, X. Zheng, Y. Deng, Y. Shao, Y. Fang, Y. Bai, C. Wang, J. Huang, *Adv. Mater.* **2017**, *29*, 1700607.
- [153] Z. Song, S. C. Watthage, A. B. Phillips, M. J. Heben, *JPE. 1* **2016**, *6*, 022001.
- [154] L. Calió, S. Kazim, M. Grätzel, S. Ahmad, *Angew. Chemie Int. Ed.* **2016**, *55*, 14522.
- [155] X. Xu, Z. Liu, Z. Zuo, M. Zhang, Z. Zhao, Y. Shen, H. Zhou, Q. Chen, Y. Yang,

- M. Wang, *Nano Lett.* **2015**, *15*, 2402.
- [156] J. H. Kim, P.-W. Liang, S. T. Williams, N. Cho, C.-C. Chueh, M. S. Glaz, D. S. Ginger, A. K-Y Jen, J. H. Kim, P. Liang, S. T. Williams, N. Cho, C. Chueh, A. K-Y Jen, M. S. Glaz, D. S. Ginger, *Adv. Mater.* **2015**, *27*, 695.
- [157] T. Ding, N. Wang, C. Wang, X. Wu, W. Liu, Q. Zhang, W. Fan, X. W. Sun, *RSC Adv.* **2017**, *7*, 26322.
- [158] L. C. Chen, C. C. Chen, K. C. Liang, S. H. Chang, Z. L. Tseng, S. C. Yeh, C. T. Chen, W. T. Wu, C. G. Wu, *Nanoscale Res. Lett.* **2016**, *11*, 1.
- [159] F. Wang, A. Shimazaki, F. Yang, K. Kanahashi, K. Matsuki, Y. Miyauchi, T. Takenobu, A. Wakamiya, Y. Murata, K. Matsuda, *J. Phys. Chem. C* **2017**, *121*, 1562.
- [160] J. Príncipe, V. C. M. Duarte, L. Andrade, *Energy Technol.* **2022**, *10*, 2100952.
- [161] Y. Li, C. Liang, G. Wang, J. Li, S. Chen, S. Yang, G. Xing, G. Xing, H. Pan, H. Pan, H. Pan, *Photonics Res. Vol. 8, Issue 10, pp. A39-A49* **2020**, *8*, A39.
- [162] M. Stolterfoht, P. Caprioglio, C. M. Wolff, J. A. Márquez, J. Nordmann, S. Zhang, D. Rothhardt, U. Hörmann, Y. Amir, A. Redinger, L. Kegelmann, F. Zu, S. Albrecht, N. Koch, T. Kirchartz, M. Saliba, T. Unold, D. Neher, *Energy Environ. Sci.* **2019**, *12*, 2778.
- [163] Q. Luo, Y. Zhang, C. Liu, J. Li, N. Wang, H. Lin, *J. Mater. Chem. A* **2015**, *3*, 15996.
- [164] D. Zhao, M. Sexton, H.-Y. Park, G. Baure, J. C. Nino, F. So, D. Zhao, M. Sexton, H. Park, G. Baure, J. C. Nino, F. So, *Adv. Energy Mater.* **2015**, *5*, 1401855.
- [165] V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, J. L. Brédas, *Chem. Rev.* **2007**, *107*, 926.
- [166] N. Suresh Kumar, K. Chandra Babu Naidu, *J. Mater.* **2021**, *7*, 940.
- [167] Y. Jiang, J. Wang, H. Zai, D. Ni, J. Wang, P. Xue, N. Li, B. Jia, H. Lu, Y. Zhang, F. Wang, Z. Guo, Z. Bi, H. Xie, Q. Wang, W. Ma, Y. Tu, H. Zhou, X. Zhan, *J. Am. Chem. Soc.* **2022**, *144*, 5400.
- [168] M. T. Hörantner, T. Leijtens, M. E. Ziffer, G. E. Eperon, M. G. Christoforo, M. D. McGehee, H. J. Snaith, *ACS Energy Lett.* **2017**, *2*, 2506.
- [169] S. N. Habisreutinger, B. Wenger, H. J. Snaith, R. J. Nicholas, *ACS Energy Lett.* **2017**, *2*, 622.
- [170] R. S. Sanchez, E. Mas-Marza, *Sol. Energy Mater. Sol. Cells* **2016**, *158*, 189.

- [171] A. Torres, L. G. C. Rego, *J. Phys. Chem. C* **2014**, *118*, 26947.
- [172] C. S. Ponseca, E. M. Hutter, P. Piatkowski, B. Cohen, T. Pascher, A. Douhal, A. Yartsev, V. Sundström, T. J. Savenije, *J. Am. Chem. Soc.* **2015**, *137*, 16043.
- [173] X. Zheng, B. Chen, J. Dai, Y. Fang, Y. Bai, Y. Lin, H. Wei, X. C. Zeng, J. Huang, *Nat. Energy* **2017**, *2*, 1.
- [174] C. H. Chiang, M. K. Nazeeruddin, M. Grätzel, C. G. Wu, *Energy Environ. Sci.* **2017**, *10*, 808.
- [175] Y. Wu, J. Wang, X. Qiu, R. Yang, H. Lou, X. Bao, Y. Li, *ACS Appl. Mater. Interfaces* **2016**, *8*, 12377.
- [176] Q. Wang, M. Eslamian, *Ultrasonics* **2016**, *67*, 55.
- [177] A. Corani, M. H. Li, P. S. Shen, P. Chen, T. F. Guo, A. El Nahhas, K. Zheng, A. Yartsev, V. Sundström, C. S. Ponseca, *J. Phys. Chem. Lett.* **2016**, *7*, 1096.
- [178] S. Chatterjee, A. J. Pal, *J. Phys. Chem. C* **2016**, *120*, 1428.
- [179] J. Woong Jung, C.-C. Chueh, A. K-Y Jen, J. W. Jung, C. Chueh, A. K-Y Jen, *Adv. Energy Mater.* **2015**, *5*, 1500486.
- [180] N. Arora, M. I. Dar, A. Hinderhofer, N. Pellet, F. Schreiber, S. M. Zakeeruddin, M. Grätzel, *Science* . **2017**, *358*, 768.
- [181] S. Chavhan, O. Miguel, H. J. Grande, V. Gonzalez-Pedro, R. S. Sánchez, E. M. Barea, I. Mora-Seró, R. Tena-Zaera, *J. Mater. Chem. A* **2014**, *2*, 12754.
- [182] Z. Zhou, X. Li, M. Cai, F. Xie, Y. Wu, Z. Lan, X. Yang, Y. Qiang, A. Islam, L. Han, Z. Zhou, X. Li, M. Cai, F. Xie, Y. Wu, Z. Lan, A. Islam, L. Han, X. Yang, Y. Qiang, *Adv. Energy Mater.* **2017**, *7*, 1700763.
- [183] X. Lin, D. Cui, X. Luo, C. Zhang, Q. Han, Y. Wang, L. Han, *Energy Environ. Sci.* **2020**, *13*, 3823.
- [184] E. Jokar, Z. Y. Huang, S. Narra, C. Y. Wang, V. Kattoor, C. C. Chung, E. W. G. Diau, *Adv. Energy Mater.* **2018**, *8*, 1701640.
- [185] H. H. Huang, Q. H. Liu, H. Tsai, S. Shrestha, L. Y. Su, P. T. Chen, Y. T. Chen, T. A. Yang, H. Lu, C. H. Chuang, K. F. Lin, S. P. Rwei, W. Nie, L. Wang, *Joule* **2021**, *5*, 958.
- [186] A. Y. Alsalloum, B. Turedi, K. Almasabi, X. Zheng, R. Naphade, S. D. Stranks, O. F. Mohammed, O. M. Bakr, *Energy Environ. Sci.* **2021**, *14*, 2263.
- [187] P. Kumnorkaew, A. Tuantranont, S. Chooapun, A. Gardchareon, S. Phadungthitidhada, D. Boonyawan, S. Chooapun, *Curr. Appl. Phys.* **2017**, *17*, 488.

- [188] G. Kakavelakis, T. Maksudov, D. Konios, I. Paradisanos, G. Kioseoglou, E. Stratakis, E. Kymakis, G. Kakavelakis, T. Maksudov, D. Konios, E. Kymakis, G. Kioseoglou, E. Stratakis, I. Paradisanos, *Adv. Energy Mater.* **2017**, 7, 1602120.
- [189] S. Chen, Y. Hou, H. Chen, M. Richter, F. Guo, S. Kahmann, X. Tang, T. Stubhan, H. Zhang, N. Li, N. Gasparini, C. Omar Ramirez Quiroz, L. S. Khanzada, G. J. Matt, A. Osvet, C. J. Brabec, S. Chen, Y. Hou, H. Chen, M. Richter, F. Guo, S. Kahmann, X. Tang, T. Stubhan, H. Zhang, N. Li, N. Gasparini, C. O. R Quiroz, L. S. Khanzada, G. J. Matt, A. Osvet, C. J. Brabec, *Adv. Energy Mater.* **2016**, 6, 1600132.
- [190] Y. Deng, Q. Dong, C. Bi, Y. Yuan, J. Huang, *Adv. Energy Mater.* **2016**, 6, 1600372.
- [191] D. Zhao, Z. Zhu, M. Y. Kuo, C. C. Chueh, A. K. Y. Jen, *Angew. Chemie Int. Ed.* **2016**, 55, 8999.
- [192] A. F. Akbulatov, L. A. Frolova, M. P. Griffin, I. R. Gearba, A. Dolocan, D. A. Vanden Bout, S. Tsarev, E. A. Katz, A. F. Shestakov, K. J. Stevenson, P. A. Troshin, A. F. Akbulatov, L. A. Frolova, A. F. Shestakov, P. A. Troshin, M. P. Griffin, D. A. Vanden Bout, S. Tsarev, K. J. Stevenson, E. A. Katz, *Adv. Energy Mater.* **2017**, 7, 1700476.
- [193] S.-K. Jung, J. Hyuck Heo, D. Woon Lee, S.-C. Lee, S.-H. Lee, W. Yoon, H. Yun, S. Hyuk Im, J. H. Kim, O.-P. Kwon, S. Jung, D. W. Lee, S. Lee, S. Lee, J. H. Kim, O. Kwon, J. H. Heo, S. H. Im, W. Yoon, H. Yun, *Adv. Funct. Mater.* **2018**, 28, 1800346.
- [194] E. Castro, T. J. Sisto, E. L. Romero, F. Liu, S. R. Peurifoy, J. Wang, X. Zhu, C. Nuckolls, L. Echegoyen, *Angew. Chemie* **2017**, 129, 14840.
- [195] X. Liu, Y. Cheng, B. Tang, Z. G. Yu, M. Li, F. Lin, S. Zhang, Y. W. Zhang, J. Ouyang, H. Gong, *Nano Energy* **2020**, 71, 104556.
- [196] X. Ren, D. Yang, Z. Yang, J. Feng, X. Zhu, J. Niu, Y. Liu, W. Zhao, S. F. Liu, *ACS Appl. Mater. Interfaces* **2017**, 9, 2421.
- [197] E. H. Anaraki, A. Kermanpur, L. Steier, K. Domanski, T. Matsui, W. Tress, M. Saliba, A. Abate, M. Grätzel, A. Hagfeldt, J. P. Correa-Baena, *Energy Environ. Sci.* **2016**, 9, 3128.
- [198] Y. Hou, X. Chen, S. Yang, C. Li, H. Zhao, H. Gui Yang, Y. Hou, X. Chen, S. Yang, C. Li, H. G. Yang, H. Zhao, *Adv. Funct. Mater.* **2017**, 27, 1700878.
- [199] R. Azmi, W. Tanyo Hadmojo, S. Sinaga, C.-L. Lee, S. Cheol Yoon, I. Hwan Jung, S.-Y. Jang, R. Azmi, W. T. Hadmojo, S. Sinaga, I. H. Jung, S. Jang, C. Lee, S. C. Yoon, *Adv. Energy Mater.* **2018**, 8, 1701683.

