

**SYNTHESIS OF SURFACE FUNCTIONALIZED Cu_2O ,
 $\text{Au@Cu}_2\text{O}$ HYBRID FOR PHOTOCATALYTIC
APPLICATION**

BY

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In

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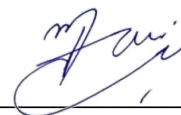
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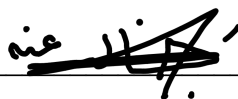
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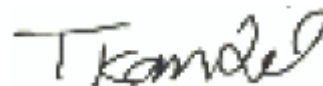
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DEDICATION

*To the glory my creator ALLAH Subhanahu Watahalah, THE ONE THE
ETERNAL REFUGE, THAT IS NEITHER BEGETS NOR IS BORN,
NOTHING IS EQUIVALENT TO HIM. Blessing to our prophet Muhammed
(SAW) and my beloved parent*

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LIST OF ABBREVIATIONS

EDX	:	Electron Diffraction X-Ray Spectroscopy
SEM	:	Scanning Electron Microscopy
SDS		Sodium Dodecyl Sulfate
MB		Methylene Blue

ABSTRACT

Full Name : MOHAMMED TAJUDEEN ABDULLAHI

Thesis Title : SYNTHESIS OF SURFACE FUNCTIONALIZED Cu_2O $\text{Au}@\text{Cu}_2\text{O}$ HYBRID FOR PHOTOCATALYTIC APPLICATION

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The environmental concern raised due to the use of conventional fuel for energy production which results in increasing the level of CO_2 and to remediate industrial dumped organic pollutants especially dyes into the ocean body, demands for alternatives renewable energy resources. There is an increasing need to develop new materials or improve the existing options to exploit the available carbon neutral energy resources such as hydrogen fuel using photo-electrochemical (PEC) water splitting or degradation of pollutants using solar light. The both processes require the design and synthesis of new materials which are cost effective, environmentally friendly, capable of harvesting maximum range of the solar spectrum, electrically and chemically stable, with suitable band-edge potentials to perform the function. In this project we accomplished the synthesis of pristine Cu_2O nanoparticles consisting and hybrid nanomaterial with the composition Au and Cu_2O . Due to the low band gap ~ 2.1 eV of Cu_2O and its suitable conduction band edge positions, it is among the most favorite semiconductors available for visible light base photocatalytic applications. The hybridization of Au and Cu_2O improved the solar absorption efficiency, photocatalytic activity and the chemical stability of these materials under working conditions.

ABSTRACT (ARABIC)

الاسم الكامل: MOHAMED TAJUDEEN ABDULLAHI

الضوئي التحفيز لتطبيق Hybrid Au @ Cu₂O و Cu₂O وتوصيف تحضير: الرسالة عنوان

كيمياء: الدقيق التخصص

2020 أبريل: الدرجة تاريخ

العضوية الصبغة ومعالجة الكربون أكسيد ثاني مستوى زيادة مع للتعامل أخرى مناطق في فعالة بيئية بإدارة الاهتمام الكربون المحايدة الطاقة موارد لإنتاج المواد تحسين / لتطوير متزايدة حاجة هناك ، المحيط جسم في الملقة الصناعية الضوئي للتحلل ضوئي وحفز المياه لتقسيم (PEC) الكهروكيميائية المواد- الصور باستخدام الهيدروجين وقود مثل أقصى حصاد على القدرة الجديدة للمواد التكلفة حيث من الفعاليين والتركيب التصميم فإن ، لذلك . العضوية للصبغة مفر لا أمر المياه لتقسيم المناسبة النطاق حافة إمكانات مع ، وكيميائيًا كهربائيًا المستقر ، الشمسي الطيف من مدى مع الهجينة النانوية والمواد ، O و Cu من يتكون مركب أصلي نانوي جزيء بإنجاز قمنا ، المشروع هذا في . منه فجوة بسبب ، العمل ظروف في المواد لهذه الكيميائي الاستقرار لتحسين السطح وهندسة Cu₂O و Au التركيب المفضلة الموصلات أشباه بين من وهي ، المناسبة التوصيل حافة مواضع و Cu₂O - 2.1 eV ~ المنخفض النطاق المرئية الضوء لقاعدة الضوئي التحفيز لتطبيقات المتاحة

CHAPTER 1

INTRODUCTION

The advancement in technology is in the forefront of developmental strive of modern era with energy being very important necessity for driving this race. Therefore, there is an ever increasing demand for energy both in the developed and developing countries. Human well-being is much related to the access to energy, due to its impact on economic development and reducing the poverty. The hardcore challenge that threatens the world development is how to ensure everyone has access to the sufficient amount of energy and safe clean water for their optimum functioning. Although, the present sources of energy like coal, gas and crude oil pose a great environmental concern to the world, still fossil fuels (oil, gas and coal) have dominated our energy sources over the years. It produces atmospheric pollutants with devastating foot prints of different degree in every part of the world. To reverse this trend, it is paramount to transit from fossil fuel based source of energy to renewable energy resource *i.e.* bioenergy, wind, hydropower and solar energy. The renewable resources have a huge potential as a source of energy with no or little environmental damage¹.

Among the renewable sources available, solar power exposing 1.2×10^{14} kJ/sec of energy to Earth's surface is the most promising option². The efficient conversion of solar power using renewable resources such as photo-electrochemical (PEC) water splitting to produce hydrogen fuel could be the cost effective and environmentally friendly alternatives to meet world energy demands. The solar spectrum could successfully provide the required energy (286 kJ mol^{-1}) input to split water at room temperature and pressure³. Therefore,

the design and synthesis of new functional materials capable of; **(i)** harvesting the maximum range of solar spectrum, **(ii)** electrically and chemically stable and **(iii)** with suitable band-edge potentials to split water are inevitable.

The advances towards tapping into visible light photoactive semiconductors has seen interest even in non-oxide based photocatalyst such as (oxy)nitride (e.g. C_3N_4 and $TaON_4$), also sulphide like MoS_4 , $CuInS_2$ and CdS semiconductors⁵. However, the narrow band gap of the mentioned photocatalyst contributed to their relatively weak reduction, that is a low negative conduction band (CB) and/or oxidation which implies a low positive valence band (VB) potentials. So there is a need to develop the materials with a suitable band gap as well as positions of valence and conduction band. The Cu_2O fulfills the necessary criteria required for H_2 production using solar light. Cuprous oxide (Cu_2O) has a band gap of 2.0-2.4 eV suitable for water redox reaction and an excellent material for photocatalytic organic dye degradation⁶.

1.1 Semiconductor Nanoparticle for Sunlight Harvesting

The mindset on how to harvest the solar power for valuable uses in electricity or to bring about chemical reaction has been around with us since the discovery of the possibility of generating electricity upon exposure of semiconductor material to sunlight. Civilization comes with a huge price, as the energy harness to meet increasing needs of energy by consumers on their pursuit for civilization and to attain comfort. Developing nations at present drive for technology are consuming energy at an unprecedented rate. This energy, is majorly produced using fossil resources. Earlier human relies on his own power to perform a task, but industrial boom facilitated invention of machines that now do those task human has done earlier and these machines run on fossil fuel directly or indirectly.

The unending race of civilization is threatening our present finite energy sources and soon we might run out of oil, scarcity will set in and energy from fossil fuel will no longer be available or affordable to us. Presently, our civilization energy up take is about 18TW ($18 \times 10^{12} \text{ W}$)⁷, and it is expected to be more than double the rate in nearest future⁸.

The solar energy with capacity to expose light on earth which can produce $3.846 \times 10^{26} \text{ W}$ of energy per second could be the potential alternative energy generation option to maintain the demands of world energy. However, to do so, we need suitable of light absorbing materials. The inorganic based semiconductor has shown great potential. The energy when captured by semiconductor is converted to electricity through photovoltaics effect, (Figure 1), as a model where the source of current parallel with a diode and as the light intensity increases so is the current generated by the photovoltaic (PV) cell. In the absent of light, the PV act as a diode⁹.

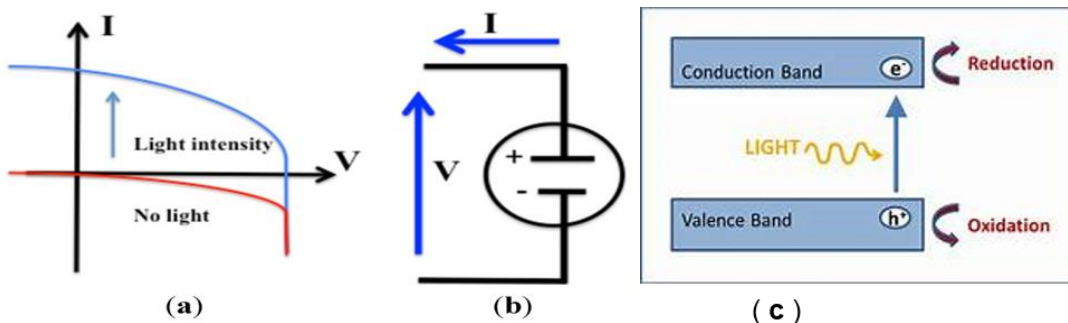


Figure 1, (a) I-V Curve of photovoltaic (PV) cell in darkness and under illumination; (b) Electrical diagram of a PV cell; (c) Semiconductor light induced redox reaction

1.2 Hybrid Nanomaterial

These are composite materials which consist of more than one constituents, connected to each other in the nanometer size regime at the same platform. It could be

a combination of inorganic semiconductors such as TiO_2 , Cu_2O , Fe_2O_3 , MnO based nanomaterial joined with plasmonic metal like Au, Ag, or Cu on the surface of the use inorganic semiconductors. These materials not only present the combined properties of individual constituents but also new properties of the hybrid as a result of electronic communication between the different domains.¹⁰ There is a decrease in the electromagnetic frequency of a semiconductor when plasmonic metal were introduced into its surface, and given that there is an inverse relation between frequency and wavelength, therefore, MNO with Au hybrid interaction will lead to a red shift in the absorption of electromagnetic radiation by the hybrid nanomaterial. The size of noble metal domain has a huge contribution to the overall new effect exhibited by the newly formed hybrid materials. For instance, a pure Au nanoparticle with 5-20 nm size range shows a collective plasmon resonance which correspond to 520-525 nm, and this was red shifted to 555-585 nm when the Au nanoparticle was attached Cu_2O ¹¹. Figure 2, shows a hybrid nanomaterial consisting of Au metal domain (in yellow color) and Cu_2O semiconductor component (wine color). This combination ensures a cheap hybrid nanomaterial consisting largely of efficient, less toxic and abundantly available materials. The architecture of the hybrid material also enables the metal to contribute maximum for charge separation.

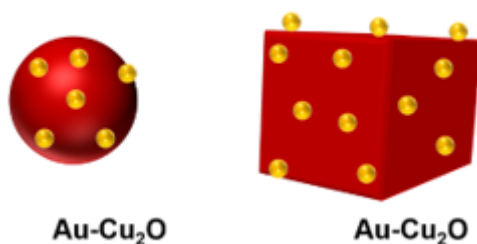


Figure 2, Gold is the yellow dots and wine color represent copper (1) oxide

Metal oxide semiconductor photocatalyst has been proven to be highly desirable for several applications. Basically, ultraviolet (UV) light absorbing semiconductors with wide band gap are usually employed as photocatalytically active materials¹¹. The semiconductor materials such as TiO_2 ¹², ZnO ¹³, among others has gain great attention due to UV light harvesting properties where as CdS ¹⁴ is the best visible light harvesting semiconductor. In the face of this remarkable usefulness of these metal oxides semiconductors, there are many shortcomings which hampers their function to be used as efficient photocatalysts. These are still matter of concerns for their use as semiconductor material at large scale. The noticed shortcomings are faster charge carrier recombination, low stability in recycling and low photo induced reaction efficiency. This warrant the need to study the photocatalytic performance of cuprous oxide to add to the recent effort by the scientists on this semiconductor material^{15,16,17}. Figure 3, represent the scheme with noble metal as core and Cu_2O as shell materials. This design is among the already well established metal-semiconductor based nanoparticles. However, noble metal being inside as core cannot contribute for charge separation, one of the key parameter which defines the best efficiency of the photocatalyst.

Cu_2O is well known for its well-placed conduction band (CB) and valence band (VB) for the overall oxidation of water splitting¹⁸. Typically, semiconductor is either that with direct band gap or indirect band gap, but Cu_2O is a good example of direct band gap semiconductor. A band gap is the minimum energy difference that is between the valence bond (VB) at the top and the conduction band (CB) at the bottom. The electron momentum at the bands are usually not of the same values. The Energy maxima in the valence band

and the energy minima in the conduction band are define by certain crystal momentum and k -vector (propagation constant) in the Brillouin zone. Basically, Cu_2O conduction band minima and valence band maxima, k -vector are the same which imply a direct band gap semiconductor. In a direct band gap, the momentum of electrons & holes is similar for both the conduction band and the valence band, this electron can emit photon. The direct band semiconductor electron in conductor band (CB) minima, recombine directly with holes in valence band (VB) maxima without change in kinetic energy and momentum, where energy in the form of light is spontaneous emission¹⁹.

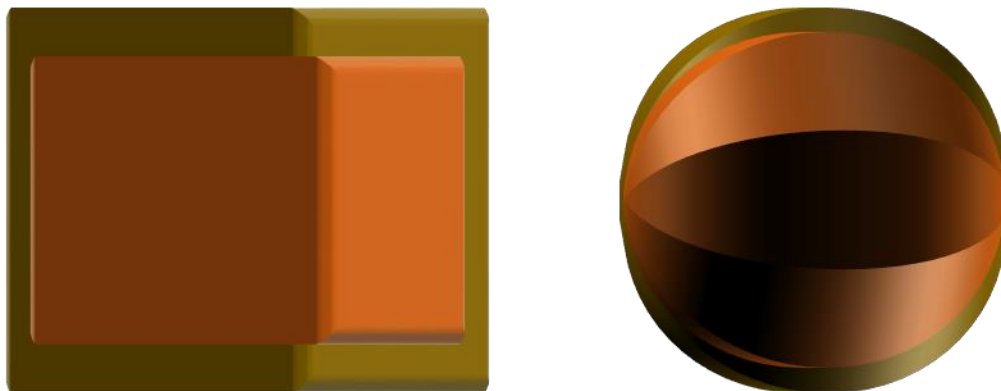


Figure 3, Cube $\text{Au}@\text{Cu}_2\text{O}$ & Octahedron $\text{Au}@\text{Cu}_2\text{O}$ in a gold shell-copper oxide core hybrid nanomaterial

1.2.1 Copper (1) Oxide Photoelectrochemistry uses

Photoelectrochemical production of hydrogen through the splitting of water from the direct harvesting of solar energy using semiconductor can ease the issue of energy conservation and storage associated with solar electricity production. The associated cost with the existing methods give PEC an edge as a promising innovative technique for ultimate solar fuel generation, in this case hydrogen²⁰. The stability and efficiency of the

system also count in determining the best choice for the water splitting method. The efficiency of solar to hydrogen (STH) water splitting system can be define as

$$STH = \left(\frac{J_{Photo} [mA/cm^2] \times 1.23V \times \eta_F}{Power [mW/cm^2]} \right) \quad 1$$

Where the symbol J_{Photo} is the photocurrent density per geometric area and η_F stand for the faradiac efficiency for hydrogen evolution. This equation is useful when sacrificial agents like methanol are not used and oxygen evolution occurs²⁰.

The value 1.23V is the reversible voltage needed for water splitting and represents the highest electrical energy that can be harvested by reacting hydrogen and oxygen to produce liquid water in a fuel cell²¹.

Therefore, in this project we would accomplish the synthesis of plasmonic metals (Au) and low bandgap semiconductor (Cu_2O) based hybrid nanoparticles using bottom up wet chemical approaches to solve the both impairments related to its use as photocatalytic applications. The strategy will focus to engineer the Cu_2O domain; **(a)** by controlling the size and shape of Cu_2O domain in the nano-regime and improving the photostability of the Cu_2O domain by combining with plasmonic mateals^{22,23}. The wet chemical synthesis gives the best opportunity to control the nucleation and growth steps by controlling heating rate/temperature, employing proper solvents and stabilizing ligands. This strategy will help stabilizing the Cu_2O domains in the nano-regime by compensating the surface energy through proper ligand binding²⁴.