- [200] J. Barbé, M. L. Tietze, M. Neophytou, B. Murali, E. Alarousu, A. El Labban, M. Abulikemu, W. Yue, O. F. Mohammed, I. McCulloch, A. Amassian, S. Del Gobbo, *ACS Appl. Mater. Interfaces* **2017**, 9, 11828.
- [201] N. Rajamanickam, P. Soundarrajan, V. K. Vendra, J. B. Jasinski, M. K. Sunkara, K. Ramachandran, *Phys. Chem. Chem. Phys.* **2016**, 18, 8468.
- [202] W. Tress, N. Marinova, O. Inganäs, M. K. Nazeeruddin, S. M. Zakeeruddin, M. Graetzel, *2014 IEEE 40th Photovolt. Spec. Conf. PVSC 2014* **2014**, 1563.
- [203] V. W. hei Lau, B. V. Lotsch, *Adv. Energy Mater.* **2022**, 12, 2101078.
- [204] H. Ishaq, I. Dincer, *Renew. Sustain. Energy Rev.* **2021**, 135, 110192.
- [205] K. C. Christoforidis, P. Fornasiero, *ChemCatChem* **2017**, 9, 1523.
- [206] G. Zhang, Z. A. Lan, X. Wang, *Angew. Chemie - Int. Ed.* **2016**, 55, 15712.
- [207] X. Peng, R. M. Kelly, Y. Han, *Biotechnol. Bioeng.* **2018**, 115, 1624.
- [208] T. Uekert, H. Kasap, E. Reisner, *J. Am. Chem. Soc.* **2019**, 141, 15201.
- [209] H. H. Wang, L. Xue, C. L. Yu, Y. Y. Qian, H. Jiang, *Dye. Pigment.* **2011**, 91, 350.
- [210] Y. Yang, S. Niu, D. Han, T. Liu, G. Wang, Y. Li, *Adv. Energy Mater.* **2017**, 7, 1700555.
- [211] J. Wang, J. Hao, D. Liu, S. Qin, D. Portehault, Y. Li, Y. Chen, W. Lei, *ACS Energy Lett.* **2017**, 2, 306.
- [212] J. Liang, X. Yang, Y. Wang, P. He, H. Fu, Y. Zhao, Q. Zou, X. An, *J. Mater. Chem. A* **2021**, 9, 12898.
- [213] C. Jiang, H. An, G. Dong, J. Feng, M. Zhang, Y. Ren, J. Ma, *Chem. Eng. J.* **2022**, 428, 131054.
- [214] Y. Wang, X. Wang, M. Antonietti, *Angew. Chemie Int. Ed.* **2012**, 51, 68.
- [215] E. Alwin, W. Nowicki, R. Wojcieszak, M. Zieliński, M. Pietrowski, *Dalt. Trans.* **2020**, 49, 12805.
- [216] T. P. Ang, Y. M. Chan, *J. Phys. Chem. C* **2011**, 115, 15965.
- [217] J. E. Ellis, D. C. Sorescu, S. C. Burkert, D. L. White, A. Star, *ACS Appl. Mater. Interfaces* **2017**, 9, 27142.
- [218] S. T. A. G. Melissen, T. Le Bahers, P. Sautet, S. N. Steinmann, *Phys. Chem. Chem. Phys.* **2021**, 23, 2853.

- [219] G. Liu, P. Niu, C. Sun, S. C. Smith, Z. Chen, G. Q. Lu, H. M. Cheng, *J. Am. Chem. Soc.* **2010**, *132*, 11642.
- [220] J. Zhang, X. Chen, K. Takanabe, K. Maeda, K. Domen, J. D. Epping, X. Fu, M. Antonieta, X. Wang, *Angew. Chemie - Int. Ed.* **2010**, *49*, 441.
- [221] Z. Teng, W. Cai, S. Liu, C. Wang, Q. Zhang, S. Chenliang, T. Ohno, *Appl. Catal. B Environ.* **2020**, *271*, 118917.
- [222] J. Wang, Z. Guan, J. Huang, Q. Li, J. Yang, *J. Mater. Chem. A* **2014**, *2*, 7960.
- [223] X. Li, J. Zhang, Y. Huo, K. Dai, S. Li, S. Chen, *Appl. Catal. B Environ.* **2021**, *280*, 119452.
- [224] Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec, S. Z. Qiao, *Nat. Commun.* **2014**, *5*, 3783.
- [225] X. Li, R. Shen, S. Ma, X. Chen, J. Xie, *Appl. Surf. Sci.* **2018**, *430*, 53.
- [226] P. Kumar, R. Boukherroub, K. Shankar, *J. Mater. Chem. A* **2018**, *6*, 12876.
- [227] K. Dai, L. Lu, Q. Liu, G. Zhu, X. Wei, J. Bai, L. Xuan, H. Wang, *Dalt. Trans.* **2014**, *43*, 6295.
- [228] W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong, A. R. Mohamed, *Nano Energy* **2015**, *13*, 757.
- [229] H. Begum, M. S. Ahmed, Y. B. Kim, *Sci. Reports* **2020**, *10*, 12431.
- [230] T. Song, B. Long, S. Yin, A. Ali, G. J. Deng, *Chem. Eng. J.* **2021**, *404*, 126455.
- [231] B. Ai, X. Duan, H. Sun, X. Qiu, S. Wang, *Catal. Today* **2015**, *258*, 668.
- [232] M. Ashraf, M. Ahmad, H. Ahmad, S. Ahmad, *Pak. J. Pharm. Sci.*, **2019**, *32*, 6617.
- [233] M. Khan, M. R. Shaik, S. F. Adil, M. Kuniyil, M. Ashraf, H. Frerichs, M. A. Sarif, M. R. H. Siddiqui, A. Al-Warhan, J. P. Labis, M. S. Islam, W. Tremel, M. N. Tahir, *Sci. Rep.* **2020**, *10*, 11728.
- [234] B. W. Sun, H. Y. Yu, Y. J. Yang, H. J. Li, C. Y. Zhai, D. J. Qian, M. Chen, *Phys. Chem. Chem. Phys.* **2017**, *19*, 26072.
- [235] G. Peng, M. Volokh, J. Tzadikov, J. Sun, M. Shalom, *Adv. Energy Mater.* **2018**, *8*, 1800566.
- [236] L. Seyfarth, J. Seyfarth, B. V. Lotsch, W. Schnick, J. Senker, *Phys. Chem. Chem. Phys.* **2010**, *12*, 2227.
- [237] A. Du, S. Sanvito, Z. Li, D. Wang, Y. Jiao, T. Liao, Q. Sun, Y. H. Ng, Z. Zhu, R.

- Amal, S. C. Smith, *J. Am. Chem. Soc.* **2012**, *134*, 4393.
- [238] Y. Li, H. Zhang, P. Liu, D. Wang, Y. Li, H. Zhao, *Small* **2013**, *9*, 3336.
- [239] J. Feng, L. Su, Y. Ma, C. Ren, Q. Guo, X. Chen, *Chem. Eng. J.* **2013**, *221*, 16.
- [240] N. Hashim, Z. Muda, M. Zobir Hussein, I. Md Isa, A. Mohamed, A. Kamari, S. Abu Bakar, M. Mamat, A. Jaafar, *J. Mater. Environ. Sci* **2016**, *7*, 3225.
- [241] T.-F. Yeh, C.-Y. Teng, S.-J. Chen, H. Teng, *Adv. Mater.* **2014**, *26*, 3297.
- [242] L. Sun, T. Du, C. Hu, J. Chen, J. Lu, Z. Lu, H. Han, *ACS Sustain. Chem. Eng.* **2017**, *5*, 8693.
- [243] Y. Zheng, Y. Liu, X. Guo, W. Zhang, Y. Wang, M. Zhang, R. Li, Z. Peng, H. Xie, Y. Huang, *ACS Appl. Nano Mater.* **2020**, *3*, 7982.
- [244] Q. Han, N. Chen, J. Zhang, L. Qu, *Mater. Horizons* **2017**, *4*, 832.
- [245] L. Wang, W. Si, Y. Tong, F. Hou, D. Pergolesi, J. Hou, T. Lippert, S. X. Dou, J. Liang, *Carbon Energy* **2020**, *2*, 223.
- [246] J. Gong, C. Li, M. R. Wasielewski, *Chem. Soc. Rev.* **2019**, *48*, 1862.
- [247] M. Lange, I. Khan, R. Dören, M. Ashraf, A. Qurashi, L. A. Prädel, M. Panthöfer, M. von der Au, A. Cossmer, J. Pfeifer, B. Meermann, M. Mondeshki, M. N. Tahir, W. Tremel, *Dalt. Trans.* **2021**, *24*, 6528.
- [248] M. Khan, M. E. Assal, M. Nawaz Tahir, M. Khan, M. Ashraf, M. Rafe Hatshan, M. Khan, R. Varala, N. Mohammed Badawi, S. Farooq Adil, *J. Saudi Chem. Soc.* **2022**, 101544.
- [249] J. Yang, D. Wang, H. Han, C. Li, *Acc. Chem. Res.* **2013**, *46*, 1900.
- [250] N. Xiao, S. Li, X. Li, L. Ge, Y. Gao, N. Li, *Chinese J. Catal.* **2020**, *41*, 642.
- [251] Z. Yu, Q. Huang, X. Jiang, X. Lv, X. Xiao, M. Wang, Y. Shen, G. Wittstock, *Anal. Chem.* **2021**, *93*, 12221.
- [252] S. Cao, J. Low, J. Yu, M. Jaroniec, *Adv. Mater.* **2015**, *27*, 2150.
- [253] C. Li, J. B. Baek, *ACS Omega* **2020**, *5*, 31.
- [254] A. S. Malik, T. Liu, M. Rittirum, T. Saelee, J. L. F. Da Silva, S. Praserttham, P. Praserttham, *Sci. Reports* **2022**, *12*, 1.
- [255] X. Zou, Y. Zhang, *Chem. Soc. Rev.* **2015**, *44*, 5148.
- [256] P. Ye, X. Liu, J. Iocozzia, Y. Yuan, L. Gu, G. Xu, Z. Lin, *J. Mater. Chem. A* **2017**,

5, 8493.

- [257] Y. Chen, Z. Qin, *Catal. Sci. Technol.* **2016**, 6, 8212.
- [258] A. R. J. Kucernak, V. N. Naranammalpuram Sundaram, *J. Mater. Chem. A* **2014**, 2, 17435.
- [259] H. Zhao, J. Wang, Y. Dong, P. Jiang, *ACS Sustain. Chem. Eng.* **2017**, 5, 8053.
- [260] D. E. Schipper, Z. Zhao, H. Thirumalai, A. P. Leitner, S. L. Donaldson, A. Kumar, F. Qin, Z. Wang, L. C. Grabow, J. Bao, K. H. Whitmire, **2018**, DOI 10.1021/acs.chemmater.8b01624.
- [261] S. Cao, Y. Chen, C. C. Hou, X. J. Lv, W. F. Fu, *J. Mater. Chem. A* **2015**, 3, 6096.
- [262] J. H. Kim, S. Han, Y. H. Jo, Y. Bak, J. S. Lee, *J. Mater. Chem. A* **2018**, 6, 1266.
- [263] W. Wang, X. Zhao, Y. Cao, Z. Yan, R. Zhu, Y. Tao, X. Chen, D. Zhang, G. Li, D. L. Phillips, *ACS Appl. Mater. Interfaces* **2019**, 11, 16527.
- [264] H. Zhou, R. Chen, C. Han, P. Wang, Z. Tong, B. Tan, Y. Huang, Z. Liu, *J. Colloid Interface Sci.* **2022**, 610, 126.
- [265] S. E. Jun, S. Choi, S. Choi, T. H. Lee, C. Kim, J. W. Yang, W. O. Choe, I. H. Im, C. J. Kim, H. W. Jang, *Nano-Micro Lett.* **2021**, 13, 1.
- [266] Y. Shi, B. Zhang, *Chem. Soc. Rev.* **2016**, 45, 1529.
- [267] Z. Sun, M. Zhu, M. Fujitsuka, A. Wang, C. Shi, T. Majima, *ACS Appl. Mater. Interfaces* **2017**, 9, 30583.
- [268] H. Zhao, S. Sun, P. Jiang, Z. J. Xu, *Chem. Eng. J.* **2017**, 315, 296.
- [269] A. Han, H. Chen, Z. Sun, J. Xu, P. Du, *Chem. Commun.* **2015**, 51, 11626.
- [270] P. Wen, K. Zhao, H. Li, J. Li, J. Li, Q. Ma, S. M. Geyer, L. Jiang, Y. Qiu, *J. Mater. Chem. A* **2020**, 8, 2995.
- [271] H. Yin, Q. Guo, D. He, J. Li, S. Sun, *RSC Adv.* **2017**, 7, 44001.
- [272] Z. Li, J. Feng, J. Cao, J. Jin, Y. Zhou, D. Cao, Z. Liang, B. Zhu, M. Li, L. Zhao, S. Wang, *Energy Environ. Mater.* **2022**, 10, 1002
- [273] Y. Miyamoto, M. L. Cohen, S. G. Louie, *Solid State Commun.* **1997**, 102, 605.
- [274] J. Zeng, Z. Chen, X. Zhao, W. Yu, S. Wu, J. Lu, K. P. Loh, J. Wu, *ACS Appl. Nano Mater.* **2019**, 2, 7969.
- [275] Z. Ma, X. Zhao, Q. Tang, Z. Zhou, *Int. J. Hydrogen Energy* **2014**, 39, 5037.

- [276] J. Feng, M. Li, *Adv. Funct. Mater.* **2020**, 30, 2001502.
- [277] T. Uekert, H. Kasap, E. Reisner, *J. Am. Chem. Soc.* **2019**, 141, 15201.
- [278] E. Liu, C. Jin, C. Xu, J. Fan, X. Hu, *Int. J. Hydrogen Energy* **2018**, 43, 21355.
- [279] N. H. Hemasiri, S. Kazim, S. Ahmad, *Nano Energy* **2020**, 77, 105292.
- [280] L.-L. Jiang, Z.-K. Wang, M. Li, C.-H. Li, P.-F. Fang, L.-S. Liao, *J. Mater. Chem. A* **2019**, 7, 3655.
- [281] X. Zheng, B. Chen, J. Dai, Y. Fang, Y. Bai, Y. Lin, H. Wei, X. C. Zeng, J. Huang, *Nat. Energy* 2017 27 **2017**, 2, 1.
- [282] D. W. deQuilettes, W. Zhang, V. M. Burlakov, D. J. Graham, T. Leijtens, A. Osharov, V. Bulović, H. J. Snaith, D. S. Ginger, S. D. Stranks, *Nat. Commun.* 2016 71 **2016**, 7, 1.
- [283] Zhen Li, Chuanxiao Xiao, Ye Yang, S. P. Harvey, D. Hoe Kim, J. A. Christians, Mengjin Yang, Philip Schulz, S. U. Nanayakkara, Chun-Sheng Jiang, J. M. Luther, J. J. Berry, M. C. Beard, M. M. Al-Jassim, Kai Zhu, *Energy Environ. Sci.* **2017**, 10, 1234.
- [284] T. Bu, X. Liu, Y. Zhou, J. Yi, X. Huang, L. Luo, J. Xiao, Z. Ku, Y. Peng, F. Huang, Y.-B. Cheng, J. Zhong, *Energy Environ. Sci.* **2017**, 10, 2509.
- [285] X. Zheng, Y. Deng, B. Chen, H. Wei, X. Xiao, Y. Fang, Y. Lin, Z. Yu, Y. Liu, Q. Wang, J. Huang, *Adv. Mater.* **2018**, 30, 1803428.
- [286] H.-S. Kim, S. H. Im, N.-G. Park, *J. Phys. Chem. C* **2014**, 118, 5615.
- [287] C.-C. Zhang, M. Li, Z.-K. Wang, Y.-R. Jiang, H.-R. Liu, Y.-G. Yang, X.-Y. Gao, H. Ma, *J. Mater. Chem. A* **2017**, 5, 2572.
- [288] N. Arora, M. I. Dar, A. Hinderhofer, N. Pellet, F. Schreiber, S. M. Zakeeruddin, M. Grätzel, *Science* . **2017**, 358, 768.
- [289] G. Kakavelakis, I. Paradisanos, B. Paci, A. Generosi, M. Papachatzakis, T. Maksudov, L. Najafi, A. E. D. R. Castillo, G. Kioseoglou, E. Stratakis, F. Bonaccorso, E. Kymakis, *Adv. Energy Mater.* **2018**, 8, 1702287.
- [290] Sergey Tsarev, I. K. Yakushchenko, S. Yu Luchkin, P. M. Kuznetsov, R. S. Timerbulatov, N. N. Dremova, L. A. Frolova, K. J. Stevenson, P. A. Troshin, *Sustain. Energy Fuels* **2019**, 3, 2627.
- [291] Q. Guo, C. Wang, J. Li, Y. Bai, F. Wang, L. Liu, B. Zhang, T. Hayat, A. Alsaedi, Z. Tan, *Phys. Chem. Chem. Phys.* **2018**, 20, 21746.
- [292] K. Eom, I. H. Yoo, Q. A. Sial, H. Seo, *Curr. Appl. Phys.* **2021**, 23, 62.

- [293] D. Kasinathan, M. Ashok, *AIP Conf. Proc.* **2020**, 2265, 030648.
- [294] S. Bhandari, A. Roy, A. Ghosh, T. K. Mallick, S. Sundaram, *ACS Omega* **2020**, 5, 422.
- [295] A. Liu, H. Zhu, M. G. Kim, J. Kim, Y. Y. Noh, *Adv. Sci.* **2021**, 8, 2100546.
- [296] S. Zhang, H. Wang, X. Duan, L. Rao, C. Gong, B. Fan, Z. Xing, X. Meng, B. Xie, X. Hu, *Adv. Funct. Mater.* **2021**, 31, 2106495.
- [297] X. Yin, P. Chen, M. Que, Y. Xing, W. Que, C. Niu, J. Shao, *ACS Nano* **2016**, 10, 3630.
- [298] M. B. Islam, M. Yanagida, Y. Shirai, Y. Nabetani, K. Miyano, *ACS Omega* **2017**, 2, 2291.
- [299] S. Pirzad Ghias Abadi, M. Borhani Zarandi, N. Jahanbakhshi Zadeh, *Synth. Met.* **2022**, 289, 117115.
- [300] S. Wang, Y. Li, J. Yang, T. Wang, B. Yang, Q. Cao, X. Pu, L. Etgar, J. Han, J. Zhao, X. Li, A. Hagfeldt, *Angew. Chemie Int. Ed.* **2022**, 61, e202116534.
- [301] M. Jakhar, A. Kumar, P. K. Ahluwalia, K. Tankeshwar, R. Pandey, *Mater.* **2022**, 15, 2221.
- [302] Y. Jing, X. Zhu, S. Maier, T. Heine, *Trends Chem.* **2022**, 4, 792.
- [303] L.-L. Jiang, Z.-K. Wang, M. Li, C.-C. Zhang, Q.-Q. Ye, K.-H. Hu, D.-Z. Lu, P.-F. Fang, L.-S. Liao, *Adv. Funct. Mater.* **2018**, 28, 1705875.
- [304] Z. Li, S. Wu, J. Zhang, Y. Yuan, Z. Wang, Z. Zhu, *Sol. RRL* **2020**, 4, 1900413.
- [305] X. Chen, Q. Liu, Q. Wu, P. Du, J. Zhu, S. Dai, S. Yang, *Adv. Funct. Mater.* **2016**, 26, 1719.
- [306] Jin-Feng Liao, Wu-Qiang Wu, Jun-Xing Zhong, Yong Jiang, Lianzhou Wang, Dai-Bin Kuang, *J. Mater. Chem. A* **2019**, 7, 9025.
- [307] J. Tian, Z. Zhou, S. Zhang, Z. Li, L. Shi, Q. Li, J. Wang, *J. Mater. Chem. A* **2021**, 9, 11753.
- [308] S. Singh, P. Anees, S. Chandra, T. K. Ghanty, *J. Phys. Chem. C* **2021**, 10, 1021
- [309] S. Qi, Y. Fan, J. Wang, X. Song, W. Li, M. Zhao, *Nanoscale* **2019**, 12, 306.
- [310] P. Kumar, E. Vahidzadeh, U. K. Thakur, P. Kar, K. M. Alam, A. Goswami, N. Mahdi, K. Cui, G. M. Bernard, V. K. Michaelis, K. Shankar, *J. Am. Chem. Soc.* **2019**, 141, 5415.

- [311] X. Tong, F. Li, J. Jin, X. Guo, J. Li, F. Yan, X. Z. Zhao, Q. Tai, *J. Phys. D. Appl. Phys.* **2021**, *54*, 144002.
- [312] N. Harindu Hemasiri, S. Kazim, S. Ahmad, *J. Mater. Chem. C* **2021**, *9*, 9865.
- [313] George W. Huber, and Sara Iborra, A. Corma*, *Chem. Rev.* **2006**, *106*, 4044.
- [314] C. Chatterjee, F. Pong, A. Sen, *Green Chem.* **2014**, *17*, 40.
- [315] J. J. Bozell, G. R. Petersen, *Green Chem.* **2010**, *12*, 539.
- [316] J. Ma, K. Liu, X. Yang, D. Jin, Y. Li, G. Jiao, J. Zhou, R. Sun, *ChemSusChem* **2021**, *14*, 4903.
- [317] J. Wang, P. Kumar, H. Zhao, M. G. Kibria, J. Hu, *Green Chem.* **2021**, *23*, 7435.
- [318] U. Nwosu, A. Wang, B. Palma, H. Zhao, M. A. Khan, M. Kibria, J. Hu, *Renew. Sustain. Energy Rev.* **2021**, *148*, 111266.
- [319] A. V. Puga, *Coord. Chem. Rev.* **2016**, *315*, 1.
- [320] S. P. Teong, G. Yi, Y. Zhang, *Green Chem.* **2014**, *16*, 2015.
- [321] A. J. J. E. Eerhart, A. P. C. Faaij, M. K. Patel, *Energy Environ. Sci.* **2012**, *5*, 6407.
- [322] P. P. Upare, Y. K. Hwang, D. W. Hwang, *Green Chem.* **2018**, *20*, 879.
- [323] X. Kong, Y. Zhu, Z. Fang, J. A. Kozinski, I. S. Butler, L. Xu, H. Song, X. Wei, *Green Chem.* **2018**, *20*, 3657.
- [324] S. Xu, P. Zhou, Z. Zhang, C. Yang, B. Zhang, K. Deng, S. Bottle, H. Zhu, *J. Am. Chem. Soc.* **2017**, *139*, 14775.
- [325] X. Y. Zhang, M. H. Zong, N. Li, *Green Chem.* **2017**, *19*, 4544.
- [326] H. G. Cha, K. S. Choi, *Nat. Chem.* **2015**, *7*, 328.
- [327] O. Casanova, S. Iborra, A. Corma, *ChemSusChem* **2009**, *2*, 1138.
- [328] D. J. Chadderdon, L. Xin, J. Qi, Y. Qiu, P. Krishna, K. L. More, W. Li, *Green Chem.* **2014**, *16*, 3778.
- [329] Z. Zhang, K. Deng, *ACS Catal.* **2015**, *5*, 6529.
- [330] Y. Yang, T. Mu, *Green Chem.* **2021**, *23*, 4228.
- [331] K. Schnatbaum, H. J. Schäfer, *Synthesis (Stuttg.)*. **1999**, *1999*, 864.
- [332] T. W. Kim, K. S. Choi, *Science (80-.)*. **2014**, *343*, 990.

- [333] S. E. Davis, L. R. Houk, E. C. Tamargo, A. K. Datye, R. J. Davis, *Catal. Today* **2011**, 160, 55.
- [334] T. Pasini, M. Piccinini, M. Blosi, R. Bonelli, S. Albonetti, N. Dimitratos, J. A. Lopez-Sanchez, M. Sankar, Q. He, C. J. Kiely, G. J. Hutchings, F. Cavani, *Green Chem.* **2011**, 13, 2091.
- [335] K. R. Vuyyuru, P. Strasser, *Catal. Today* **2012**, 195, 144.
- [336] B. You, X. Liu, N. Jiang, Y. Sun, *J. Am. Chem. Soc.* **2016**, 138, 13639.
- [337] B. You, X. Liu, X. Liu, Y. Sun, *ACS Catal.* **2017**, 7, 4564.
- [338] B. You, N. Jiang, X. Liu, Y. Sun, *Angew. Chemie Int. Ed.* **2016**, 55, 9913.
- [339] N. Jiang, B. You, R. Boonstra, I. M. Terrero Rodriguez, Y. Sun, *ACS Energy Lett.* **2016**, 1, 386.
- [340] H. Ait Rass, N. Essayem, M. Besson, *ChemSusChem* **2015**, 8, 1206.
- [341] D. H. Nam, B. J. Taitt, K. S. Choi, *ACS Catal.* **2018**, 8, 1197.