1.2.2 Noble Metal Nanoparticle

Surface plasmon resonance (SPR) is very well associated with noble metal nanoparticles (NPs) due to the behavior of their free surface electrons that oscillate with the same frequency of the incident electromagnetic radiation²⁵. Noble metal nanoparticles are unique in their capacity to exhibit local surface plasmon resonance (LSPR) optical properties. The presence of resonating plasmon is attributed to the loads of free electrons and stabilities in chemical environment as seen in the case of gold (Au) and Silver (Ag) nanoparticle. These nanoparticles are being exploited for the plasmonic field applications because of its large LSPR support for wide region of the electromagnetic radiation spectrum. However, the LSPR of Ag nanoparticle has a stronger intensity than observed in other noble metals, perhaps, its low refractive index could account for this performance in case of silver^{26,27}. However, the chemical stability of silver is compromised under working condition. The ease of fabrication of Au nanoparticles along with its high chemical stability prompted their use as a plasmonic metal nanoparticle much more than any other metal based materials such as Ag and Cu. The noble metal based nanoparticles have also considerably gained attention as a sensor²⁸. Biological/Chemical sensor usefulness of a nanomaterial is determined by the refractive index sensitivity of nanoparticles.

1.2.3 Semiconductor Nanoparticle

Metal oxides have gained tremendous use as a semiconductor such as TiO_2 , WO_3 , and CuO due to their ability to harvest sunlight. They could be categorized as either p-type or n-type depending on their conduction band and valence band position. Among which copper oxide is a p-type semiconductor with wide distribution on the earth, relatively cheap and non-toxic transitional metal oxide. It can exist in various forms such as Cu_4O_3 , CuO

and Cu_2O ²⁹. The first two is less commonly used in such applications compare to Cu_2O . Figure 4, shows the crystal structure of Cu_2O (Cubic Bravais lattice), with the space group $\text{Pn}\bar{3}\text{m}$ (224) and has a lattice constant of $4.2696 \pm 0.0010 \text{ \AA}$ ³⁰. Copper atom is coordinated to two oxygen linearly and oxygen atoms which occupies the body center and the edge of the cubic unit cell, individually coordinated to four copper atoms in a tetragonal fashion.

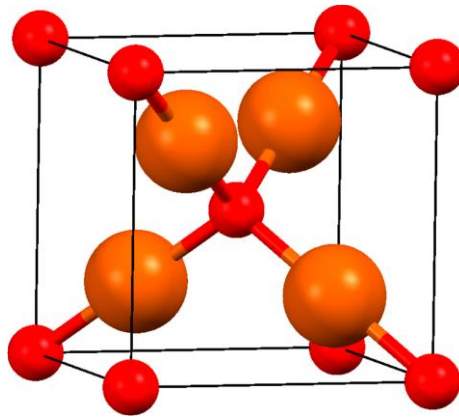


Figure 4, shows the crystal structure of Cu_2O (Cubic Bravais lattice), with the space group $\text{Pn}\bar{3}\text{m}$ (224) and has a lattice constant of $4.2696 \pm 0.0010 \text{ \AA}$. Copper in orange and oxygen in red color.

Furthermore, the valence band gap and the conduction band are presented in Figure 5, Cu d^{10} orbitals constitute the upper valence bond and the s-orbital like character constitute the lower conduction band, which is the Cu 4s orbitals³¹. Interestingly, the allowed transition is ($\Gamma_8^+ \longrightarrow \Gamma_8^-$ and $\Gamma_7^+ \longrightarrow \Gamma_8^-$) and the absorption transitions ($\Gamma_8^+ \longrightarrow \Gamma_6^+$ and $\Gamma_7^+ \longrightarrow \Gamma_6^+$) are forbidden in nature. The allow transition resulted in the much higher absorption coefficients at their corresponding wavelengths. The forbidden nature of the

lower energy direct transition of Cu_2O makes it behaves more like an indirect semiconductor even though it is a direct semiconductor³².

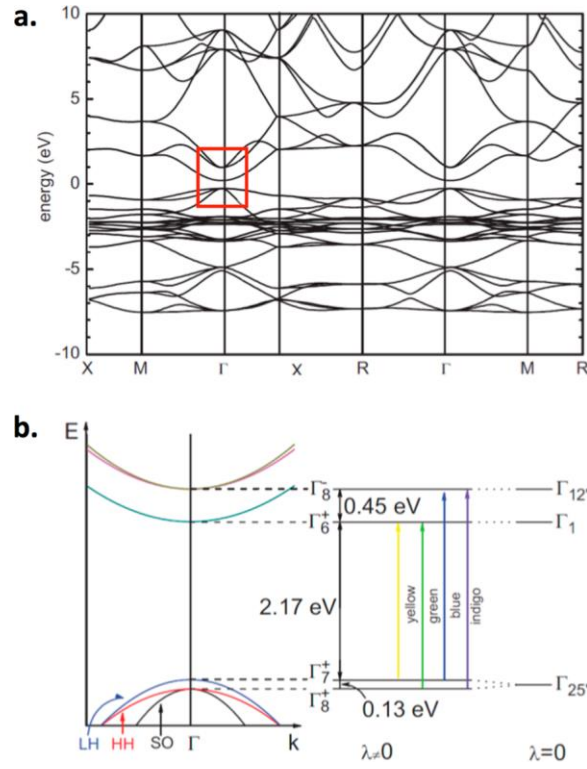


Figure 5, (a) Estimated band structure of Cu_2O . (b) A view on bandgap highlighted in red in (a)³⁰

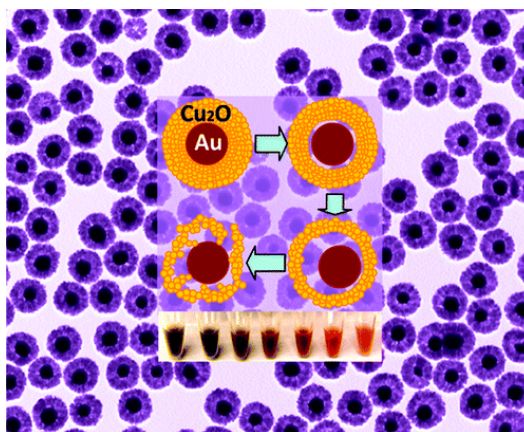
[CHAPTER 2]

[LITERATURE REVIEW

2.1 The Development of Semiconductor Nanoparticle

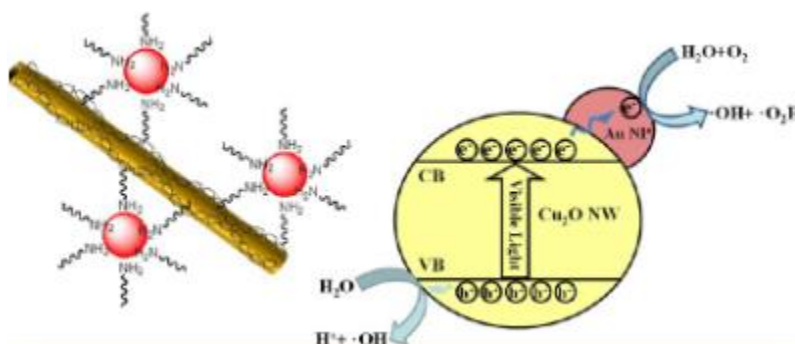
The solution synthesized nano-gold-copper oxide of specific dimension showed very high electronic properties with an optimized photocatalytic viability³³. Varying the concentration of the reducing agent present in the reaction, nucleation of the expected product takes different forms with promising facet present on the surface, that significantly determine the electro-optical properties of the pristine Cu₂O semiconductor target nanotube³³. Addition of metal as core nanocrystal further pushed the electrical conductivity and optical properties of gold-copper oxide for better solar energy utilization. In their work, Kuo et al., showed the facet dependent photocatalytic properties of the synthesized Cu₂O nanoparticles. The pure Cu₂O nanoparticles with octahedral morphology and bounded by {111} facets were 1100 times more conductive compared to the pure Cu₂O having cube shape and crystal bounded by {100} facets. The Cu₂O nanoparticles when hybridized with Au core, showed the enhanced, electrical and photocatalytic properties³⁴. It is possible to achieve Au nanoparticles with octahedral geometry and this concentrated nano-shape gold crystal were used as seed crystals to grow Au/Cu₂O hybrid. The conductivity of these hybrid nanoparticles became 10,000 fold more than pure Au octahedra³⁵. The work also showed how the photodegradation of organic pollutant using Au-Cu₂O core shell heterostructure outperformed the pristine Cu₂O nanoparticles. The improved photocatalytic performance was attributed to the efficient photoinduced charge separation due to metal and metal oxide interfacial electronic communication³⁶.

The photothermal activities for the photodegradation of organic pollutant and water splitting of core-shell noble metal-semiconductor nanocubes, octahedral and nanobars were also reported. Wang et al, Reported, Scheme 1, the facet dependent heat production properties of Au-Cu₂O. They synthesized the round shaped gold nanocrystals with opposite corner distance of 41 and 57 nm and the nanocube, octahedral Au-Cu₂O using hydrothermal method³⁷. But the nanobars were synthesized by the seed-mediated growth method. Au nanorods were added during the synthesis of Cu₂O³⁷. The absorption band of nanocubes and octahedral Au-Cu₂O having a surface plasmon resonance (SPR) in the near-infrared (NIR) region from Au core with octahedral shape having SPR band around 808 nm were used for light excited heat production. The cube shape Au-Cu₂O solution upon irradiation could reach 65° C after 5min. The surface plasmon resonance band of their Au domains matches that of the illuminating light wavelength. In the case of nanobars, gold nanorods, were used that has {100} facet bounded in Au-Cu₂O hybrid with promising tunable longitudinal Au SPR absorption band in the broad NIR range from approximately 1050 to 1400 nm, hence displaying a much better photothermal properties³⁸.



Scheme 1, Image of Cu_2O Shell with Au Core³⁸

Yang et al., reported that the absorption band of Au surface plasmon resonance in the Au- Cu_2O heteronanostructures depend on the surface facets of single crystalline Cu_2O shells. The light scattering effect of the Cu_2O shell was minimized due to its small crystallite size which enable the easy identification of the surface plasmon resonance (SPR) absorption band of the Au cores and the thickness of the Cu_2O shell. There was no effect of shell thickness on the SPR absorption band of Au, beyond the lower shell limit required, but it depends strongly on the exposed particle surfaces³⁹.



Scheme 2, Au@ Cu_2O photocatalytic effect³⁹

The research work by Pan et al., dwells on the surface functionalization of nanocomposites by functional groups such as amine, thiol and carboxylates, which provides a linkage between the noble metal and the semiconductors hybrid. Specifically, a poly(σ -anisidine)-

capped Cu₂O nanowires (NWs) were used to provide a very strong hydrophobic host-guest interaction with oleylamine-capped Au NPs to form metal-semiconductor which enabled the separation of nucleation of free nanocrystal and the control of the size of the Au NWs. Also the photodegradation of methylene blue was tested in aqueous solution for these hybrid materials. Pristine Cu₂O NW exhibited very low photocatalytic activity as compared to Au-Cu₂O nanocomposites. The time-resolved photoluminescence spectroscopy was used to probe the surface electron process at the heterostructure interface³⁷.

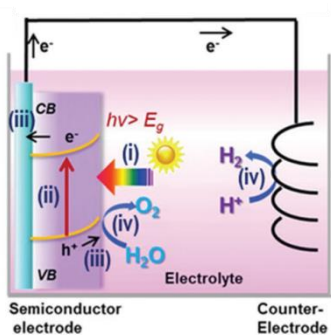
Cuprous oxide (Cu₂O) is a p-type semiconductor. The vacancies in Cu enable it to accept electron, bases on which it was hypothesized that Cu₂O is a p-type semiconductor,³⁸ with theoretical and experimental facts support the hypothesis has gain widely acceptance^{39,40}. However, controversy still lace the exact nature of the vacancies in copper. Papadimitriou earlier reported, by the use of dep-level transient spectroscopy (DLTS) that the hole traps were associated to CuO reefs⁴⁰. Paul, recently, use DLTS in the identification of two trap states in Cu₂O, which was attributed to single and double Cu vacancies⁴¹. Also, it was observed and reported that the electric conductivity was due to single Cu Vacancies i.e. two 3-fold coordinated oxygen with one Cu missing or split Cu vacancies, this implies neighboring Cu atom moves toward Cu vacancy and coordinates four oxygen's, this assertion is credited to scientist, although, the disagree on which of the possibilities is more stable thermodynamically^{42,43}. The formation energies of the oxygen interstitials, other intrinsic acceptors in either octagonal or tetragonal coordination are much higher than for vacancies.

Wan-Chen, reported the synthesis of Cu₂O in cubic, octahedral, and rhombic structure, working in room condition, in aqueous medium by using surfactant sodium dodecyl sulfate

(SDS), Copper (2) oxide chloride (CuCl_2), sodium hydroxide (NaOH), reductant $\text{NH}_2\text{OH}.\text{HCl}$ and each morphology was tested on methyl orange to grade there photodegradation and state the inability of facet with $\{100\}$ face to degrade methyl orange⁴⁴. The *in-situ* growth of noble metal nanoparticles onto semiconductor, in which Cu_2O was synthesis using wet-chemical reduction and the subsequent introduction of the noble metal to a targeted facet of the semiconductor was reported. Cu_2O nanotubes were prepared by adding CuCl_2 and NaOH , into distilled water under magnetic stirring and- ascorbic acid was added as reducing agent, the contents were further stirred for 15min to harvest Cu_2O nanocube. The product was washed then noble metal solution was added to achieve the desired hybrid product.⁴⁵.

Fujishima and Honda, for the first time, discovered TiO_2 as PEC active catalyst with $\sim 0.1\%$ quantum efficiency⁴⁶. Since then there is a steady progress in the field with respect to both materials synthesis and engineering of the PEC setups, thereby reaching the efficiencies of 12.7% using a p-GaInP₂/GaAs as photoanode material or 14% using a Z-scheme tandem cell having Rh-engineered AlInPO_x photocathode and RuO_2 as photoanode^{47,48}. It is worth mentioning, although the choice of materials plays a role for the successful harvesting of solar energy but it is the surface engineering of materials which defines its practical applicability⁴⁹. For example, to harvest the maximum range of solar spectrum, materials having bandgap between 1.6 and 2.4 eV could be meritorious but they are chemically unstable on photo-excitation under aqueous environments such as photoelectrochemical (PEC) water splitting⁵⁰. Therefore, we need to tailor the surfaces to exploit the full available potential.

There are four main features which defines the overall success of PEC water splitting reaction; **(i)** band gap energy and the conduction and valence band edge positions, **(ii)** transportation of the exciton to the surface, **(iii)** separation of charge carriers, and **(iv)** surface reaction leading to stable product as shown in Scheme 3⁵¹. The three among these four decisive factors not only depend on the chemical composition but also the size, morphology, crystallinity and surface chemistry of photoelectrode materials.



Scheme 3: Schematic illustration of the photoelectrochemical cell operation using n-type semiconductor; the water splitting reaction steps (i–iv) reproduced from the Kment et al⁵¹.

Among semiconductors, Cu_2O with small band gap ~ 2.1 eV and suitable conduction band edge position, naturally abundant, cost efficient, non-toxic fulfils all the basic criteria required for photocatalysis and water splitting⁵². Although intrinsically, Cu_2O is p-type semiconductor but it can be synthesized as n-type by varying the reaction conditions and methodology⁵⁷. Owing to its technological importance, the progress for the synthesis of Cu_2O nanostructures is documented, especially facet dependent catalytic applications of Cu_2O based particles⁵³. However, most of these synthetic methods resulted in microsize particles. Cu_2O in combination with metal and metal oxide as hetero-particles have also been tested and showed better results but still these reports were significantly below the

theoretically expected photocurrent density (14.5 mA cm^{-2})⁵⁴⁻⁵⁶. There are two main drawbacks for using Cu_2O in practical applications: **(1)** short carrier diffusion length (20-100 nm) upon light absorption (related to particles size) and **(2)** its self-photocorrosion upon contact with water (surface chemistry).