Appendix A. Supplementary Figure

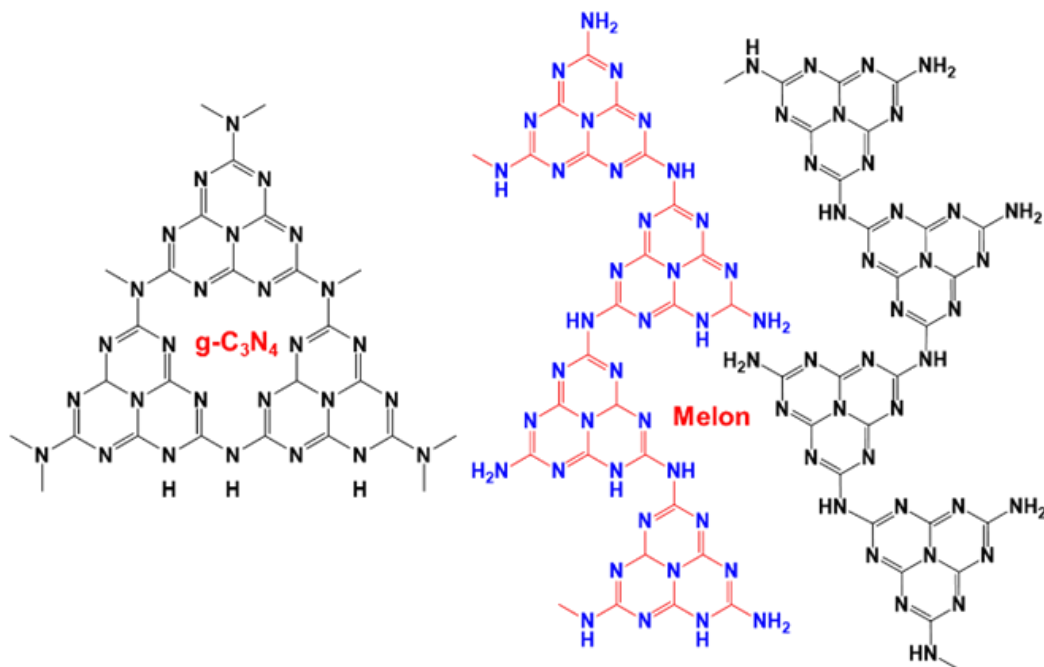


Figure S. 1. Structures of g-C₃N₄ and melon.

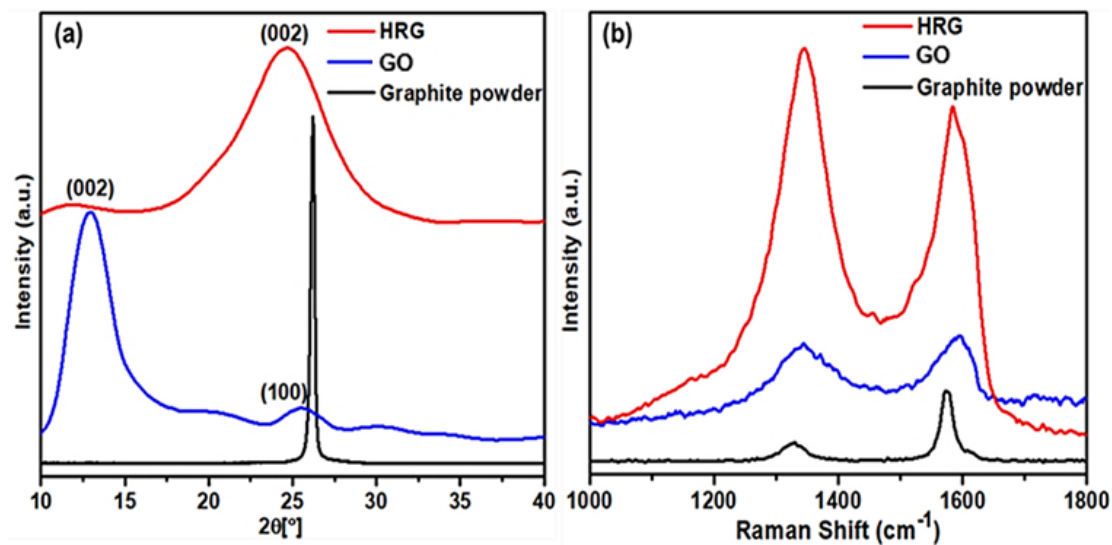


Figure S. 2. XRD and Raman patterns of as-synthesized graphite powder, GO, HRG catalyst.

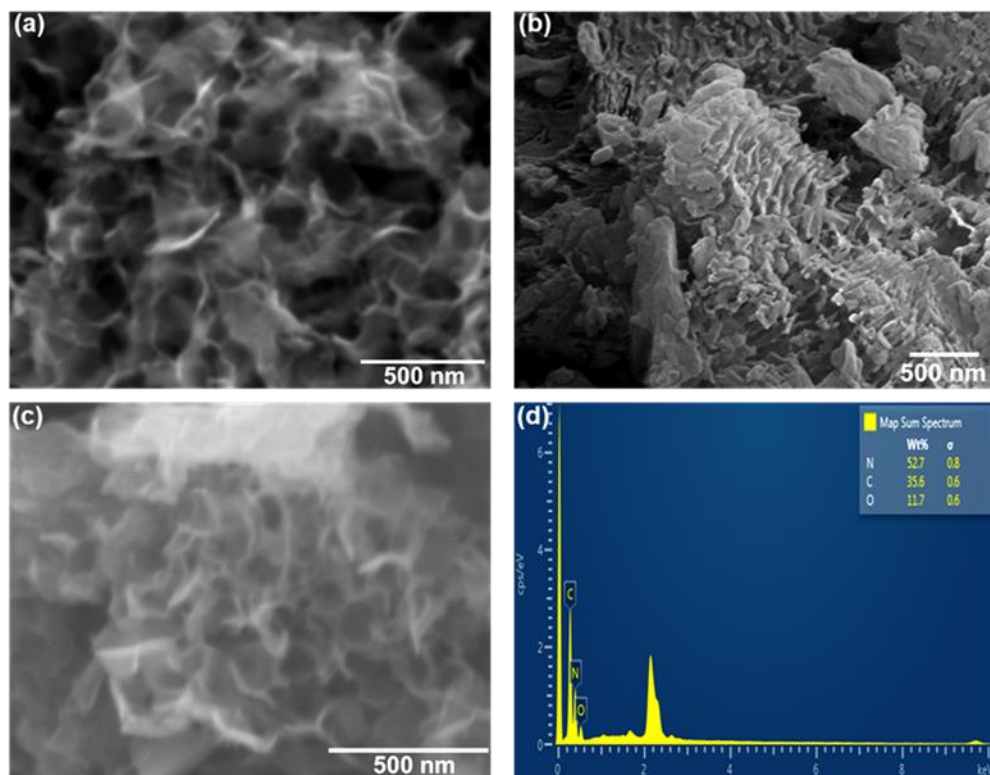


Figure S. 3. FE-SEM images of (a) HRG, (b) melon, (c) 1 % HRG@melon nanocomposite and (d) EDX spectrum recorded from the 1 % HRG@melon nanocomposite showing the composition.

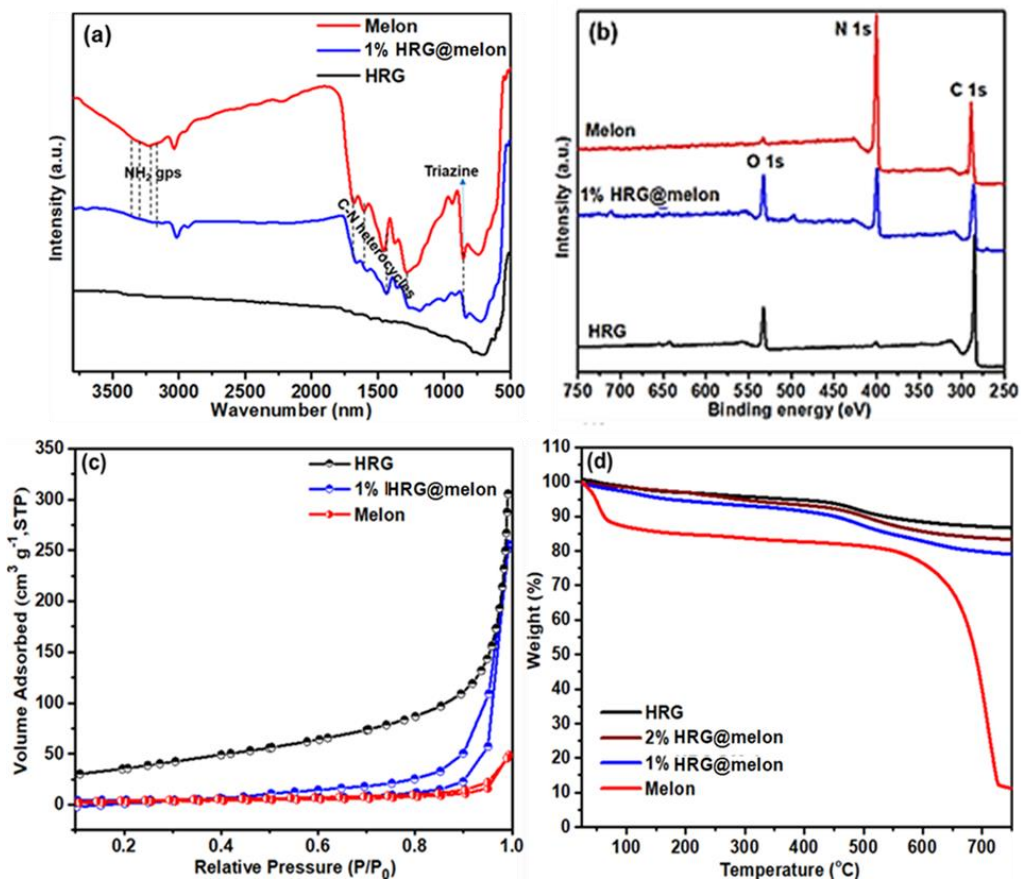


Figure S. 4. (a) FTIR spectra of melon, HRG and 1% HRG@melon nanocomposite and (b) XPS survey spectra of melon, HRG and 1% HRG@melon nanocomposite. (c) Nitrogen adsorption-desorption isotherms plots for HRG, melon and a 1% HRG@melon nanocomposite. The BET trace shows that the addition of HRG to melon increases the surface area. (d) TGA trace of HRG, melon and an HRG@melon nanocomposite.