2.1.1 Statement of Problem

Environmental concern associated with energy generation from fossil fuel and its limited supply, warrant a new frontier, hoped at replacing the current source of energy to a safe, clean and sustainable source of energy. Materials that can find usefulness in this area of study is currently being searched and developed across the globe. Copper (1) Oxide captured our interest for its uniqueness as a visible light spectrum harvester, a semiconductor, with band gap of about 2.1eV suitable to serve the intended purpose of harvesting the maximum portion of sunlight spectrum.

We will also introduce plasmonic metal to further boost visible spectrum harvesting ability of the semiconductor (Cu_2O) nanoparticle, and the morphology of interest is cube and octahedral that will be tested against organic dye like methyl blue (ME) contaminated water. Bearing in mind, the key role of absorption step in the pollutant removal process, the unique morphology of the synthesis Cu_2O with active facets exhibit excellent adsorption performance.

2.1.2 Project Objectives

The main objective of the project is to develop nanostructured Cu_2O , $\text{Au/Cu}_2\text{O}$ hybrid nanoparticles for visible light catalyzed applications.

In contribution, we will concentrate on the following objectives;

1. Optimization of the synthesis of Cu_2O nanoparticles and $\text{Au/Cu}_2\text{O}$, hybrid nanoparticles with various sizes and morphologies of both Au and Cu_2O components.
2. Characterization of the as-prepared hybrid nanoparticles using various advanced spectroscopic (UV-Visible, photoluminescence), scanning electron microscopy (SEM), and X-ray based techniques.
3. Engineering the surface of Cu_2O with focus to maximize harvesting the solar spectrum and to minimize photo-corrosion on contact with water through synthesis hybridization of Au on the surface of pristine Cu_2O nanoparticles.
4. Photocatalyzed degradation of organic pollutant using these hybrid nanoparticles.
5. Compilation of the data for future exploration of industrial application of the synthesized nanocomposite materials.

CHAPTER 3

RESEARCH METHODOLOGY

Hydrated copper (II) chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 97%) and hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$; 99%) were purchased from Aldrich. Sodium dodecyl sulfate (SDS) were acquired from Mallinckrodt, Sodium hydroxide (NaOH) was gotten from Fluke, Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) was purchased from Fisher, Copper Acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) were purchased from Aldrich. All chemical was used as purchase without further purification. Deionized water gotten from research institution of king Fahd university of petroleum and minerals.

3.1 Nanomaterial Synthesis

The proposed project includes the synthesis of hybrid nanoparticles containing copper, oxygen and Au. The metal oxide (Cu_2O), optimization of size, morphology and crystal structure and its hybridization with Au to form hybrid materials. This would be realized by controlling the nucleation and growth process of these components employing non-aqueous as well as aqueous medium. These materials are used as photocatalyst for organic dye degradation. The research methodology was divided in three different steps.

3.1.1 Synthesis of Cu_2O , $\text{Au}@\text{Cu}_2\text{O}$ Based Multi-Component Nanomaterials

3.1.2 Non-Aqueous Synthesis

The synthesis for the formation of nanoparticles proceeds through bottom-up non-aqueous high temperature solution method. Non-aqueous high temperature solution

syntheses have been developed to control the size, morphology, faceting, crystallinity and surface functionalities of such nanomaterials^{23,57}. The non-aqueous synthesis is especially helpful for the synthesis of nanoparticles because the reaction kinetics can be easily controlled by taking snapshot of the reaction by monitoring the chemical events through changes in physical appearance, spectroscopically or microscopically. This helps to control the nucleation and growth process which are the key parameters to easily add/incorporate multiple domains in a single nanoparticle so called multicomponent or heterostructure nanoparticle.

In a rinse and oven dried breaker, 4ml ethylene glycol and 0.024g (0.37mmol) of copper acetate was added sequentially, stirred, then 4ml ethylene glycol, again stirred before sonication, and 8ml of ethylene glycol, follow by the addition of 0.024g (0.37mmol) of glucose to facilitate reduction of copper (II) to copper (I). Sonication continued for 20min, more 24mg of glucose was added, the reaction temperature was set at 40⁰C, expected color change not observed then 0.5mg glucose was introduce and finally the nanoparticles were washed with ethanol.

In an attempt to achieve the expected nanoparticle, the stated procedure was adjusted, into a round bottom flask; ethylene glycol (8ml), followed by the addition of copper acetate immediately. The mixture was placed in the sonicating water bath set at 50⁰C and sweeping vibration mode, when a clear solution is formed, 148mg of glucose was added and the flask was covered with a septum rubber, a balloon filled with nitrogen gas was connected through the septum into the flask using a needle.

Copper(II)chloride, benzoyl alcohol and Sodium hydroxide was used in this synthesis procedure; 20mg CuCl_2 , was poured into an 8ml benzoyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$) in a flask, under stirring till the temperature reaches 60°C , at about 45min of reaction time NaOH in ethanol was added dropwise. Figure 5, is the UV-Vis-spectra of copper oxide synthesis using non aqueous medium, where it is observed that there was no absorption related to Cu_2O phase, that normally lies in the visible region around 450nm – 550nm.

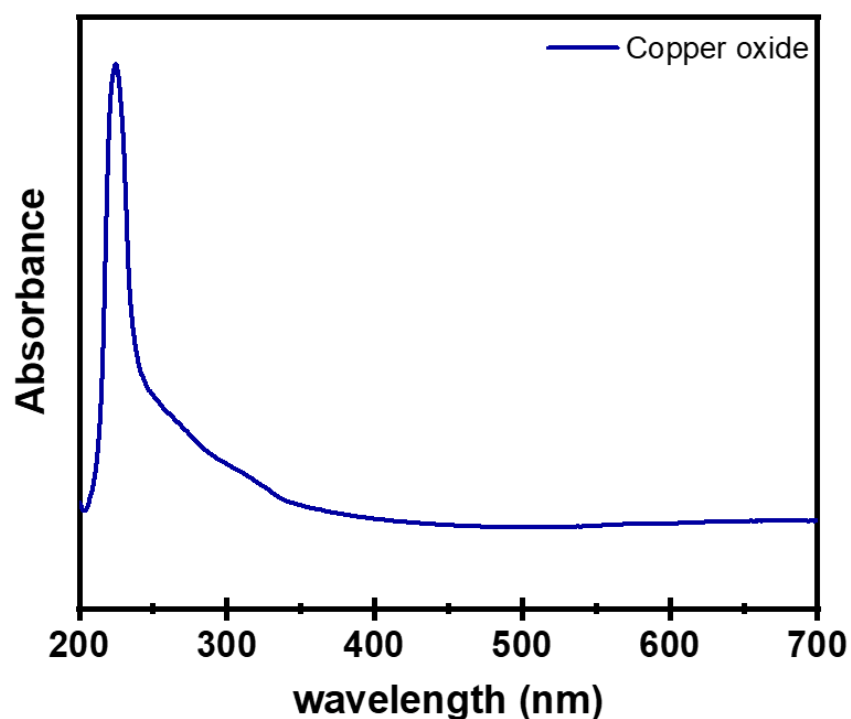
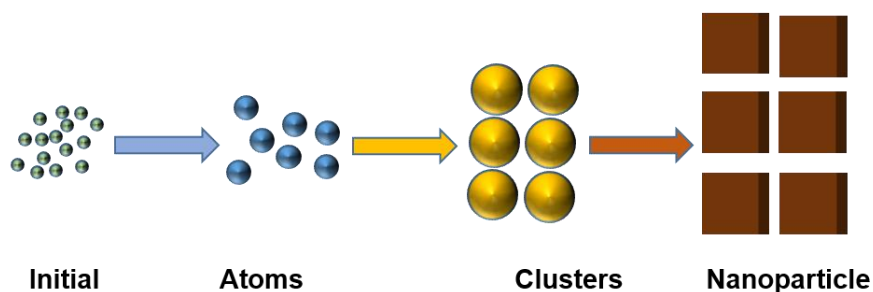


Figure 5, UV-Vis Spectra of Non-Aqueous Synthesized cube shaped Cu_2O

3.1.3 Aqueous Synthesis

The synthesis of hybrid nanoparticles was accomplished by employing bottom-up aqueous room temperature solution synthesis method. Sonication assisted, with temperature around 30-35°C, syntheses have been developed to control the size, morphology, faceting, crystallinity and surface functionalities of Au and Cu₂O hybrid materials nanomaterials. The aqueous synthesis is especially helpful for the synthesis of multicomponent nanoparticles because the reaction kinetics can be easily controlled by taking snapshot of the reaction by monitoring the chemical events through changes in physical appearance, spectroscopically or microscopically. This helps to control the nucleation and growth process which are the key parameters to easily add/incorporate multiple domains in a single nanoparticle so called multicomponent or heterostructure nanoparticle. Scheme 4, shows the bottom-up approach of nanoparticle synthesis.



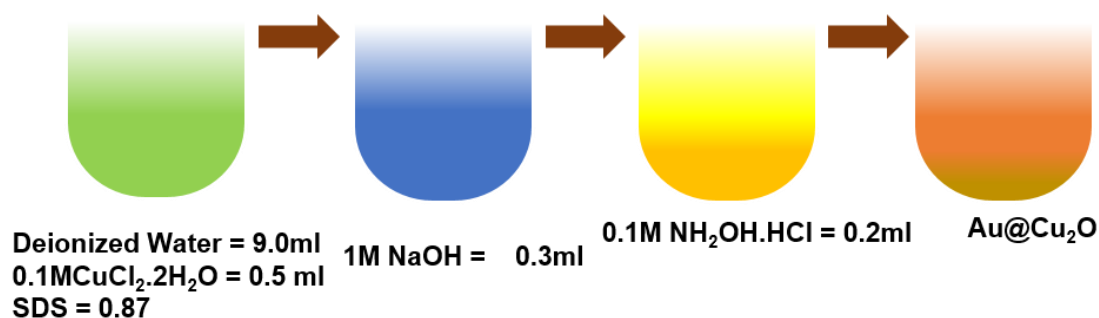
Scheme 4, Bottom-up synthesis of nanoparticle

3.1.4 One Step Synthesis

In one step synthesis of Au@Cu₂O hybrid nanoparticles, metal nanoparticles would be synthesized *in situ* using benzyl alcohol as a solvent and oleyl amine as reducing agent using chloroauric acid or copper acetate or copper acetylacetonate as precursor compounds¹⁵. The growth of Cu₂O domain would be realized by heating up method and

growth of Au or Cu domains onto preformed metal oxide nanoparticles acting as seed particles^{14,15,23,32}. The number of domains of metal components attached to single particle will be controlled by changing the solvent polarity to localize the surface plasmons of metal component onto the surface of Cu₂O NPs as demonstrated by the author and many other researchers for the synthesis of other metal@metal oxides based multicomponent nanoparticles^{15, 32}. The one-step synthesis is shown in scheme 2 below.

A round bottom flask was used as the reaction apparatus, into which 9.0ml deionized water was added, 0.5ml of 0.1M CuCl₂.2H₂O introduced, this was followed by the addition of sodium dodecyl sulfate (SDS) and placed into a sonicates water bath set at 35⁰C temperature and vibration time of 20min, as the SDS fully dissolve, as shown in Scheme 5, a light greenish color was noticed and 0.3ml of 1M NaOH was added and the mixture color changes to blue, when 0.2ml of 0.1M NH₂OH.HCl was added into the mixture, the color immediately changes to yellow. This signifies the formation and subsequent growth of nanoparticle which is the copper (I) oxide (Cu₂O). finally, 1ml of 0.002mM HAuCl₄ was added to form gold deposited nanomaterial hybrid, after 1hour growth time, Au-Cu₂O was collected through centrifuge by washing with deionized water, and ethanol.



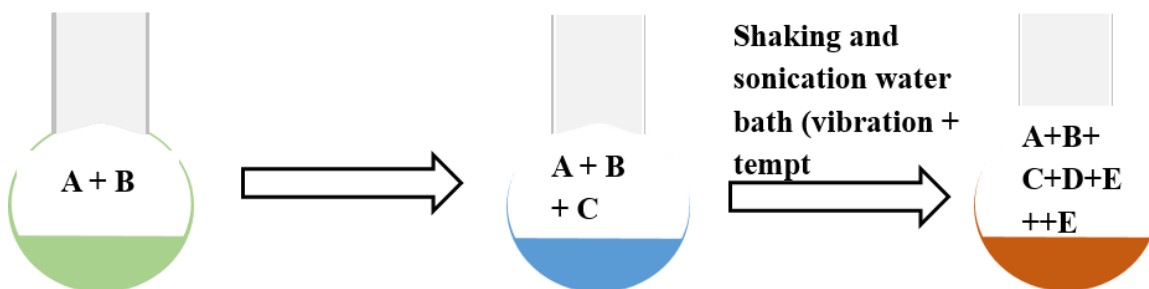
Scheme 5, Schematic of In-situ synthesis cube and octahedron shaped Cu₂O

3.1.5 Two Step Synthesis

The two step synthesis involves the synthesis of metal oxide nanoparticles separately in the first step followed by growth of metal components. The *in situ* synthesis of metal domains in multicomponent nanoparticles gives less control to play the size and morphology of these metal nanoparticles. To elucidate the influence of the size and morphology of plasmonic domains on the overall performance of photoelectrode in the present project, in the first step the Cu₂O with various size and shapes shall be synthesized separately. These nanoparticles shall be used as seed particles to grow metal domains in the second step. Moreover, the sizes of different components and number of metal domains grown onto Cu₂O domain will be varied by proper choice of precursors compounds to surfactant ratios, nature of solvent and reaction kinetics as demonstrated by the author for other metal@metal oxides based multicomponent nanoparticles^{15,21}.

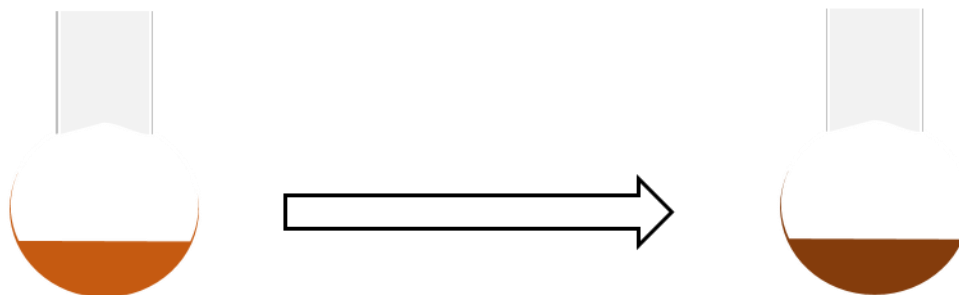
The synthesis of cube shaped Cu₂O nanoparticles was carried out in dried round bottom flask using 2ml of the freshly prepared 0.1M solution of CuCl₂·2H₂O, 11ml deionized water and 0.48g sodium dodecyl sulfate (SDS) was added slowly under shaking on span of few minutes, before it was placed on a sonication water bath, set at 35°C and vibration time for 10min. Immediately the vibration stops, 1ml of 1.0M NaOH was added randomly, the vibration of the sonication water bath was turn-on again, then 1.6ml of 0.1M NH₂OH.HCl was added randomly and the vibration was allowed to stop. The nanoparticles are allowed to grow under aging process for 1hour. The nanoparticles were collected by first washing three times with deionized water to remove the unreacted reactant follow by washing twice with ethanol and the nanoparticle was stored in a sample vial.

In Scheme 6, synthesis route of copper (1) oxide. A = DI Water, B = $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, C = SDS, D = NaOH, E = $\text{NH}_2\text{OH} \cdot \text{HCl}$ and $\text{A+B+C+D+E} = \text{Cu}_2\text{O}$.



Scheme 6, Cube morphology Cu_2O nanoparticle synthesis

The product from scheme 6, was washed with deionized water several times to remove unreacted substance, this was transferred into a round bottom flask using 10ml deionized water, and placed on a sonication water bath set at 35°C temperature with vibration time of 10min, as the vibration stops, 0.3ml of 0.001M HAuCl_4 was added as shown in scheme 7 the color change to brown.



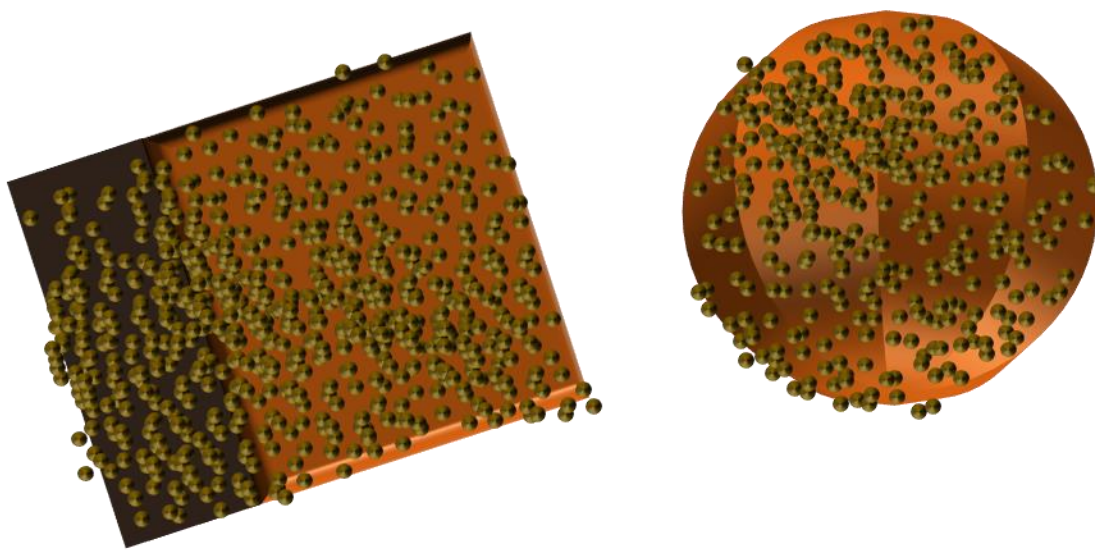
Scheme 7, Cube Shaped Cu_2O nanoparticle, decorated with Au Nanoparticle.

3.1.6 Synthesis of $\text{Au}@\text{Cu}_2\text{O}$ Hybrid Nanoparticles

The second methodology to stabilize the Cu_2O surface from photo-corrosion as well as enhance visible light harvesting efficiency is being based on growth of the few Au

nanoparticles on the surface of Cu_2O domain. This was achieved through injection of Au or Ag precursor at suitable time while the Cu_2O domain has developed.

A schematic presentation for the synthesis of proposed materials is shown in Scheme 8.



Scheme 8, Schematic representation of the synthesis of heterodimer and multimers $\text{Au}@\text{Cu}_2\text{O}$ hybrid nanoparticles

In order to synthesize cube and octahedral morphology of Cu_2O with decorated gold nanoparticles as shown in scheme 5, 50ml round bottom flask was charged with 11ml deionized water, 0.6ml of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1M) and 0.087g sodium dodecyl sulfate (SDS). The mixture is kept on shaking before set on sonication (Temperature 35°C , Vibration 25min), as the SDS dissolved, 1.5ml of 1M NaOH was added for cube while to obtain octahedral shape Cu_2O , 1.2ml was added, follow by 3ml of 0.1M $\text{NH}_2\text{OH} \cdot \text{HCl}$ and sonication continue for few minute. The color change from blue to deep yellow and nanoparticle is allowed to grow by again for 1 hour and then washed with deionized water three times. The resulting nanoparticles were transferred back into the round bottom flask

with 10ml deionized water sonicate for few minute before 0.3ml HAuCl₄ (0.001m) was added into it and the hybrid nanomaterial is allowed to grow.

3.1.7 Characterization of Multi-Component Nanoparticles

To confirm the size, shape, composition, phase and optical properties of the as synthesized materials will be characterized using SEM, TEM, XRD and UV-visible spectroscopy.

Photocatalytic applications

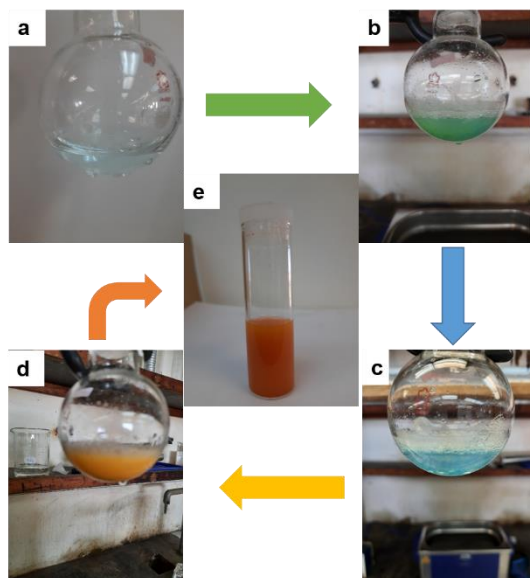
The hybrid nanoparticles are used for visible light assisted photo-catalysis for the degradation of organic pollutants in water as well for the water splitting reaction. For the photoelectrochemical (PEC) splitting of water, the photoelectrodes shall be fabricated on FTO substrates using drop casting (due to the colloidal nature of proposed materials). The photoelectrode surfaces and thickness will be characterized using scanning electron microscopy (SEM). Their photo-electrochemical efficiency shall be tested using Pyrex container 3-electrode cell with a 0.5 M Na₂SO₄ electrolyte (pH 7.0 ± 0.1) connected to argon gas cylinder. A Pt wire as auxiliary electrode), FTO coated with different M-Cu₂O hybrid composites as working electrode, and a saturated calomel electrode (SCE) as reference electrode.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Spectroscopy Characterization

The structure and composition of the nanoparticles were probed to have a deep insight on the fundamental properties of the synthesized nanomaterials with different morphologies towards the photocatalytic degradation of methylene blue and photoelectrocatalytic splitting of water. Spectroscopic characterization was performed to get full grasp of usefulness of Cu_2O and $\text{Au@Cu}_2\text{O}$ in different applications and the importance of the morphologies and their hybridization of the semiconductor nanoparticle with noble metal in boosting the stability and efficiency of the nanomaterials. The kinetics of the as synthesis Cu_2O and the hybrid $\text{Au@Cu}_2\text{O}$ are monitored to have a quality insight on the reaction transition from the initial to the final stage. This is observed through color changes that occurs as each reactant were introduced into the synthesis pot. Starting from the colorless deionized water (Scheme 9a), to a light green color on addition of surfactant (SDS) (Scheme 9b), the color becomes blue as a base (NaOH) is introduced indicating the production of more OH ions (Scheme 9c), and the addition of the reducing agent ($\text{NH}_2\text{OH.HCl}$) changes the color to yellow (Scheme 9d), finally as the nanoparticle grow the color of the reaction becomes orange (Scheme 9e).



Scheme 9, Shows the synthesis steps with the corresponding color changes, from colorless through light green, blue, yellow and finally orange color.

4.2 Scanning Electron Spectroscopy (SEM) Image

The morphology of the synthesized nanoparticles both pristine and as well as decorated with Au nanomaterial were obtained using high-end-field emission scanning electron microscope (FESEM, Tescan-Lyra-3) in the department of chemistry of King Fahd University of Petroleum and Minerals. The samples were well prepared to ensure they are stabilized and possess electrical conductivity their insertion the SEM chamber to record SE micrographs. Scanning electron microscope (SEM) is a technique that uses a focused radiation of high energy electrons to produce several coherent signal at the surface of the well prepared dried sample of the nanomaterial. The signals that emerge from the electron-nanomaterial interactions exposes the information about the nanomaterial orientation, crystallinity structure, chemical composition and it topography. The accelerated electrons generated in SEM are energetically strong enough to dissipate, several signal through the electron-nanoparticle interaction when the incident electrons are

decelerated. The signals used by a scanning electron microscope to generate result from beam atoms interaction at various depths within the nanomaterial can be of several types, such as secondary electrons (SE) which have a low energy on the order of 50 eV, which limits their mean free path in nanoparticle, back-scattered electrons (BSE) and diffracted backscattered electrons (EBSE) are beam electrons that are reflected from the nanoparticle elastic scattering, and are valuable in illustrating contrasts in composition of multiphase sample. Figure 6-13, shows the SEM image of all the synthesized morphologies for both Cu₂O as well as Au@Cu₂O hybrid versions. SEM image (Figure 6) represent cube Cu₂O that was synthesized without the addition of sodium dodecyl sulfate (SDS). In the absence of surfactant SDS, the expected morphology was not achieved. It resulted in irregular shape with broad size distribution. Figure 7-9 shows the as synthesized Cu₂O upon addition of surfactant sodium dodecyl sulfate in the synthesis procedure at varying amount, (Figure 10) correspond to the cube shape image of Au decorated Cu₂O, (Figure 11) SEM image of octahedral shape Cu₂O, and Figure 12 show the image of octahedral Cu₂O, (Figure 13) the SEM for the Au decorated Cu₂O with octahedral crystallinity structure.

The SEM image show (Figure 6) that a dark cubic Cu₂O of 10 μ m sized nanoparticle with lot of dirty like wool material covering which can be undoubtedly attributed to the in ability of the reactant to be exhaustively utilized in the cause of the reaction, as the reacting medium, in this case deionized water could not facilitate the complete mix ability of the precursor salt, the base and the reducing agent. This was the consequence of not using surfactant SDS, which would have allowed for the proper reactant interactions.

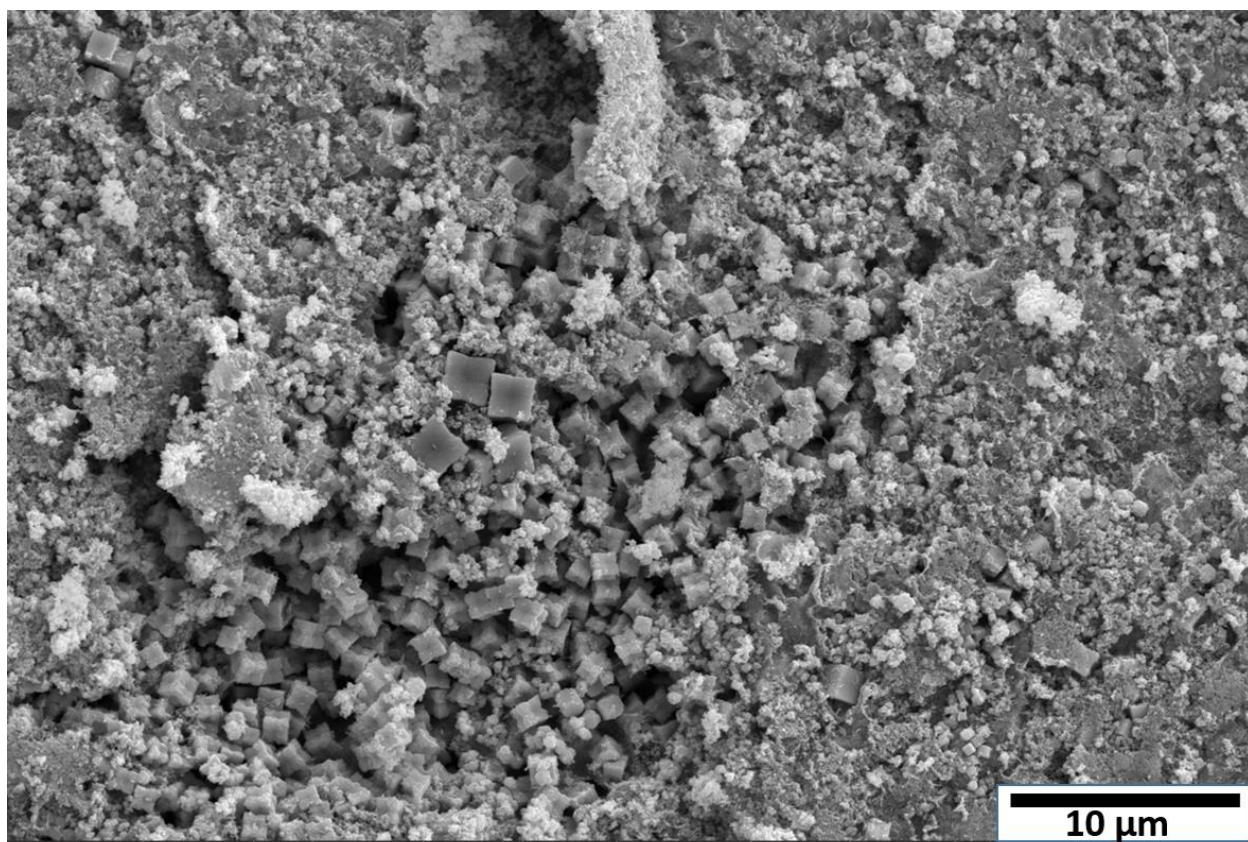


Figure 6, SEM image of the Cu₂O, synthesized without sodium dodecyl sulfate (SDS), a surfactant.

The established image (Figure 6) that resulted when surfactant (SDS) was not used in the synthesis of Cu₂O necessitated the need to add a controlled amount of SDS in the subsequent reaction. Figure 7, show an improved SEM image Cu₂O with more uniform size, preferably clear than the previous synthesized nanoparticle without using SDS. The nanoparticle is about 10 μm, and the tread like material on the Cu₂O cube are from the unreacted reactant courtesy of the control amount of the added surfactant.

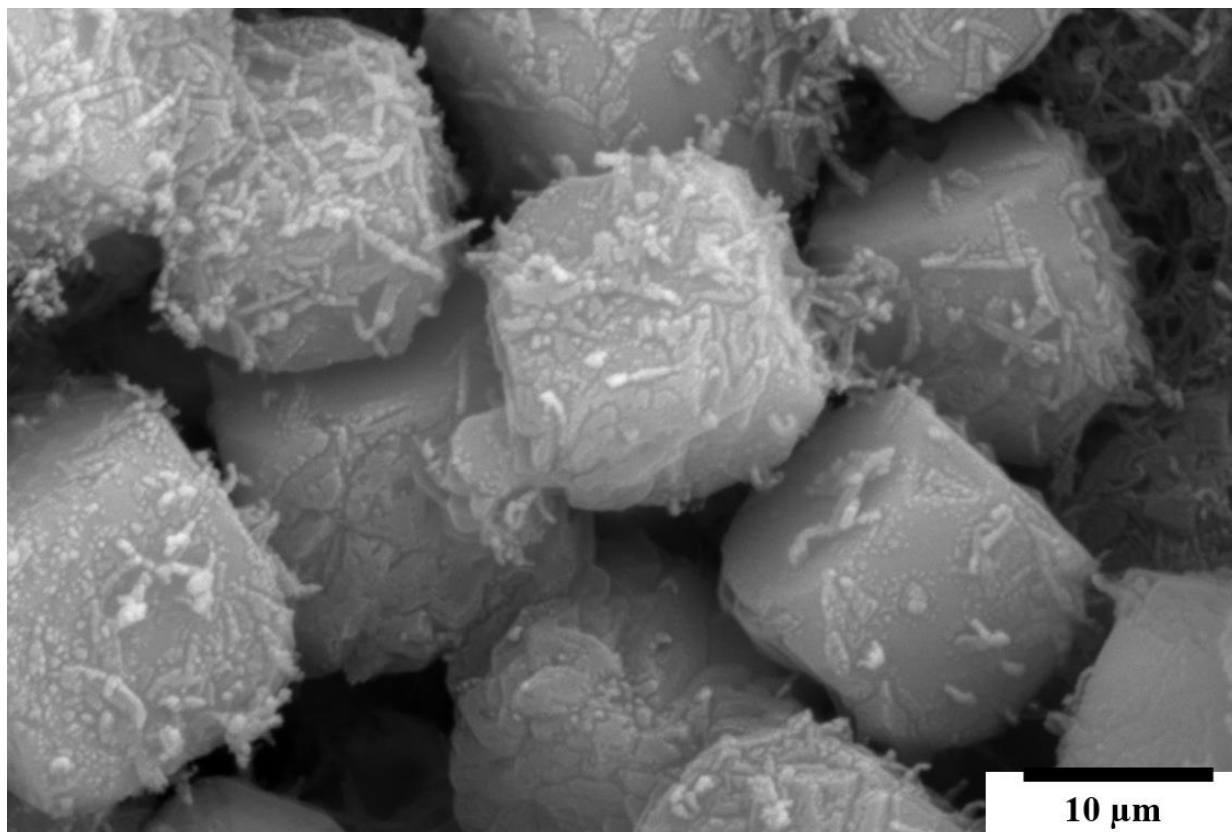


Figure 7, Bears the SEM image of Cube Cu_2O synthesized with addition of 0.087mg of SDS.