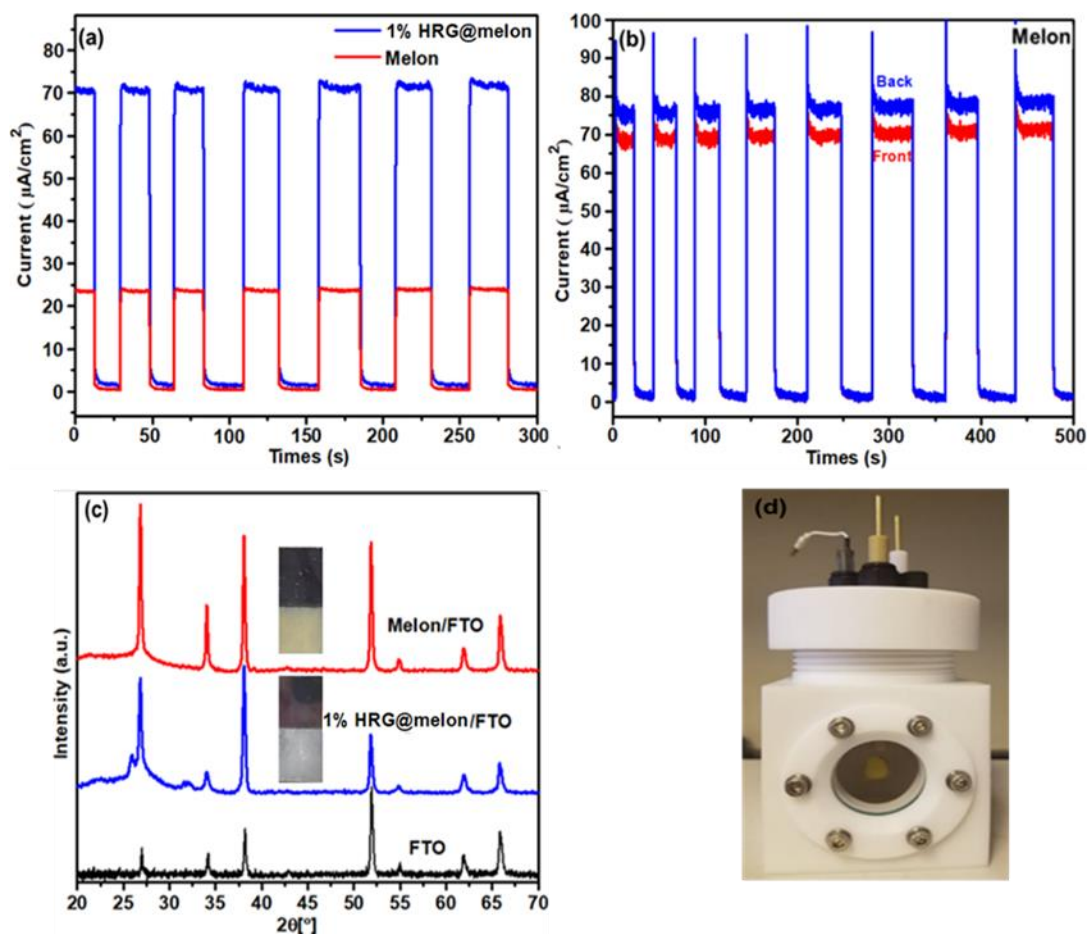


Figure S. 5. (a) Photocurrents of a melon and 1% HRG@melon electrode at 1.23 V vs. RHE in 0.5 M KOH aqueous solution (b) Photocurrents of a melon electrode at 1.23 V vs. RHE in an aqueous 0.5 M KOH solution containing 10% (volume/volume) triethanolamine. The electrode was illuminated from the front (red color) and backsides (blue color). (c) XRD diffractogram of pure melon/FTO, HRG@melon nanocomposite/FTO and bare FTO electrodes. (d) Digital image of the photoelectrochemical cell used for experiments.

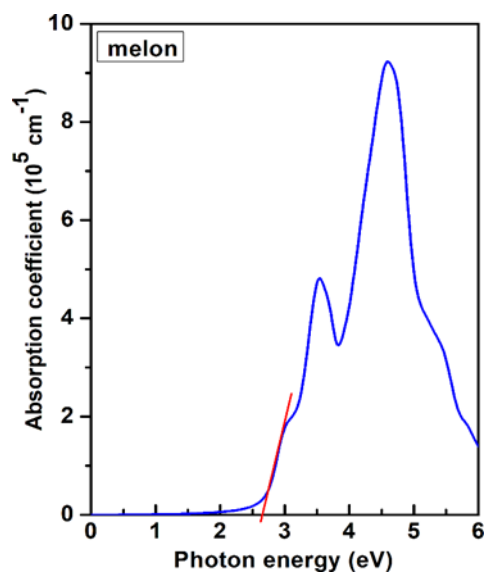


Figure S. 6. Absorption coefficient of melon with an optical bandgap of 2.66 eV.

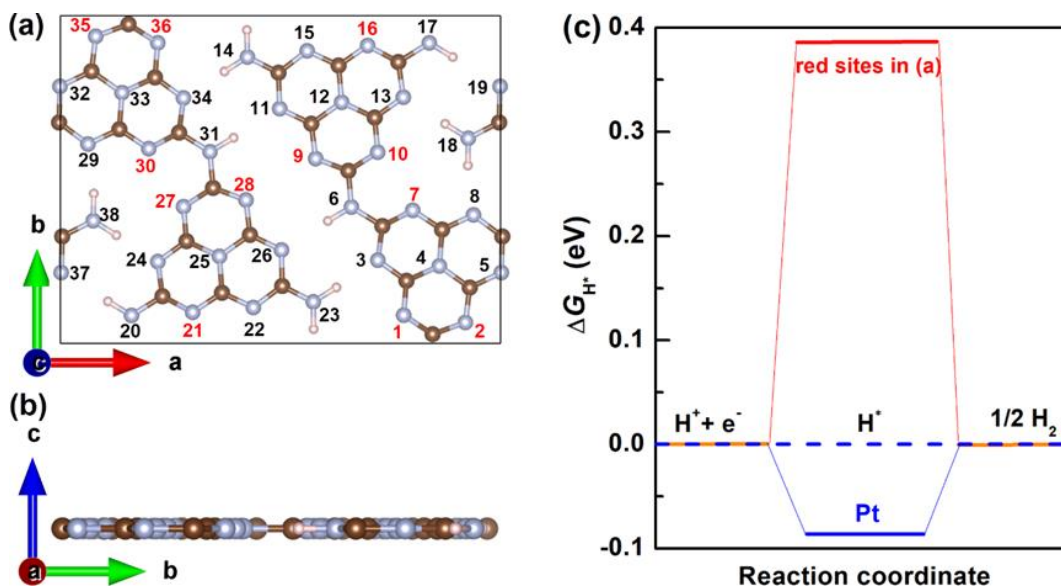


Figure S. 7. (a) Top and (b) side views of the crystal structure of melon with the N sites numbered. The red colored N sites are found to be highly HER active. The obtained values of ΔG_{H^*} are shown in Table S4. (c) ΔG_{H^*} compared to that of Pt.

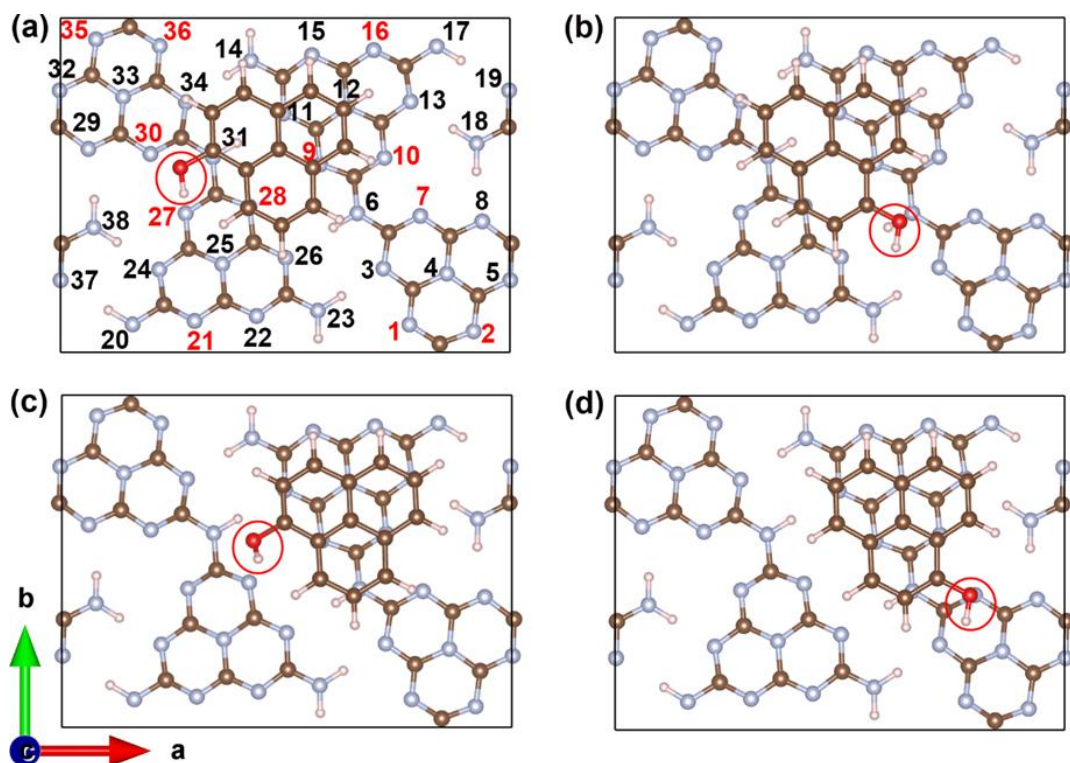


Figure S. 8. HRG placed (a, b) above the void area of melon and (c, d) above the heptazine of melon with an OH functional group attached at two different sites (red circles). Red color highlights the favorable sites for high HER activity. In cases (a) and (d) we consider all N sites for the H adsorption. In cases (b) and (c) we only consider the favorable sites for high HER activity (red color in (a)). Site 9 is considered to be the best site for high HER activity. The obtained values of ΔG_{H^*} are shown in Table S-3.

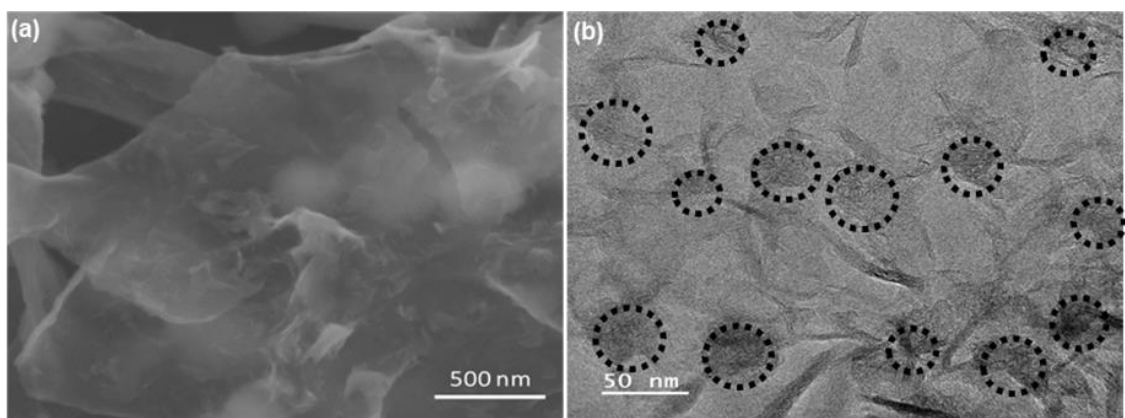


Figure S. 9: (a) FE-SEM image of the pristine C_3N_3 and HR-TEM image of 2% Ni_2P/C_3N_3 nanocomposite

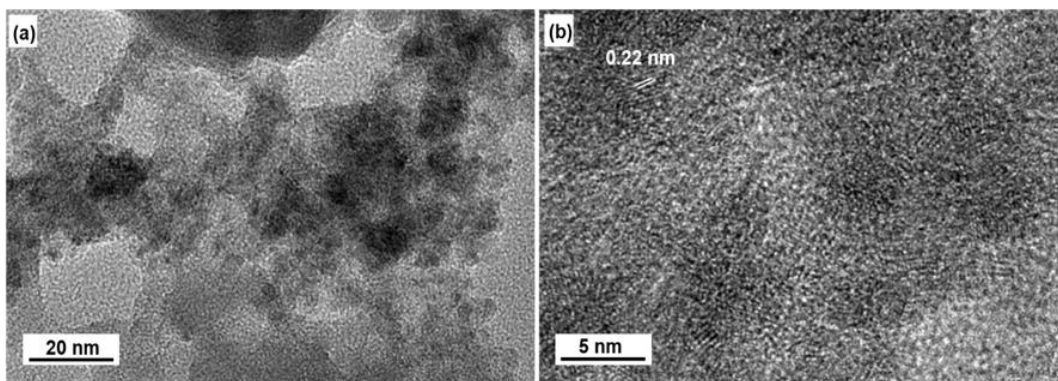


Figure S. 10: (a) HR-TEM image of the 2% Ni₂P/C₃N₃ nanocomposite and (b) HR-TEM image of the pristine Ni₂P.