Upon increasing the amount of SDS as surfactant, a monomorphic cube shape Cu_2O nanoparticle as shown in Figure 8 are obtained. The average size of the nanoparticles was about 3 μm . The SEM image reflect an improvement in control on size as well as the cleanness of the nanoparticle facet with the right amount of surfactant used during synthesis and the proper dissolution of the surfactant before the addition of base for pH adjustment.

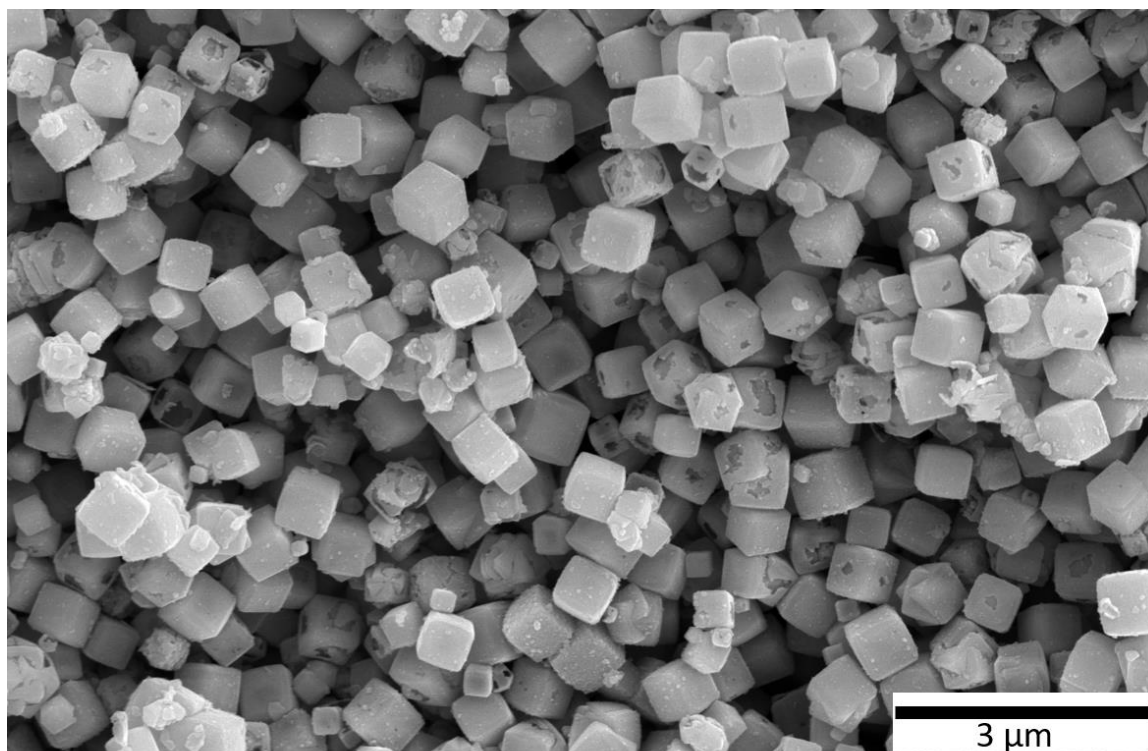


Figure 8, SEM image of Cube Cu₂O with all reaction condition maintained

As more growth time for the as prepared nanoparticle, this further show (Figure 9) the clear cubic morphology of the synthesized Cu₂O.

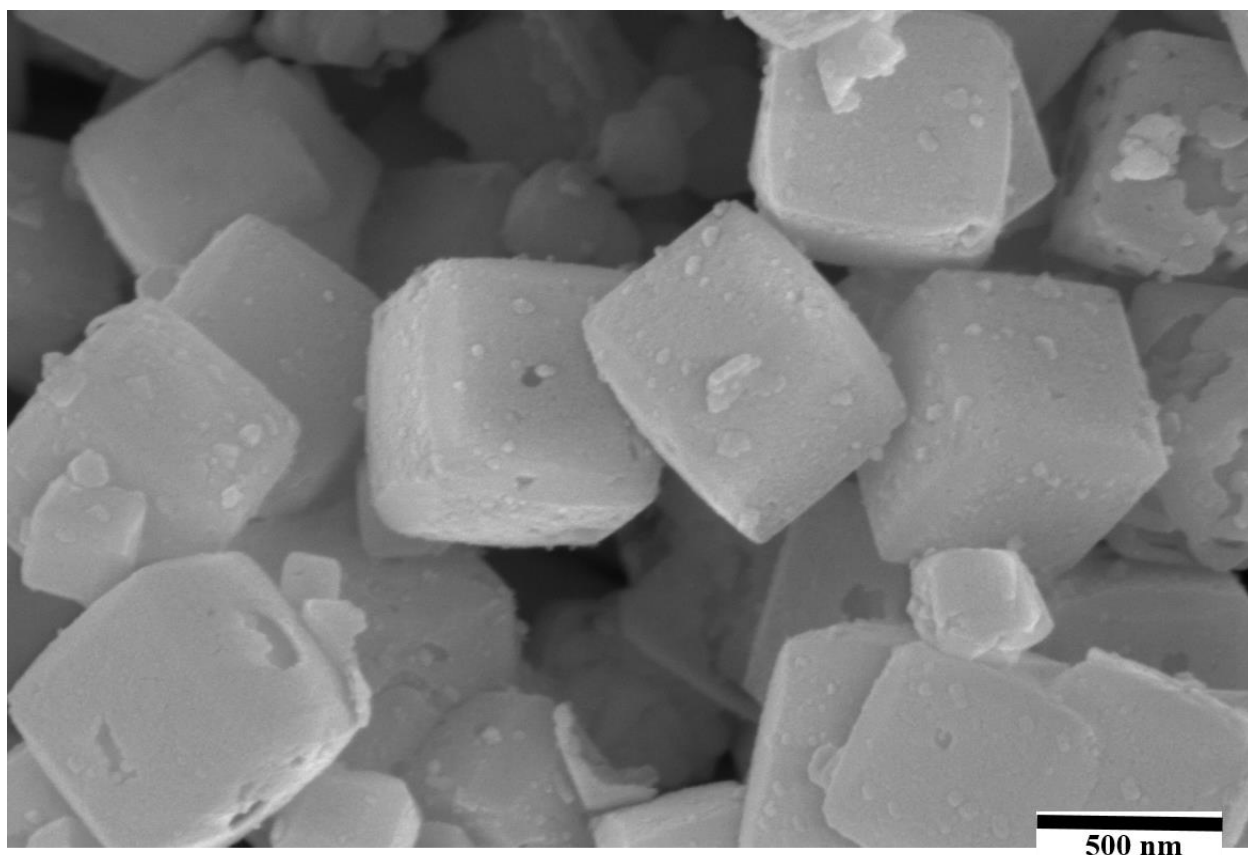


Figure 9, SEM image of cube Cu₂O nanoparticle with synthesis longer growth time.

The scanning electron microscopy (SEM) image (Figure 10) show the achieved carefully deposition of gold (Au) on a cubic Cu₂O, the facet of Au growth on the copper oxide tallies with the result from XRD, that shows the selective deposition of Au on a certain Cu₂O lattice plane, the plane is (111), (200), (220), and (311). EDS mapping also show how well dispersed deposited the is the Au nanoparticle on the cubic plane of the semiconductor Cu₂O, from which it was confirmed that the percentage of Au nanoparticle was 0.7% that bided to the selected lattice plane of the cube Cu₂O nanoparticle.

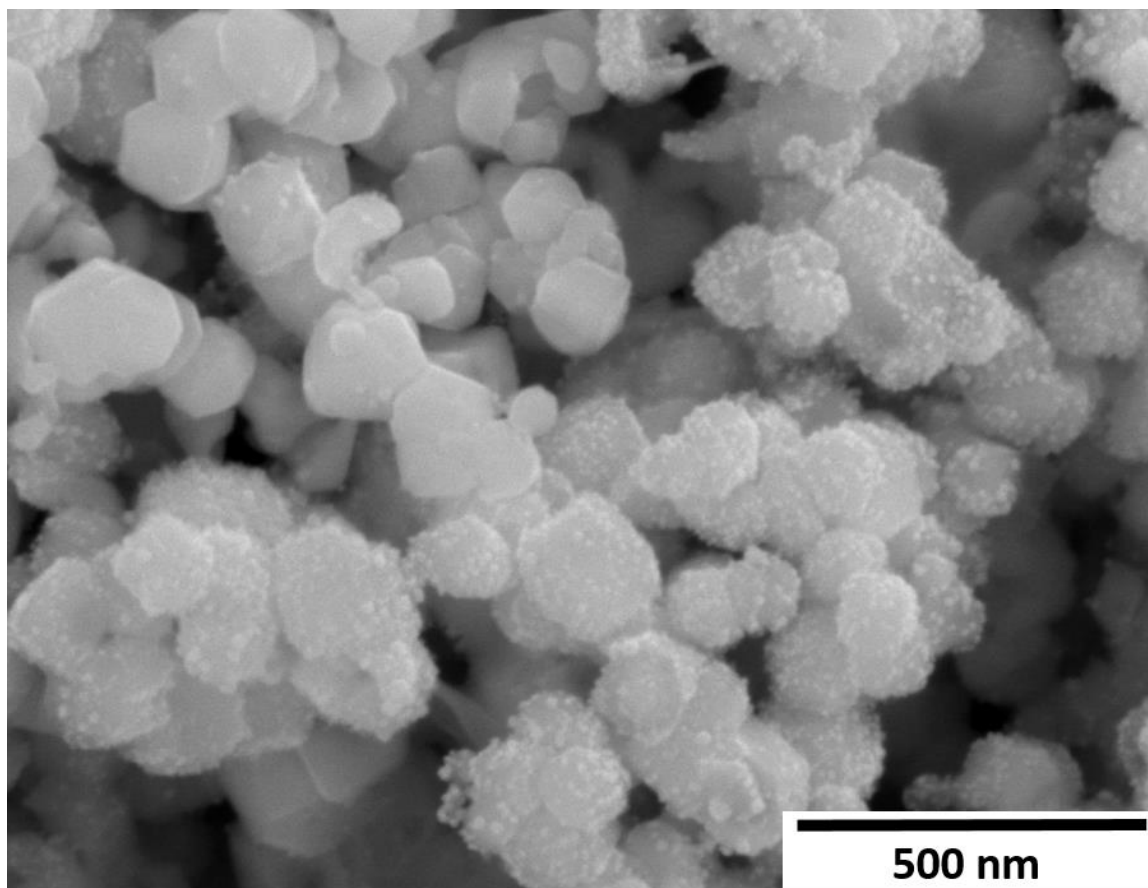


Figure 10, SEM image of cube Cu_2O semiconductor, that is decorated with Au nanoparticle ($\text{Au}@\text{Cu}_2\text{O}$ hybrid nanomaterials)

The SEM image of pristine (Figure 11) octahedral Cu_2O is shown. A nanoparticle of $1\ \mu\text{m}$ size octahedral semiconductor consisting of copper and oxygen with an octahedral shape was synthesis using reaction procedure similar to the cubic semiconductor reaction condition of 35°C temperature with sonication vibration of 20 min and reactant addition sequence, at an appropriate nanoparticle growth time of an hour.

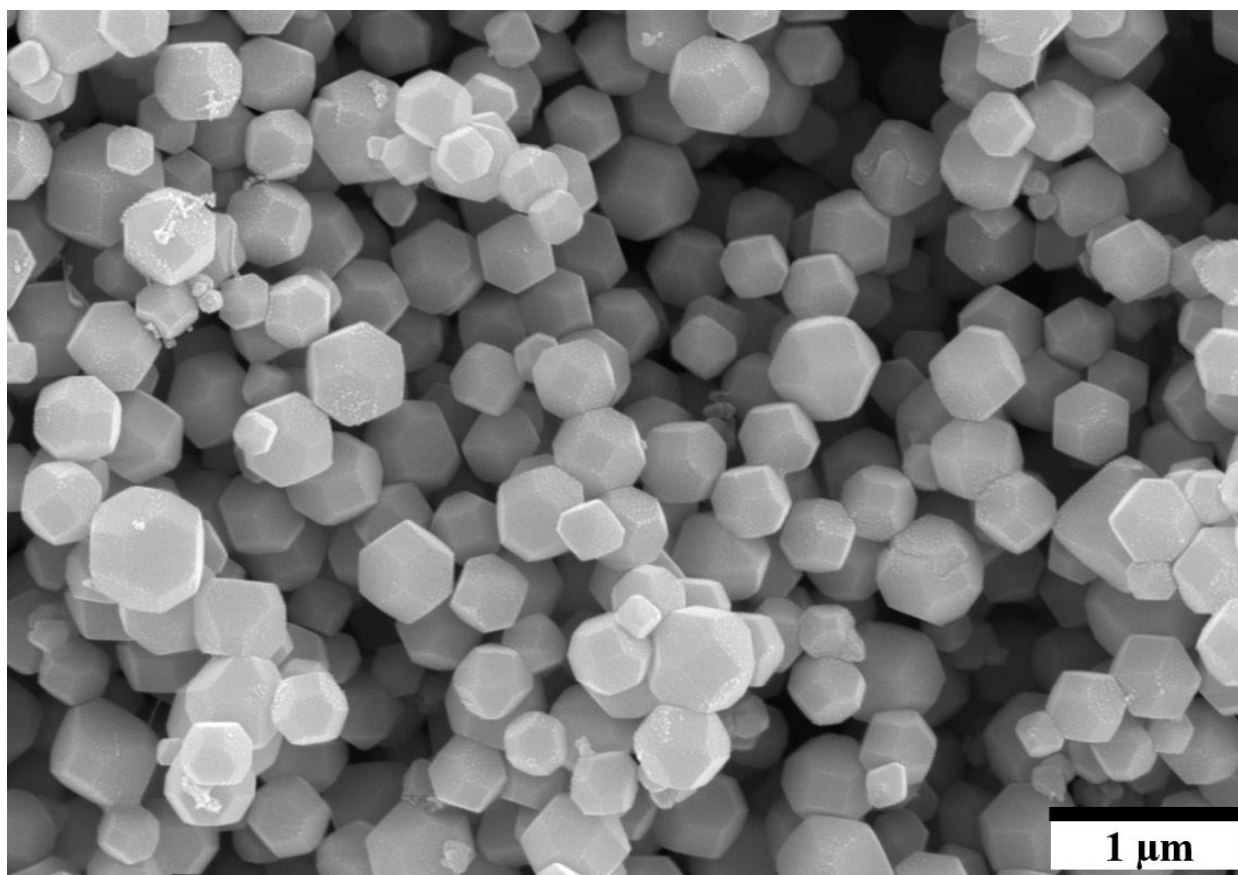


Figure 11, SEM image of octahedron Cu₂O nanoparticle

The as synthesized octahedral nanoparticle Cu₂O was decorated with Au nanoparticle.

Figure 12, show the SEM image of Au@Cu₂O octahedral with 500 nm size nanomaterial, the selective attachment of the Au on octahedral Cu₂O lattice plane.

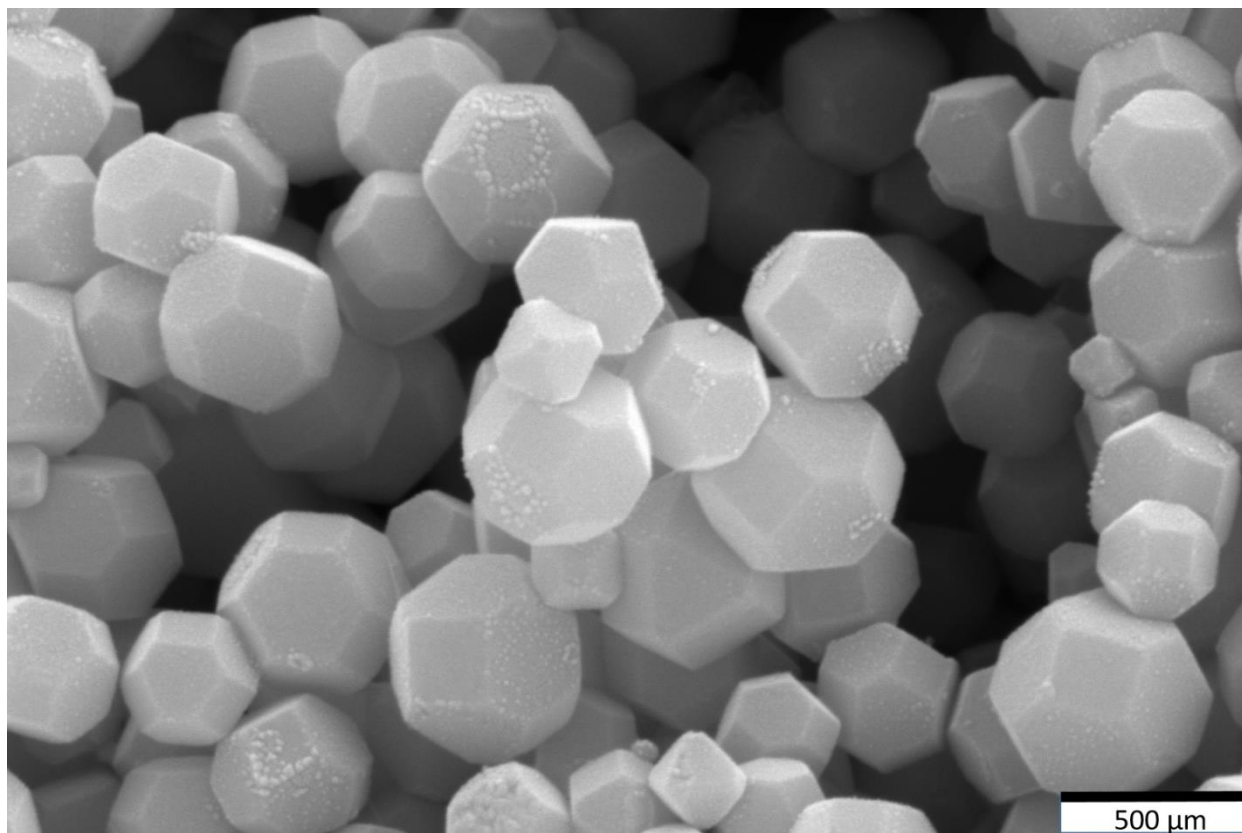


Figure 12, SEM image of octahedral Cu_2O with Au decoration

The selective attachment of the Au is more obvious when the nanomaterial size was 300 μm . Figure 13, present the SEM image of octahedral Cu_2O with Au deposited at some facet, EDS mapping shown the percentage composition of Au which is 3.8% of the total elemental constituent of the hybrid nanomaterial $\text{Au@Cu}_2\text{O}$. Also the XRD diffractogram correspond to the SEM image where the octahedral lattice plane (110) lack the deposited Au nanoparticle.

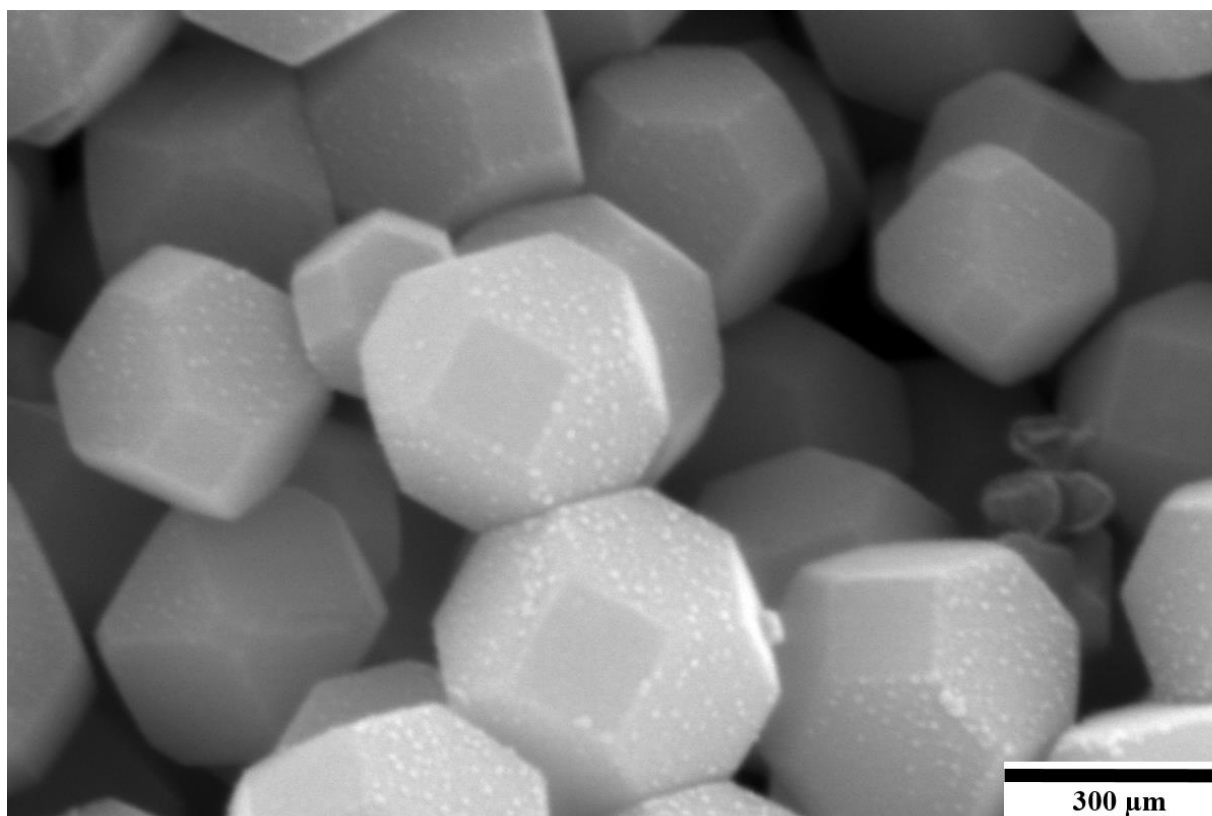


Figure 13, SEM image of pristine octahedron Cu_2O with selective facet Au decoration.

4.3 Energy-dispersive X-ray (EDX) Spectroscopy

Energy – dispersive X-ray spectroscopy (EDX, Oxford-Xmax) enabled us to confirm the elemental composition of the as synthesized nanomaterials. The detected elemental make-up of the nanomaterials is in a good agreement with the data collected and reported by other spectroscopic data (Raman, XRD). Figure 14-16 below shows the percentage composition of the synthesized Cu_2O nanoparticles and corresponding hybrid nanoparticles with gold and silver for all different morphologies. In Figure 14, the composition make-up of copper and oxygen is shown, the mapping intensity of Cu indicate that it is the most dominant element in the nanoparticle and O_2 is the least dominant. This

can be seen on the graph with Cu taking 89.5% and O₂ constitute 10.5% by the weight. This is in good agreement with the Cu₂O.

Table 1, the calculated mass ratio of copper and oxygen and percentage composition is reported.

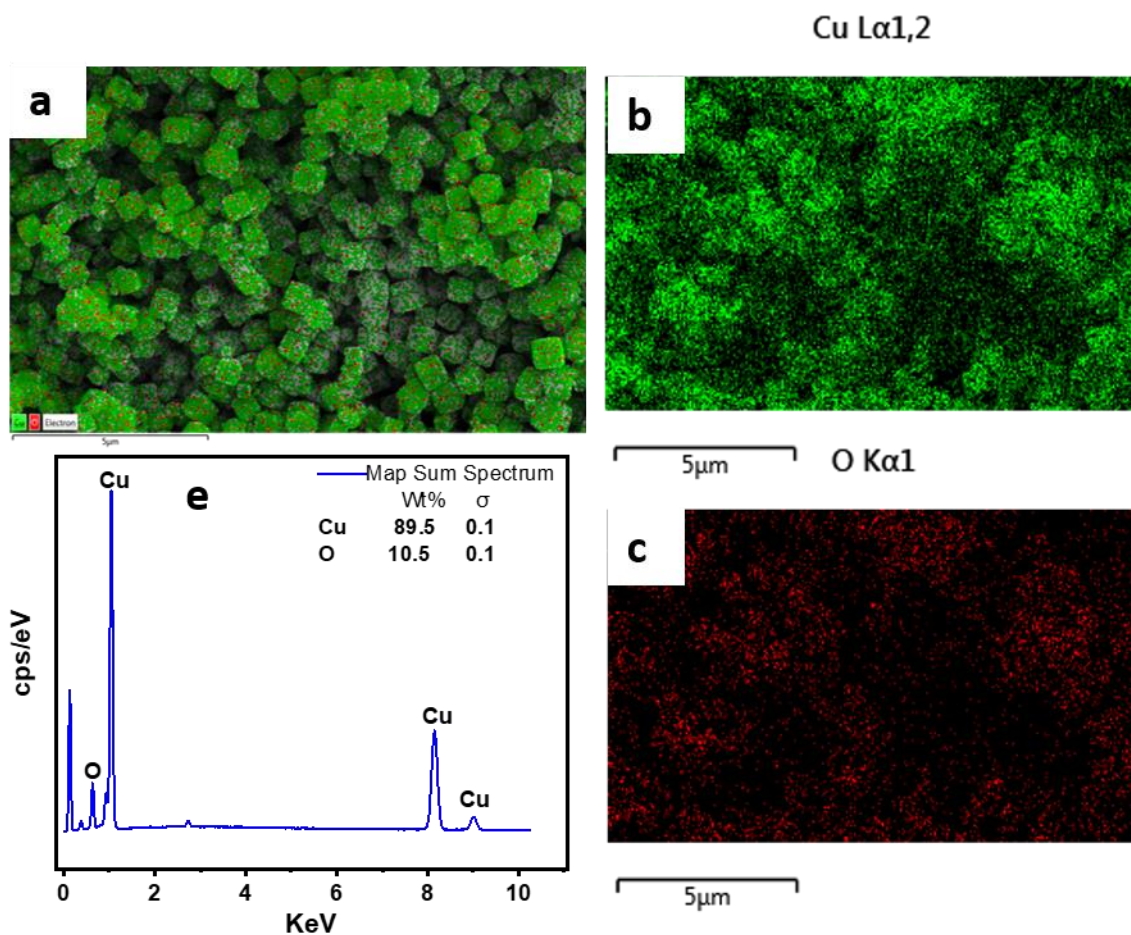


Figure 14, EDX mapping of the cube shaped Cu₂O with the elemental compositions. The SE micrographs, (a) overlay image and (b to c), the EDX mapping of elements Cu & O and (d) EDX spectrum.

The EDX elemental mapping for the gold decorated cube shape Cu₂O nanomaterial, Figure 15, present the relative elemental amounts that constitute the hybrid nanomaterials. In the EDX image the well synthesized hybrid nanomaterial with uniformity of shape, the Au image is least intense blue color, O image more intense green color and the Cu image is

much more intense red color. Also the table on the graph indicate 83.4% composition of Cu, 16.0% constitute O and Au constitute 0.7 percent of the hybrid nanomaterial. The EDX data graph also show, through the relative intensity of the peak associated to Cu, O and Au. Confirmed the above information on percentage in amount of the element.

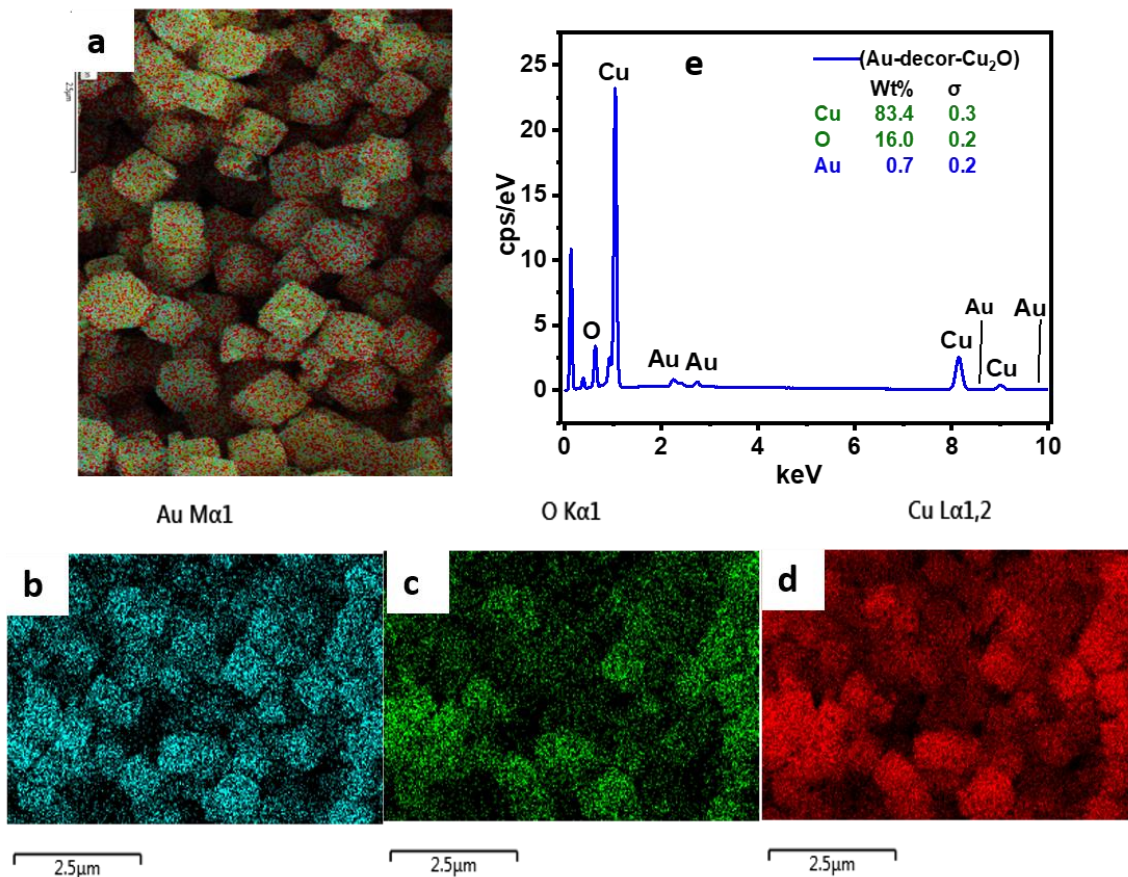


Figure 15, EDX mapping of the cube shape Au@Cu₂O with the elemental compositions. The SE micrographs, (a) overlay image and (b to c), the EDX mapping of elements Cu & O and (d) EDX spectrum

The octahedral shaped Cu₂O was analyzed using EDX to obtain the comparative percentage composition of each individual element in the hybrid nanomaterials. The image mapping shows the order of intensity varies in intensity from Cu, O, and Au in that other.