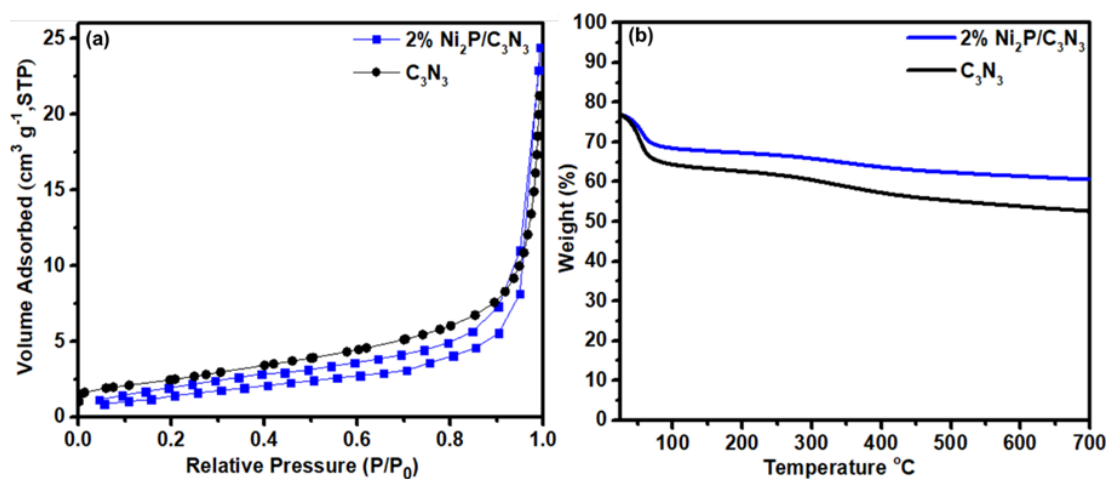


Figure S. 11: (a) Nitrogen adsorption-desorption isotherms plots of pure C₃N₃ and 2% Ni₂P/C₃N₃ nanocomposite samples. BET analysis shows that the addition of Ni₂P to the C₃N₃ samples increase surface area and (b) TGA data plot of pure C₃N₃ and 2% Ni₂P/C₃N₃ nanocomposite samples.

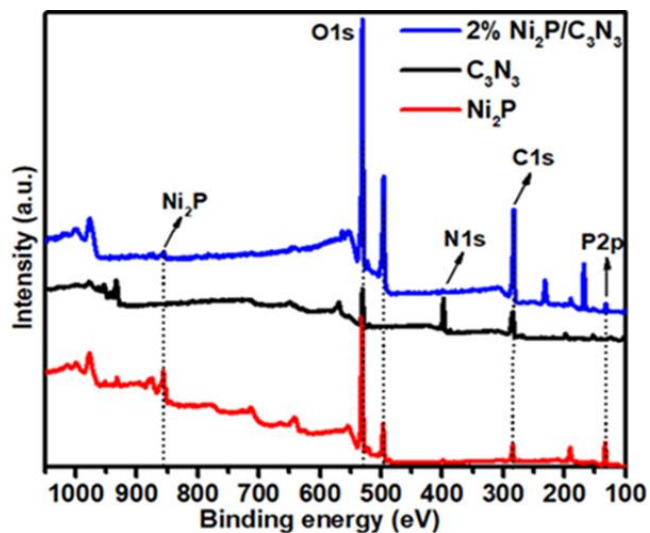


Figure S. 12: XPS survey of pure C₃N₃, 2% Ni₂P/C₃N₃ and Ni₂P

Vessel 5	(Sample)	Ni_P_Elements31(1)		Orig.	Date:	11/12/20 12:48
Pre-DF: 1	Wt.[g]:	Vol.[mL]:	100		Blank corr.:	off
P213.618						
Conc.1	201.2	0.8925	0.44	6.460	µg/L	>KAL
Conc.2	0.2012	0.8925	0.44	0.0065	mg/L	>KAL
Ints.	449911	2008	0.45			>KAL
Single values (Ints.): #1: 450734 #2: 447623 #3: 451377						
Ni231.604						
Conc.1	1308	2.162	0.17	35.93	µg/L	>KAL
Conc.2	1.308	2.162	0.17	0.0359	mg/L	>KAL
Ints.	1379137	2278	0.17			>KAL
Single values (Ints.): #1: 1376531 #2: 1380126 #3: 1380753						

Figure S. 13: ICP -OES data of 2% Ni₂P/C₃N₃ nanocomposite

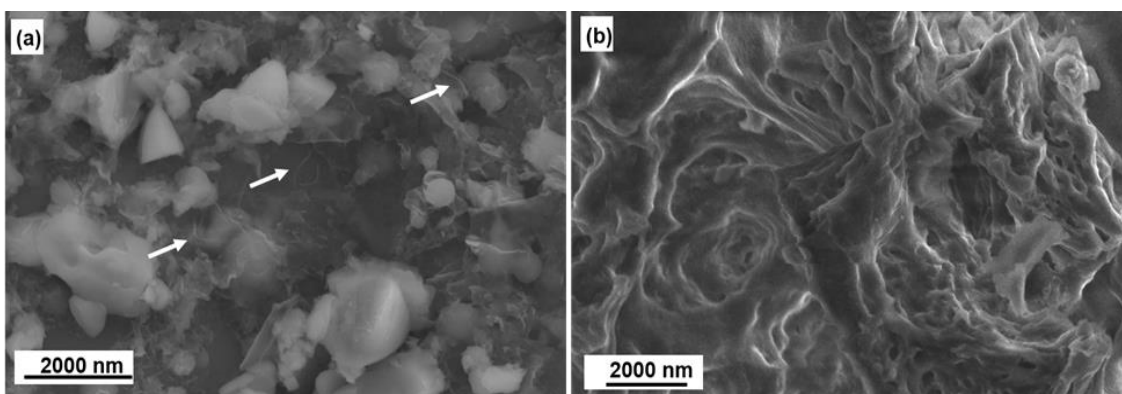


Figure S. 14: SEM image indicating the 2D layers structure of; (a) C₃N₃ and (b) C₃N₅

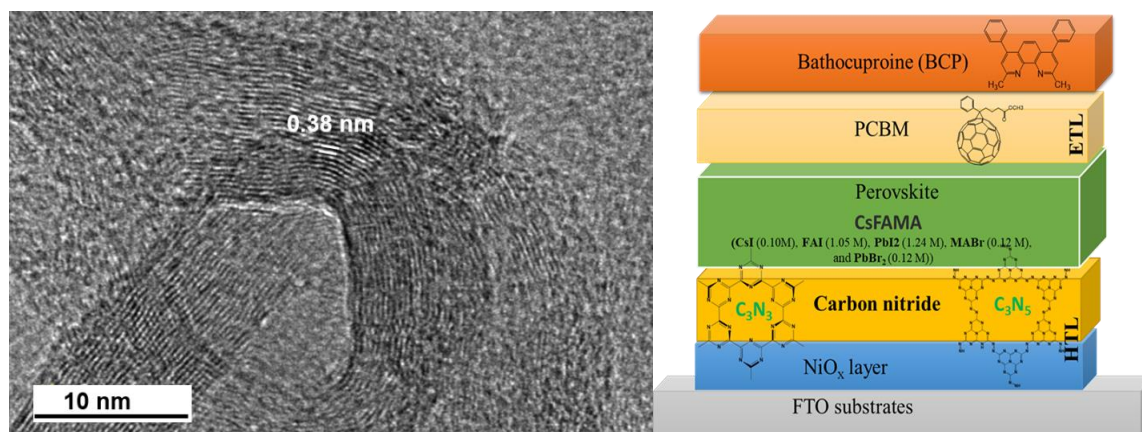


Figure S. 15: High resolution TEM image indicating the crystalline nature of C_3N_3 before washing with mineral acids and Layer by layer fabricated device.

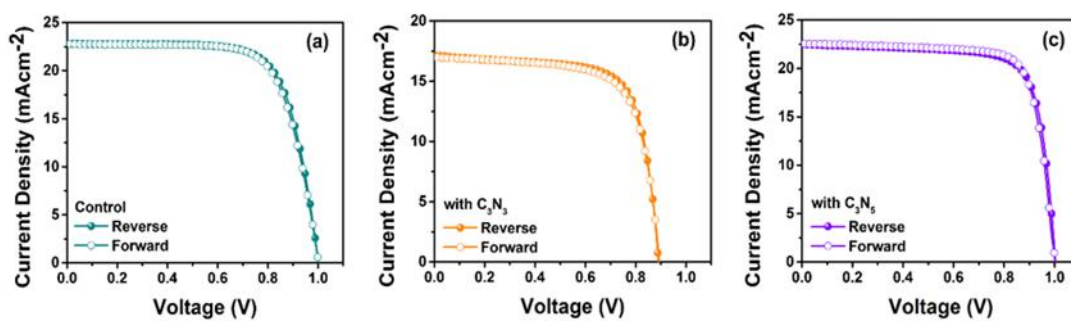


Figure S. 16: Reverse and forward scan J - V curves under simulated AM 1.5G illumination of (a). control, (b) with C_3N_3 , and (c) with C_3N_5 devices.

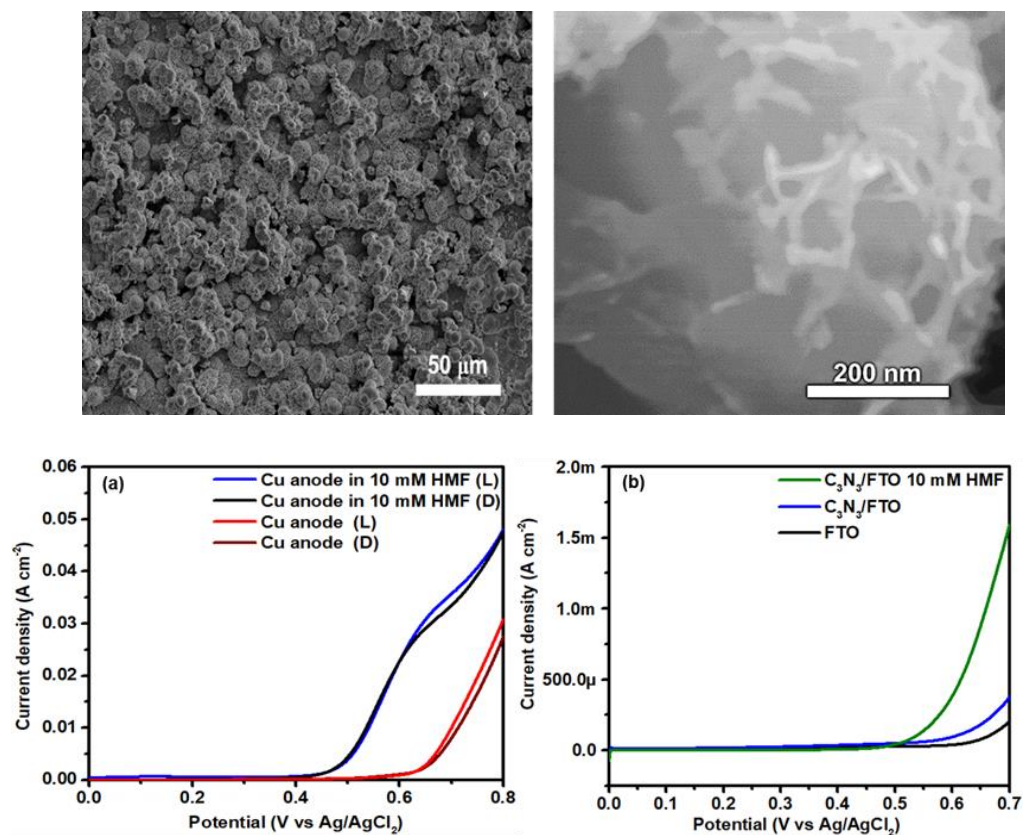


Figure S. 17: The scanning electron microscope images of the Cu containing C3N3 (a) overview, (b) HRSEM showing lamellar sheets (a) LSV polarization curves of Cu photoanode, in 1 M KOH aqueous electrolyte under visible light irradiation for hydrogen evolution reactions with 10 mM HMF (b)) LSV polarization curves of $\text{C}_3\text{N}_3/\text{FTO}$ photoanode, in 1 M KOH aqueous electrolyte under visible light irradiation for hydrogen evolution reactions with 10 mM HMF.

Appendix B. Supplementary Table

Table S. 1. Elemental Analysis of HRG, Melon and HRG@melon composites

Sample ID#	Weight	% Carbon	% Hydrogen	% Nitrogen
Blank	-	79	172	89
K Factor	0.94	16.72	8.87	5.88
Cystine (Control Run)	1.12	29.61	5.71	9.89
Melon	1.07	35.77	3.37	61.59
1% HRG@ melon	1.10	38.01	2.97	55.44
HRG	1.27	9.95	0.90	2.50

Table S. 2. Summary of PEC performance for 1% HRG@melon nanocomposite, CN-rGO, and g-C₃N₄.

Year	Photoanode material	Electrolyte	Potential (V) (vs. RHE)	Light intensity	Photocurrent ($\mu\text{A cm}^{-2}$)	Ref.
2021	1% HRG @melon/FTO	0.1 M KOH + 10% TEOA	1.23	100 mW cm ⁻² , AM 1.5	630	This work
2021	1% HRG @melon/FTO	0.1 M KOH	1.23	100 mW cm ⁻² , AM 1.5	70	This work
2018	CN-rGO film/FTO	0.1 M KOH + 10% TEOA	1.23	100 mW cm ⁻² , AM 1.5	660	5
2018	CN-rGO film/FTO	0.1 M KOH	1.23	100 mW cm ⁻² , AM 1.5	72	5
2018	g-C ₃ N ₄ nano rod arrays /FTO	0.5 M Na ₂ SO ₄	1.23	100 mW cm ⁻² , AM 1.5	11	6
2016	g-C ₃ N ₄ /FTO	0.1 M KCl	0.8 V (vs.Ag/AgCl)	100 mW cm ⁻² , AM 1.5	20	7

2015	g-C ₃ N ₄ /FTO	0.2 M Na ₂ SO ₄	1.23	$\lambda > 420$ nm, 200 W Xe lamp	30	8
2015	g-C ₃ N ₄ /FTO	0.1 M Na ₂ SO ₄	1.55	1 Sun	30	9

Table S. 3. Gibbs free energy difference (ΔG_{H^*} (eV)) for melon and HRG@melon with OH functional group attached to HRG. Red color represents the favorable sites for high HER activity.

N site	ΔG_{H^*} (eV) melon	ΔG_{H^*} (eV) HRG above void area; OH outside	ΔG_{H^*} (eV) HRG above void area; OH inside	ΔG_{H^*} (eV) HRG above heptazine. OH outside	ΔG_{H^*} (eV) HRG above heptazine. OH inside
1	0.39	0.35			0.31
2	0.39	0.31			0.33
3	1.04	1.03			1.13
4	2.14	2.12			2.14
5	1.04	0.35			0.38
6	2.22	2.11			2.17
7	0.39	0.14	0.23	0.31	0.33
8	0.71	0.77			0.96
9	0.39	0.03	0.20	0.01	0.26
10	0.39	0.20	0.25	0.38	0.24
11	1.04	1.00			1.03
12	2.14	2.13			2.14
13	1.14	1.11			1.06
14	1.24	1.18			1.19
15	0.71	0.67			0.71
16	0.39	0.23	0.32	0.28	0.28
17	1.04	2.17			2.18
18	1.24	0.92			1.21
19	1.04	0.94			0.89
20	1.04	2.19			2.09
21	0.39	0.22	0.54	0.21	0.27
22	0.71	0.86			0.87
23	1.24	0.96			1.26
24	1.14	1.09			0.93
25	2.14	1.97			2.09
26	1.04	0.99			0.94
27	0.39	0.22	0.25	0.18	0.09
28	0.39	0.13	0.19	0.39	0.15

29	0.71	0.91			0.90
30	0.39	0.26	0.26	0.16	0.08
31	2.22	2.14			2.06
32	1.04	0.32			0.36
33	2.14	2.12			1.93
34	1.04	1.04			0.47
35	0.39	0.33			0.33
36	0.39	0.28			0.30
37	1.04	0.90			1.03
38	1.24	1.12			1.10

Table S. 4. Photovoltaic statistics of the devices without the interfacial layer.

Device	V_{oc} (mV)	J_{sc} (mAcm ⁻²)	FF (%)	PCE (%)
1	1007.3	22.76	72.46	16.61
2	995.6	22.47	72.35	16.18
3	1004.7	22.54	71.15	16.11
4	1009.9	22.65	72.17	16.51
5	1001.9	22.79	73.07	16.69
Statistics	1003.88±4.9	22.64±0.12	72.24±0.62	16.42±0.23

Table S. 5. Photovoltaic statistics of the devices with C₃N₃ interfacial layer.

Device	V_{oc} (mV)	J_{sc} (mAcm ⁻²)	FF (%)	PCE (%)
1	860.29	16.71	68.77	9.89
2	888.30	16.79	70.71	10.55
3	899.31	16.86	70.84	10.74
4	896.15	17.44	70.19	10.97
5	890.16	17.21	71.74	10.99
6	865.29	17.26	71.69	10.71
Statistics	883.2±14.9	17.04±0.27	70.66±1.00	10.64±0.37

Table S. 6. Photovoltaic statistics of the devices with C₃N₅ interfacial layer.

Device	V_{oc} (mV)	J_{sc} (mAcm ⁻²)	FF (%)	PCE (%)
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1	999.63	22.40	75.98	17.02
2	998.57	22.24	76.41	16.97
3	1000.85	22.69	75.13	17.06
4	1003.48	22.52	75.95	17.17
5	1003.29	22.39	75.78	17.02
6	1003.15	22.43	74.26	16.71
Statistics	1001.5±1.9	22.45±0.14	75.59±0.70	16.99±0.14

Table S. 7. R_s , R_{sh} , and HF extracted from J - V curves of PSCs.

Device	Scan direction	R_s (Ω)	R_{sh} ($k\Omega$)	HF (%)
Control	Reverse	52.33	42.78	1.44
	Forward	62.48	34.71	
with C_3N_3	Reverse	61.19	11.49	3.75
	Forward	70.17	8.91	
with C_3N_5	Reverse	45.97	47.07	-0.85
	Forward	42.12	73.17	

Vitae

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Languages

English – A1

Urdu/Pashto – A1

Summary

I am interested in chemical aspects of energy and sustainability, in particular the conversion of solar energy into renewable fuels and valuable feedstock. Thus, electro- and photocatalysis for environmental and energy storage/harvesting applications are central point of my work at the interface of synthetic chemistry, engineering of nanomaterials. A central theme of my study to mimic from natural photosynthesis process to produce solar fuel. Therefore, my future research goal is to use bias-free perovskite based photoelectrochemical devices as an artificial leaf for photoreforming of waste plastics and waste biomass to into “green” hydrogen fuel and selective value-added chemical.

Education

A. Academics Qualification

- **Doctor of Philosophy (Ph.D.) in Chemistry**, 01/2018 – 05/2022, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, Dammam, KSA
Dissertation title “*Engineered 2D Carbon Nitride based Nanocomposites for Solar Energy Conversion Applications*”.
- **Master of Philosophy (M.Phil.) in Chemistry**, 06/2012–11/2015, Thesis title “*Phytochemical investigation of Hyoscyamus albus*”.
- **Master of Science (M. Sc.) in Chemistry**, 09/2009 – 03/2011

B. Professional Degrees in Teaching

Bachelor of Education (B.Ed.) 03/2012 – 04/2013

Thesis title “*Physical Facilities in Science Laboratories at Govt and Private Schools of KPK*”.

Professional Experience

Job Title (Nature)	Organization	Experience (from-to)
Lecturer B / Research Assistant (Teaching and Research)	Department of Chemistry, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, 31261 KSA	01/2018-till date
Research Associate (Research)	Department of Chemistry, University of Malakand, KP Pakistan	2013-2015
Lecturer (Teaching)	Government Degree College Madyan, KP Pakistan	2011-2012 and 2016-2017

Research Details

A. Research Interests

1. Pre-treatment of Synthetic Waste Polymers and Extraction of Selective Lignin from Waste Biomass for Photoreforming Applications.

I have successfully designed a novel protocol for the pre-treatment of synthetic waste polymers such as waste plastics and extraction of selective β -O-4 lignin monomer from several waste biomass sources.

2. Band gap Engineering of Photocatalyst for Photoreforming, Photovoltaics and Overall Water Splitting

Recently, I have engineered band gap of novel photocatalysts – including metal oxides and carbon-based nanomaterials to develop light-driven, high-yield organic transformations. My aim is to enhance the sustainability and economic value of solar fuels by developing processes that simultaneously produce fuels and drive value-added organic transformations.

3. Designing of Materials with Controlled Morphologies, Crystallinities, and Chemically Active Surfaces

In the near past, I have successfully engineered state of the art morphologies, crystallinities, particle size, and surface functionalities (low and high index surfaces) by solid state chemistry, wet chemistry, magnetron sputtering, and electrochemical techniques. The materials are found exceptionally stable and productive in as catalysts for energy conversion / storage and environmental applications.

4. The Kinetics and Mechanistic Performance Studies of the Fabricated Materials

My fundamental interest lies in using designed materials for energy and environmental applications. I have worked with photocatalytic and photo electrocatalytic water splitting to generate hydrogen. I have already extended my expertise to perovskite solar cells, and photoreforming of waste materials, lately.

I firmly believe that without a proper understanding of any process, it is hard to design or improve the performance of existing materials. Therefore, I am utilizing various tools and methods for the investigation of energy storage and conversion. These tools/techniques include electrochemical impedance spectroscopy (**EIS**) (e.g., Nyquist plot, Mott-Schottky (**MS**) analysis), Voltammetry (**CV** and **LSV** for Active Surface Area, Tafel slopes, oxidation states, and current density), Galvanostatic charge-discharge (**GCD**), Amperometry, Faradaic Efficiency (**FE**), Intensity Modulated Photon Spectroscopy (**IMPS**), Incident Photon-to-current Efficiency (**IPCE**), Solar to Hydrogen Efficiency (**STH**), GC- analysis for hydrogen and oxygen quantification etc.

5. The computational analysis (DFT & MD simulations) for CO₂ capture, and Water Splitting mechanistic Studies.

B. Research Projects Involved/Completed

1. **Halliburton Energy Services, Dhahran, KSA Funded Research Project:** Programmed mesoporous nanomaterials as carriers for control transportation and release of antiscalants. **Project # CHEM -2453, Completed** in October 2019

C. Instrumentation Expertise

- **Thin films and electrodes fabrication** via spin coating, Dr. Blade, drop casting and electrodeposition techniques
- **Optical characterization techniques** such as Photoluminescence (PL) and UV-Vis/DRS for charge separation, band position studies, Kubelka-Munk functions, and Tauc's plots analysis
- **Crystal phase, oxidation states and defects determination techniques**, i.e., , XRD, and XPS
- **Morphological and related surface characterization** such as SEM, TEM, and BET
- **Electrochemical Analyses** such as LSV, CV (I-V for reaction pathways, kinetic studies via Tafel plots, over and onset potential analyses, etc.), Chronoamperometry (I-t curves for determining electro and photostability of the material), Electronic impedance spectroscopy (EIS) and Mott-Schottky plots for charge flow /capacitance and band positions determination.
- **Quantification analysis** through GC-MS (TCD) for H₂ & O₂ generation.
- **Structure Elucidation** of organic semiconductors, lignin, and value-added products from photoreforming using NMR spectrometer (¹H, ¹³C, ¹⁵N and HSQC etc.).
- **Photo and electro efficiency determination** through electrochemical techniques such as faradaic efficiency (FE), Incident photon to current efficiency (IPCE), solar to hydrogen efficiency (STH), etc.