The representation in Figure 16 shows, percentage of Au is 3.8% which is more than that present in cube shape morphology, O remain relatively the same 16.0% and Cu reduce to 80.2% from the percentage observed in cubic morphology. The EDX spectrum also present the fact that the image mapping intensity are in agreement.

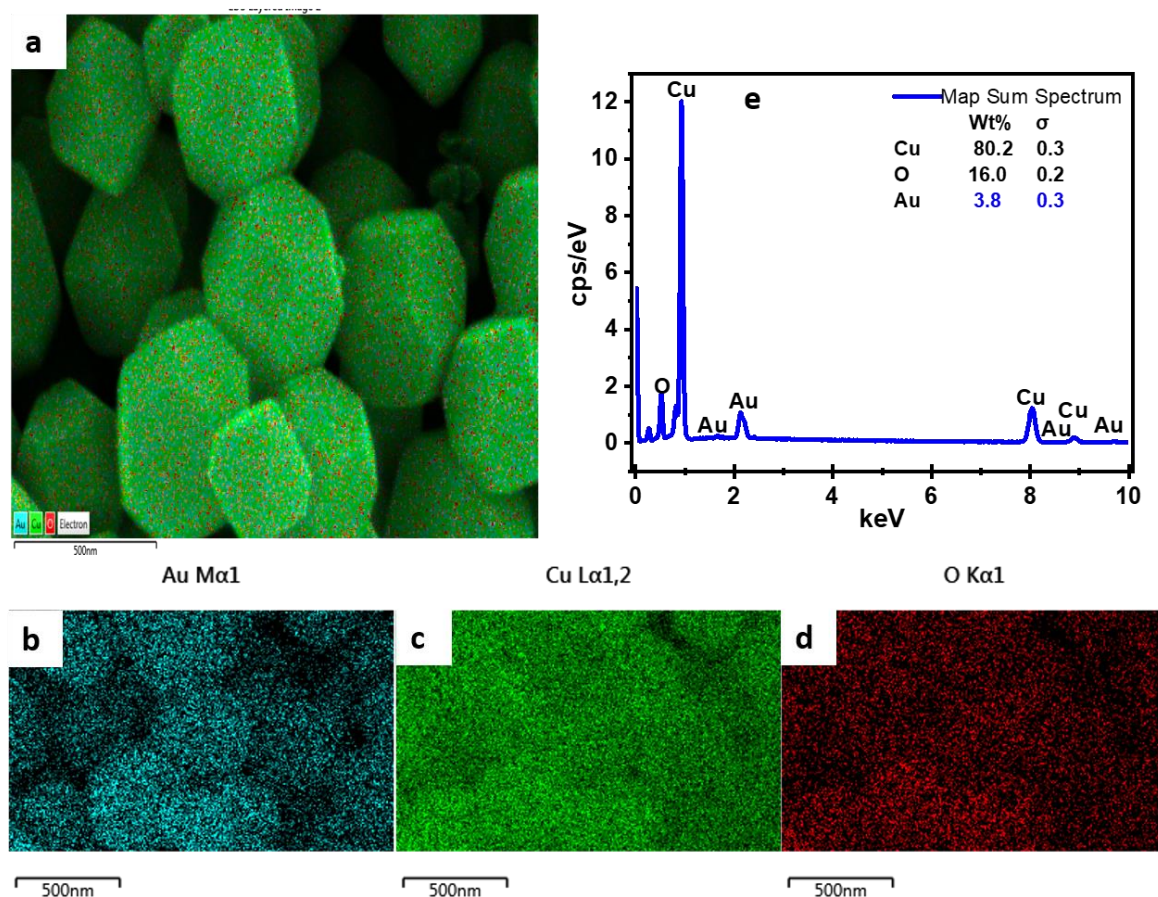


Figure 16, EDX mapping of the octahedron shaped Au@Cu₂O with the elemental compositions. The SE micrographs, (a) overlay image and (b to c), the EDX mapping of elements Cu & O and (d) EDX spectrum.

The nanomaterial synthesized in two shapes of cube and octahedral in the pristine form and the hybridized form, Table 1, present each nanostructure elemental percentage composition and their mass ratio. In the cube Cu₂O, the Cu percentage is 89.5% and O is 10.5% this agrees with the calculated theoretical mass ratio, while for Au decorated Cu₂O is compose of 0.7% of Au, 83.4% for Cu and 16.0% of O and their corresponding mass ratio are 0.007:0.833:0.159 respectively. The octahedral Cu₂O decorated with Au, has 3.8%

of Au, 80.2% of Cu, and 16.0% and the calculated theoretical mass ratio for the hybrid octahedral nanomaterial are 0.038:0.802:0.16.

Nanostructure	Element	Percentage	Mass ratio
Cube Cu ₂ O	Cu	89.5	0.896:0.105 (Cu:O)
	O	10.5	
Cube Au@Cu ₂ O	Au	0.7	0.007:0.833:0.1598 (Au:Cu:O)
	Cu	83.4	
	O	16.0	
Octahedral Au@Cu ₂ O	Au	3.8	0.038:0.802:0.16 (Au:Cu:O)
	Cu	80.2	
	O	16.0	

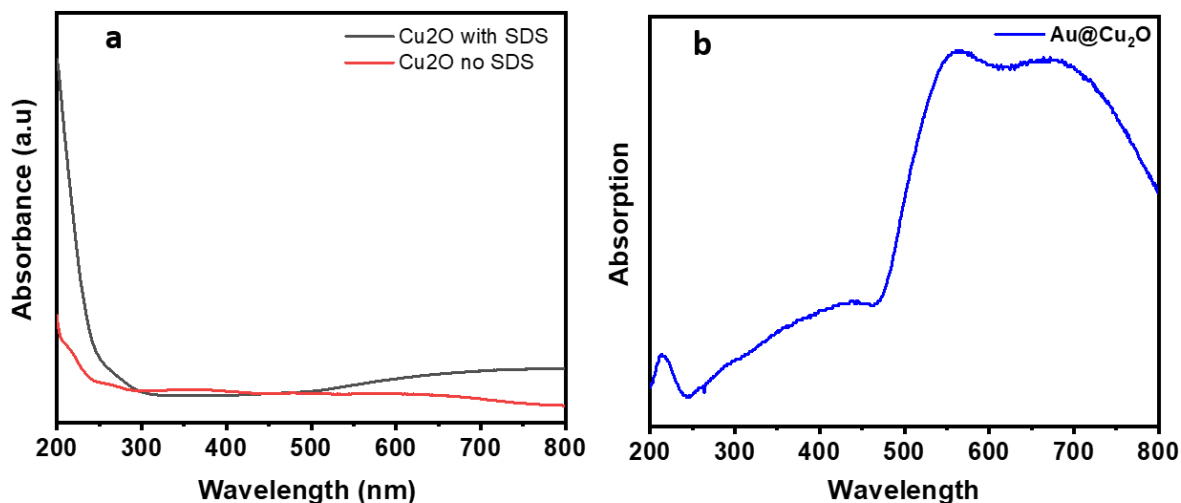
Table 1, Show the calculated theoretically, mass ratio of Cu and O in Cu₂O and the Au, Cu, and O in Au@Cu₂O

4.4 Ultraviolet-Visible (UV-Vis) Spectroscopy

The ultraviolet and visible (UV-Vis) spectral were measured in range between 0 to 800 nm. The UV-Vis range also stretch the range of human visual sharpness of approximately 400 to 750 nm, which support the spectroscopic usefulness in characterizing the absorption, transmission and reflectivity of the synthesized nanoparticles and the hybrid version. The UV-vis spectra were measured using Genesys 10S UV-Vis spectrometer.

The absorbance observed for Cu₂O that has been synthesized by adding sodium dodecyl sulfate as surfactant covers more range in the solar spectrum, it shows an absorption from above 800 nm to 530 nm (Figure 1a). In general, Cu₂O nanoparticles synthesized without SDS show UV-Vis spectra absorption ranging from little bit above 800 nm to 540 nm.

From the observation it can be inferred that the surfactant, in this case sodium dodecyl sulfate (SDS) facilitated the formation of nanoparticles with the appropriate orientation, suitable for the efficient visible spectrum. This in return, helps to harvest the maximum portion of solar spectrum which is suitably desired in photocatalytic application. The decoration of the Cu_2O cubes with plasmonic metal nanoparticles in this case a gold, the resultant UV-Vis spectra shows an increase in the absorbance intensity range of the hybrid nanomaterials from 800 nm to 460 nm (Figure 1b) this reflects the contributive plasmonic property of gold on the semiconductor nanoparticles. Figure 17, (a, b) show the corresponding UV-Vis spectra of the Cu_2O and the hybrid Au- Cu_2O nanoparticles.



Figure, 17 (a) Shows UV-Vis spectra absorption of Cu_2O cube synthesized with and without SDS. (b) Present the UV-Vis spectra of Au decorated Cu_2O cube shaped nanoparticle, with spectra extended up to 460 nm due to the plasmonic contribution of the Au nanoparticle.

The reaction kinetic of the synthesis was monitored through ultraviolet-visible spectroscopy to a full glimpse on the transition stages per minute, illustrating with an Au decorated Cu_2O at 15 min timed interval. The first observed spectra at 15 min, show an absorption at 800

nm only, at 30 min the spectra pattern changes with more absorption at 540 nm and the spectra at 45 min shows high absorption both 540 nm and 800 nm, this is likely due to the nanomaterial formation stages from atoms to cluster and finally to the nanomaterial. Figure 18, give an insight into the nanomaterial formation kinetic mechanism.

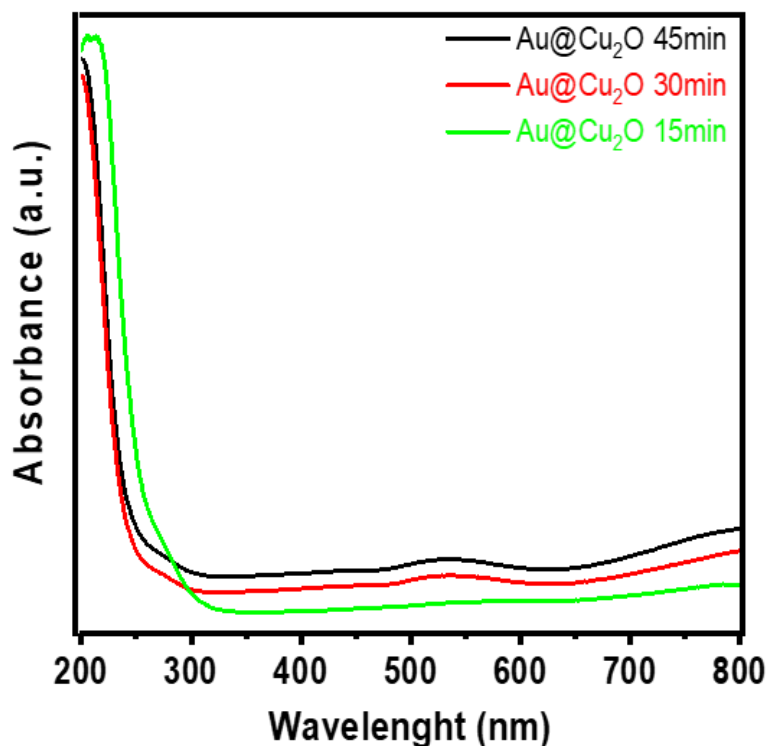


Figure 18, showing the sequential change in the absorption upon growth Au domain onto the surface of Cu₂O cube shape nanoparticles. After 45 minutes, we can clearly see the plasmon band centered at 530 nm. The growth of Au domains has also enhanced the absorption efficiency due to Au-Cu₂O hybrid nanoparticles.

The UV-Vis spectra for the nanoparticles with morphologies other than cube was also measured using the above stated instrument, the spectra for the octahedral shaped Cu_2O nanoparticle are shown in Figure 19. The washed Cu_2O nanoparticles were analyzed using and UV-Vis spectra were measured Figure 19a. The spectrum indicated an absorbance at 800 nm to 650 nm. The Figure 19b represent the effect of the introduced gold on the visible light absorbance of the octahedral shaped Cu_2O with Au nanomaterial. It showed strong absorption in the visible region and a distinctive Plasmon band centered at 520 nm due to the presence of Au nanoparticles. Overall, the Cu_2O with octahedron shape decorated with Au showed better absorption the visible range than alone Cu_2O .

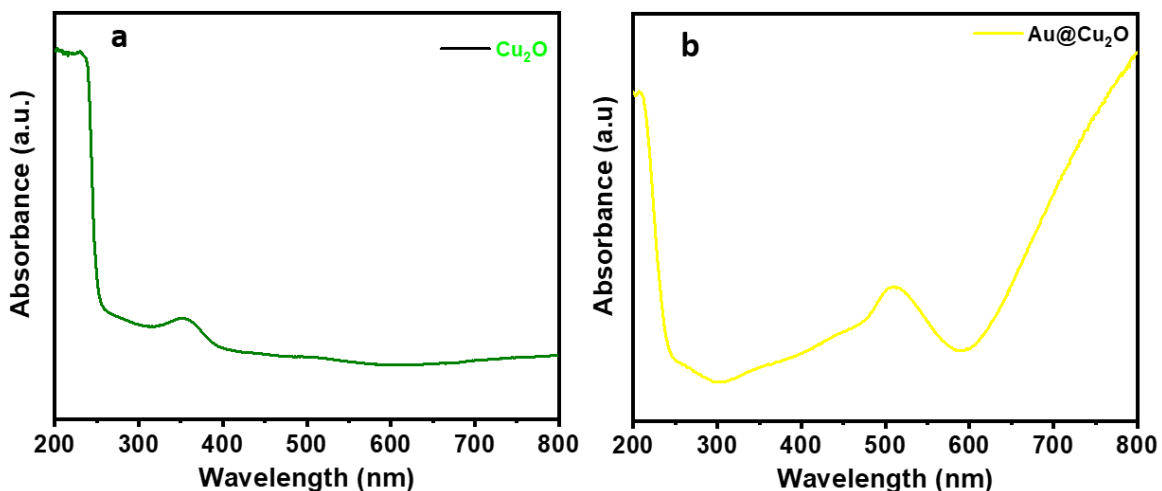


Figure 19, (a) A UV-Vis-Spectra of the as synthesized octahedral Cu_2O , showing absorption at 800 nm till 650 nm, (b) A very high intense absorbance peak around 800 nm which can be attributed to Cu_2O and another peak extension at 520 nm assumed to be as a result of the plasmon effect of the Au nanoparticle.

4.5 RAMAN Spectroscopy

Raman spectra were measured on iH320 Horiba spectrometer with charge-coupled device (CCD) using monochromatic laser (300mW, 532nm), grating of 1200cm^{-1} and an aluminum substrate. Raman spectroscopy furnish chemist with the information on the crystal structure of the synthesized nanoparticle and hybrid nanomaterial in this case Cu_2O and Au nanoparticles decorated Cu_2O . The Cu_2O and Au- Cu_2O cube and octahedral morphology were characterized using Raman spectroscopy, they exhibit a characteristic Raman bands at 218cm^{-1} , 523cm^{-1} and 623cm^{-1} . These correspond to characteristic Raman Band for the Cu_2O as reported earlier by Yilin Deng on Raman spectroscopy study of copper oxide during electrochemical oxygen evolution reaction. The Raman spectra of the pristine Cu_2O and the Au doped Cu_2O are shown in Figure 20 (a, b) below.