Research Publications

S/No	A. Papers	IF (JIF Q)
1.	M Ashraf , N Ullah, and M N Tahir* “Engineered Metal Organic Framework (MOFs) for Photocatalytic, Electrocatalytic and Photoelectrochemical Water Splitting” <i>Invited review for Energychem</i>	Ready for submission
2.	M Ashraf , N Ullah, and M N Tahir* “Photoelectrochemical reforming of Biomass intermediates integrated with H ₂ fuel over <i>In-Situ</i> Fabricated Artificial Leaf of Carbon Nitride C ₃ N ₃ on Cu Foil” <i>Green Chemistry</i>	Ready for submission
3.	M Ashraf , W Tremel*, and M N Tahir* “Photocatalyst engineering and operando characterization for efficient solar energy conversion” <i>Adv. Mater.</i>	Ready for submission
4.	M Ashraf , R Ali, N Ullah, F Raziq, Z Huabin, U Schwingenschlöggl and M N Tahir* “Engineered carbon nitride C ₃ N ₃ with non-noble metal Ni ₂ P co-catalyst for Photoelectrochemical water splitting” <i>Appl. Catal. B APCATB-D-22-07648</i>	Under review 24.33 (Q1)
5.	M Ashraf , R Ali, N Ullah, I Khan, S Ahmad, S Wooh, W Tremel*, U Schwingenschlöggl* and M N Tahir* “Bandgap Engineering of Melon using Highly Reduced Graphene Oxide for Enhanced Photoelectrochemical Hydrogen Evolution” <i>Adv. Mater.</i>	Under review 32.09 (Q1)
6.	M Ashraf , N Ullah, and M N Tahir* “Mechanistic insight to the Emerging Solar Conversion Technologies: Prospects and challenges” <i>ACS Sustainable Chemistry & Engineering</i> <i>Manuscript ID: sc-2022-06801a</i>	Under review 9.2 (Q1)
7.	I Khan, N Baig, A Bake, M Haroon, M Ashraf , A Al-Saadi, M N Tahir, S Wooh* “Electrochemically Decorated Free Standing and Highly Porous Laser-Induced Graphene for Overall Alkaline Water Splitting” <i>J. Mater. Chem. TA-ART-11-2022-008635</i>	Under review 14.51 (Q1)
8.	N. H. Hemasiri, M. Ashraf , S. Kazim, R. Graf, R. Berger, N. Ullah, M. N. Tahir, and S Ahmad “Interface Tweaking of Perovskite Solar Cells with Carbon Nitride-based 2D Materials” <i>Nano Energy NANOEN-D-22-02270</i>	Revision submitted 19.06 (Q1)
9.	M. Ashraf , N. H. Hemasiri, S. Kazim, N. Ullah, M. N. Tahir, and S Ahmad “Interface engineering with low band gap 2D carbon nitrides for perovskite solar cells fabrication” <i>Sustain. Energy Fuels</i>	6.81 (Q1)
10.	M. Ashraf , M. S. Ahmad, M. N. Tahir, Y. Inomata, T. Kida, N. Ullah, “Transition Metal Nanoparticles as Nanocatalysts in Organic Coupling Reactions” <i>Coord. Chem. Rev.</i>	24.83 (Q1)
11.	S. Mushtaq; Z. Aslam; R. Ali; U. Aslam; S. Naseem; M. Ashraf ; M. M. Bello “Surfactant modified waste ash for the removal of chloro and nitro group substituted benzene from wastewater” <i>Water Sci. Technol.</i>	2.43 (Q2)
12.	M. Khan. M. E. Assal, M. N. Tahir, M. Khan, M. Ashraf , and S. F. Adil “Graphene/Inorganic Nanocomposites: Evolving Photocatalysts for Solar Energy Conversion for Environmental Remediation” <i>J. Saudi Chem. Soc.</i>	4.75 (Q2)
13.	S.S Shah; H. Yang; M. Ashraf ; M. A. A. Qasem; M. A. Aziz* “Preperation of highly stable and electrochemically active three-dimensional interconnected graphene frameworks from jute sticks” <i>Chem. Asian J.</i> EMID: asia.202200567	4.83 (Q1)
14.	I. Hussain; N. Abbas; M. Ahmad; Xi Chen; M Ashraf ; M.Z Ansari; K. Zhang. “Glycol-assisted Cu-doped ZnS polyhedron-like structure as binder-free novel electrode materials” <i>J. Saudi Chem. Soc.</i> JSCS-D-22-00140R1	4.75 (Q2)
15.	M. Haroon, M. Ashraf , N. Ullah, M. N. Tahir, A. Al-Saadi., SERS and EC-SERS detection of local anesthetic procaine using Pd loaded highly reduced graphene oxide nanocomposite substrate. <i>Spectrochim. Acta A Mol. Biomol. Spectrosc.</i> 2022, 278, 5, 121381	4.83 (Q2)
16.	M Khan*, M Ashraf , M. R. Shaik, S F. Adil1, M. S. Islam1, M. Kuniyi, M. Khan, M. R. Hatshan, R. H. Alshammari, M. R. Siddiqui and M. N. Tahir “Pyrene	5.54 (Q1)

	Functionalized Highly Reduced Graphene Oxide-Palladium Nanocomposite: A Novel Catalyst for the Mizoroki-Heck reaction in Water” <i>Front. Chem.</i> DOI: 10.3389/fchem.2022.872366	
17.	M Mansha, T Ahmad, N Ullah, S Akram Khan, M Ashraf , S Ali, B Tan and I khan. “Photocatalytic Water-Splitting by Organic Conjugated Polymers: Opportunities and Challenges”. <i>Chem. Rec.</i> e202100336	6.93 (Q1)
18.	SF Adil, M Ashraf , M Khan, ME Assal, MR Shaik, M Kuniyil, A Al-Warthan and M N Tahir* “Advances in Graphene/Inorganic Nanoparticle Composites for Catalytic Applications”. <i>Chem. Rec.</i> e202100274	6.93 (Q1)
19.	Lange, M. A.; Khan, I.; Opitz, P.; Ashraf, M. ; Qurashi, A.; Prädell, L.; Panthöfer, M.; Cossmer, A.; Pfeifer, J.; et al. A Generalized Method for High-Speed Fluorination of Metal Oxides by Spark Plasma Sintering Yields Ta ₃ O ₇ F and TaO ₂ F with High Photocatalytic Activity for Oxygen Evolution from Water . <i>Adv. Mater.</i> 2021 , 33 (20), 2007434.	32.09 (Q1)
20.	Ashraf, M. ; et al., A High-Performance Asymmetric Supercapacitor Based on Tungsten Oxide Nanoplates and Highly Reduced Graphene Oxide Electrodes, <i>Chem. Eur. J.</i> 2021 , 27,6973 –6984,	5.21 (Q1)
21.	Ashraf, M. ; Khan, I.; Baig, N.; Hendi, A. H.; Ehsan, M. F.; Sarfraz, N. A Bifunctional 2-D Interlayered B-Cu ₂ V ₂ O ₇ /Zn ₂ V ₂ O ₆ (CZVO) Heterojunction for Solar-Driven Non-sacrificial Dye Degradation and Water Oxidation . <i>Energy Technol.</i> 2021 , 2100034.	4.14 (Q2)
22.	Lange, M.; Khan, I.; Dören, R.; Ashraf, M. ; Qurashi, A.; Prädell, L. A.; Panthöfer, M.; von der Au, M.; Cossmer, A.; Pfeifer, J.; et al. High-Speed Solid State Fluorination of Nb ₂ O ₅ Yields NbO ₂ F and Nb ₃ O ₇ F with Photocatalytic Activity for Oxygen Evolution from Water. <i>Dalt. Trans.</i> 2021 , 24 (50), 6528–6538.	4.56 (Q1)
23.	Hussain M A, Shad I, Malik I, Amin M, Amjad F, Tahir M. N , Ullah N, Ashraf M , Irfan M. I. “Design, characterization, and enhanced bioavailability of hydroxypropylcellulose-based novel bioconjugates for inclusion of a fluoroquinolone antibiotic–gemifloxacin” <i>Cellul. Chem. Technol.</i> 2021 , 55 (9-10), 1019-1027	1.46 (Q3)
24.	Ashraf, M. ; Khan, I.; Usman, M.; Khan, A.; Shah, S. S.; Khan, A. Z.; Saeed, K.; Yaseen, M.; Ehsan, M. F.; Tahir, M. N.; et al. Hematite and Magnetite Nanostructures for Green and Sustainable Energy Harnessing and Environmental Pollution Control: A Review. <i>Chem. Res. Toxicol.</i> 2020 , 33, 6, 1292–1311. (Front Cover)	3.97 (Q2)
25.	M. Sarif, J. Hilgert, I. Khan, R. A. Harris, S. Plana-Ruiz, Ashraf, M. ; E. Pütz, J. Schemberg, M. Panthöfer, U. Kolb, M. Nawaz Tahir, W. Tremel; Selective Synthesis of Monodisperse CoO Nanooctahedra as Catalysts for Electrochemical Water Oxidation. <i>Langmuir</i> 2020 , 36, 46, 13804–13816	4.33 (Q1)
26.	Khan, M.; Shaik, M. R.; Adil, S. F.; Kuniyil, M.; Ashraf, M. ; Frerichs, H.; Sarif, M. A.; Siddiqui, M. R. H.; Al–Warthan, A.; Labis, J. P.; et al. Facile Synthesis of Pd@graphene Nanocomposites with Enhanced Catalytic Activity towards Suzuki Coupling Reaction. <i>Sci. Rep.</i> 2020 , 10 (1), 11728.	4.99 (Q1)
27.	A. R. Shaikh, Ashraf, M. et al . “Amino acid Ionic Liquids as a potential candidate for CO ₂ capture: Combined Density Functional Theory and Molecular Dynamics Simulations”. <i>Chem. Phys. Lett</i> 2020 , 745, 137239.	2.75 (Q2)
28.	Hussain M A, Shad I, Malik I, Amjad F, Tahir M. N , Ullah N, Ashraf M , Sher M. Design, characterization, and enhanced bioavailability of	6.21 (Q1)

	hydroxypropylcellulose-naproxen conjugates. <i>Arab. J. Chem.</i> 2020 13, 5717–5723	
29.	Hussain M A, Shad I, Malik I, Amjad F, Tahir M. N, Ullah N, Ashraf M , Sher M. Hydroxypropylcellulose-flurbiprofen conjugates: design, characterization, anti-inflammatory activity, and enhanced bioavailability. <i>Saudi Pharm. J</i> 2020 , 28 869–875	4.56 (Q2)
30.	Basheer, C.; Kamran, M.; Ashraf, M. ; Lee, H. K. “Enhancing Liquid-Phase Microextraction Efficiency through Chemical Reactions”. <i>TrAC - Trends Anal. Chem.</i> 2019 , 1: 426–433	14.90 (Q1)
31.	Ashraf, M.; * M. Ahmad, H. Ahmad, S. Ahmad. “Phytochemical investigation of Hyoscymus albus” <i>Pak. J. Pharm. Sci</i> 2019 , 32(2):661-667.	0.86 (Q3)
S/No	B. Book Chapters	Status
32.	Sarfraz, N.; Ashraf, M. ; Khan, I.; “Magnetic Iron Oxide Nanocomposites: An overview on Their Types, and Applications”. <i>Elsevier-Publisher of Scientific Books & Journals (Smart Polymer Nanocomposites)</i>	Published
S/No	C. Patents	Status
33.	Ashraf, M. ; Khan, I.; Baig, N.; Hendi, A. H “Hybrid photoactive heterojunction and method of preparation thereof” US. Patent 11,453,599	Published
34.	Ashraf, M. ; N. Ullah, I Khan, N. Tahir “Synthesis of Tungsten Oxide Nanoplates and Highly Reduced Graphene Oxide as an Electrodes Materials for Energy Storage Devices” US. Patent 11,455,084	Published

Posters, Seminars, & Conferences (selected)

- **Muhammad Ashraf**, A Bifunctional 2-D Interlayered $\text{Cu}_2\text{V}_2\text{O}_7/\text{Zn}_2\text{V}_2\text{O}_6$ (CZVO) Heterojunction for Solar-Driven Non-sacrificial Dye Degradation and Water Oxidation, **1st Gulf Association International Conference and Exhibition 2022** Kingdom of Bahrain (Speaker)
- **Muhammad Ashraf**, Muhammad Nawaz Tahir., : Synthesis of Pd @Highly Reduced Graphene Oxide (HRG) Nanostructures for Efficient Catalytic Reaction, *Chem. Index* 2019 Kingdom of Bahrain (19377) (Poster)
- **Muhammad Ashraf**, Roshan Ali, Nisar Ullah, Udo Schwingenschlögl* and Muhammad Nawaz Tahir*, : Bandgap Engineering of Melon using Highly Reduced Graphene Oxide for Enhanced Photoelectrochemical Hydrogen Evolution, “**KAUST Research Conference: Accelerating Solar Energy Research towards meeting Vision 2030 Goals**” (9-10 May 2022), 4700 King Abdullah University of Science and Technology (KAUST) Thuwal 23955-6900, Kingdom of Saudi Arabia (Poster)

Other Professional Skill Enhancement Activities

I also involved in the collaborative projects with **Prof. Wolfgang Tremel** from Institute für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Mainz,

Germany, and **Prof. Shahzada Ahmad** from BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940, Leioa, Spain and **Prof. Udo Schwingenschlögl** from Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

Referees

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