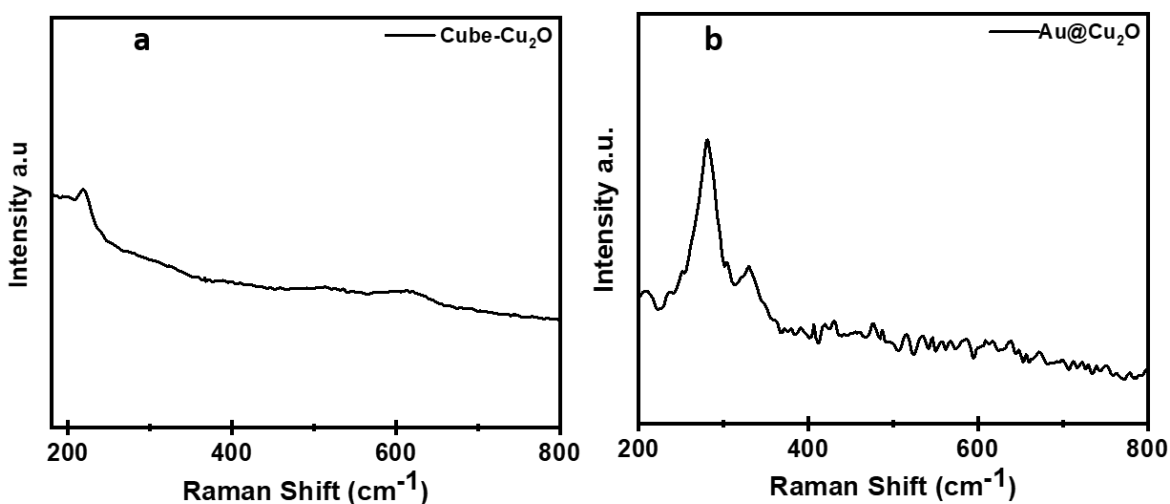


Figure 20, In (a) Raman shift pattern at 218cm^{-1} and 623 cm^{-1} was present which were due to Cu_2O cube, (b) shows Raman band at 218 cm^{-1} , 523cm^{-1} and 623 cm^{-1} , the high intensity band at 218 cm^{-1} and the observed band at 523 cm^{-1} resulted from the Au hybridized Cu_2O .

The Raman characterization of octahedral morphology is represented in figure 5 for both the pristine octahedral and the Cu_2O decorated with Au. The octahedral Cu_2O shaped nanoparticle on the show (Figure 21a) a strong Raman band at 218cm^{-1} and low band at 623cm^{-1} and when the octahedral Cu_2O (Figure 21b) is decorated to Au, Raman band was observed at 218 cm^{-1} , 523 cm^{-1} and 623 cm^{-1} . A unique band at 260 cm^{-1} which also give more credence to the Au deposited on the Cu_2O .

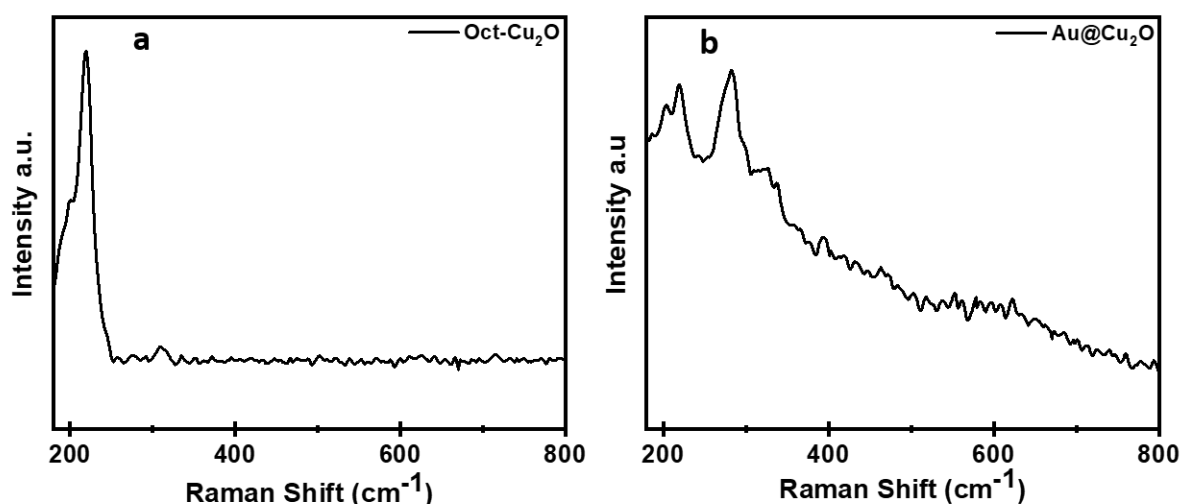


Figure 21, (a) Raman band of octahedron Cu_2O is presented with intense band at 218 cm^{-1} with less obvious band at other Raman shift, which is attributed to the morphology of the pristine nanoparticle, (b) Shows the plasmon resonance contributive effect of Au on pristine octahedron Cu_2O , with the 260 cm^{-1} in addition to 523 cm^{-1} and 623 cm^{-1} band been due to Au decorative effect on Cu_2O .

4.6 X-ray Diffraction (XRD)

The patterns of the X-ray diffraction were measured using the Rigaku Miniflex II instrument with a monochromator $\text{CuK}\alpha 1$ ($1.5406\text{\AA}$) at 30kV, 15mA. The XRD patterns were recorded in the static scanning mode from (2θ) 20° to 80° at a detector angular speed

of 4°min^{-1} and step size of 0.02° . The arrangement of atoms in a solid can be elucidated with aid of XRD. The distance between atoms in a lattice is approximately equivalent to the wavelength of the X-rays, when the beam of X-rays radiation falls on a crystal, the resultant deflection by the crystals are captured by a photographic plate which is obtain as an output. It is a technique used to examine the morphological crystal structure of the synthesized Cu_2O and $\text{Au-Cu}_2\text{O}$ based nanoparticles. In Figure 22, pristine Copper oxide synthesized without SDS and with SDS is shown with diffractograms having reflections at (2θ) 29° , 37° , 43° , 61° , 74° , and 77° . The diffraction reflection at 29° is attributed to the (110) facet of Cu_2O , that at 37° is associated to a Cu_2O nanoparticle with a facet of (111), diffraction reflection at 43° correspond to (200), while the facet (220) is in tendon with 61° . Also the diffraction reflection at 74° and 77° correspond to the facet (311) and (222) respectively.

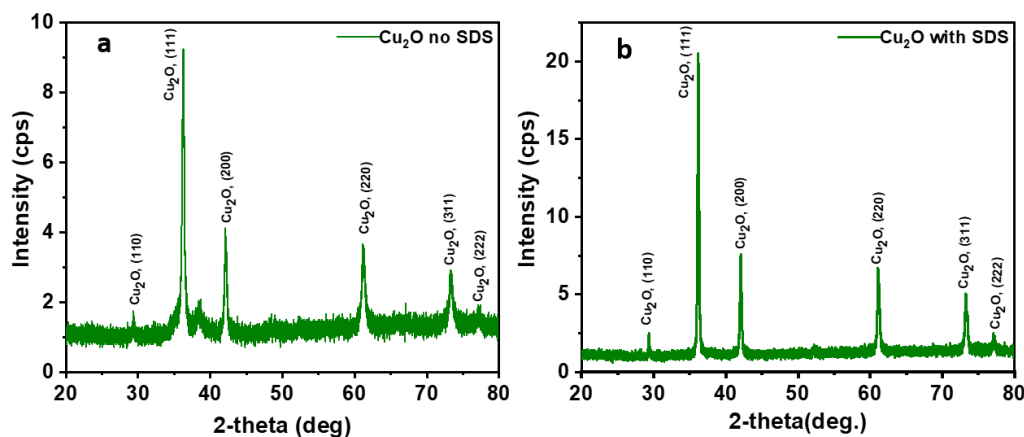


Figure 22, (a) XRD diffractogram of as synthesized Cu_2O without the use of a surfactant (SDS), extra reflection in the pattern at 37° could be due to impurity CuO . (b) Shows the XRD pattern for a Cu_2O synthesized using surfactant (SDS), all the reflections in the diffractogram

matches well with the Cu_2O ($\text{Pn}\bar{3}\text{m}$). This confirms the phase purity of as synthesized Cu_2O nanocubes.

The XRD diffractogram of the as synthesized cube shape Cu_2O semiconductor nanoparticle decorated with noble metal (Au) were investigated to ascertain the contributive effect of the Au on the crystal structure of the Cu_2O semiconductor. Figure 23, here below, present the unique XRD pattern of the hybrid nanomaterial between Cu_2O and Au. The very obvious diffraction reflections at 38° and 77° shows the presence of Au domains with the facet (111) and (311) respectively.

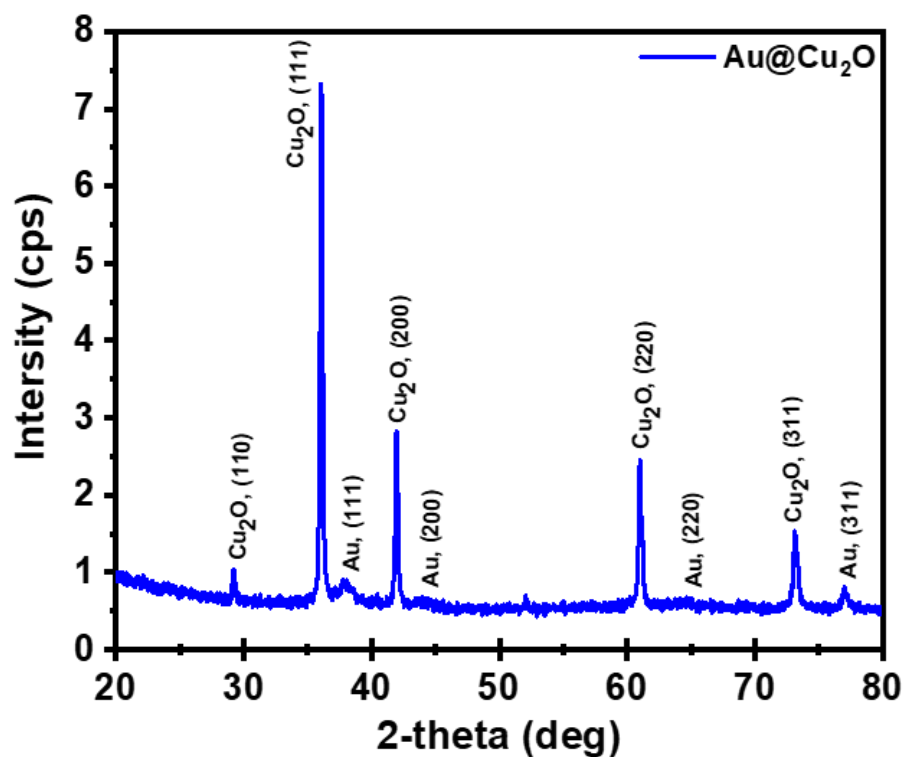


Figure 23, Show the XRD diffractogram of cube shape Cu_2O decorated with Au nanoparticles.

The XRD pattern of the Cu_2O nanoparticles with octahedral morphology was also investigated using the same instrument as stated above under similar set of conditions. The diffraction pattern is shown in Figure 24. The all reflection could be indexed to phase pure Cu_2O with space group (here write space group). All the reflection observed can be easily indexed to octahedron lattice phase

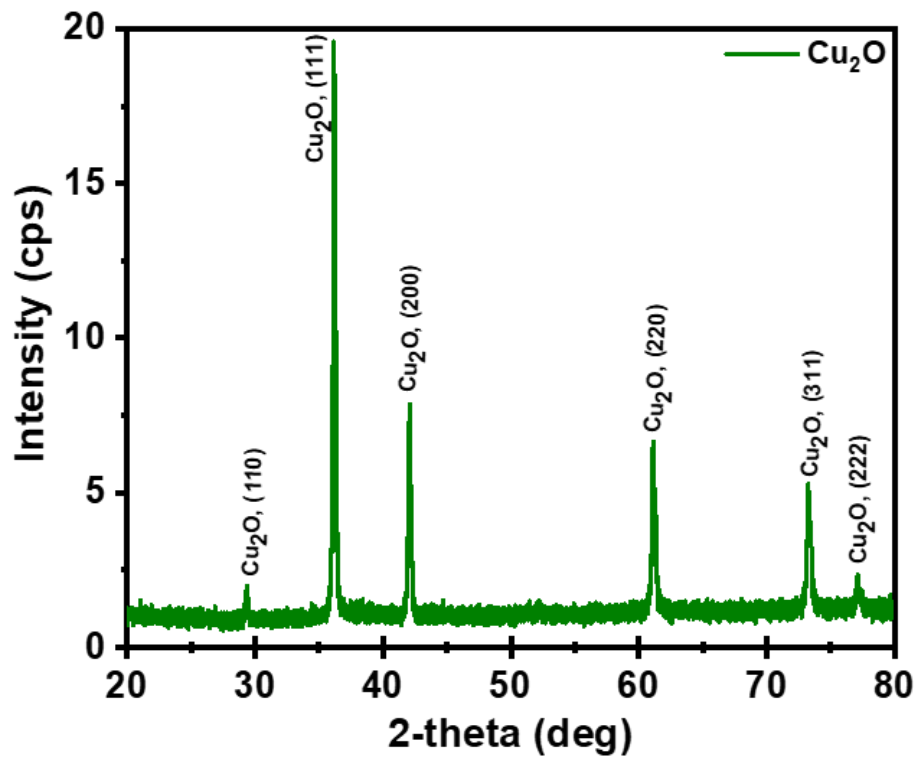


Figure 24, Represent the XRD diffractogram of octahedral shaped Cu_2O ,

Furtherance to the XRD pattern observed with the octahedron shape Cu_2O that is not a hybridized with Au nanomaterial, the crystal structure of the hybridized nanomaterial was measured to obtain the crystal structural contribution of the newly introduced Au nanoparticle on the semiconductor nanoparticle. The pattern of the octahedral nano-

structure Cu_2O , decorated with Au is detailed in Figure 25. The purity of the nanomaterial was attested by the fact that the diffraction pattern shows no any extra diffraction other than the expected pattern, usually when extra pattern is present that suggest the presence of impurity in the synthesized nanomaterial. This claim is further confirmed from the EDX analysis, as the elemental mapping only present the element of copper and oxygen in case of pristine Cu_2O and Au, Cu and oxygen for hybrid nanomaterials.

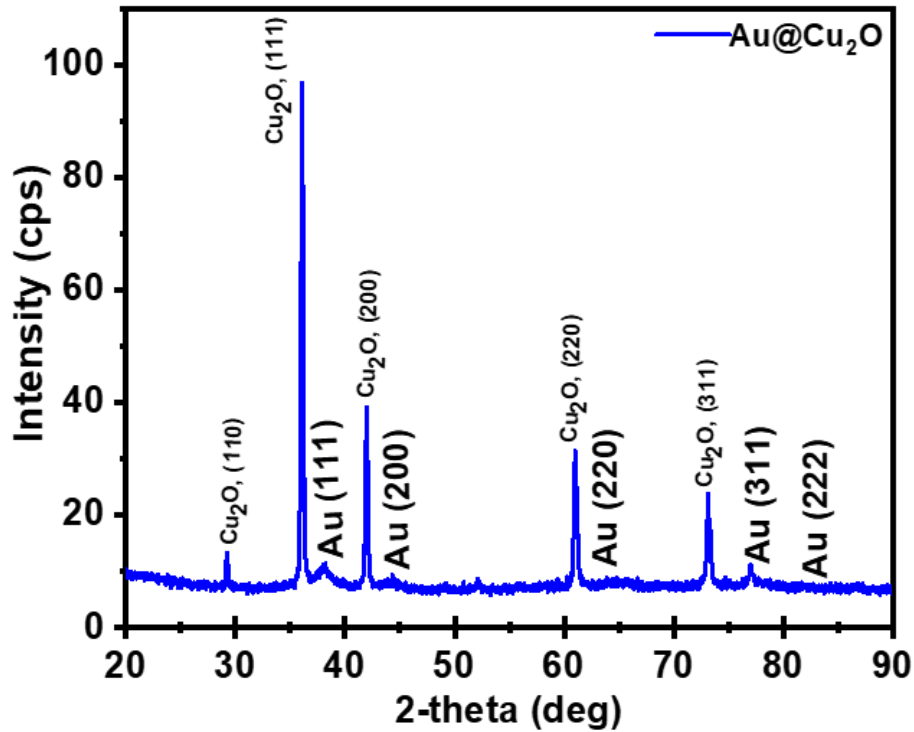
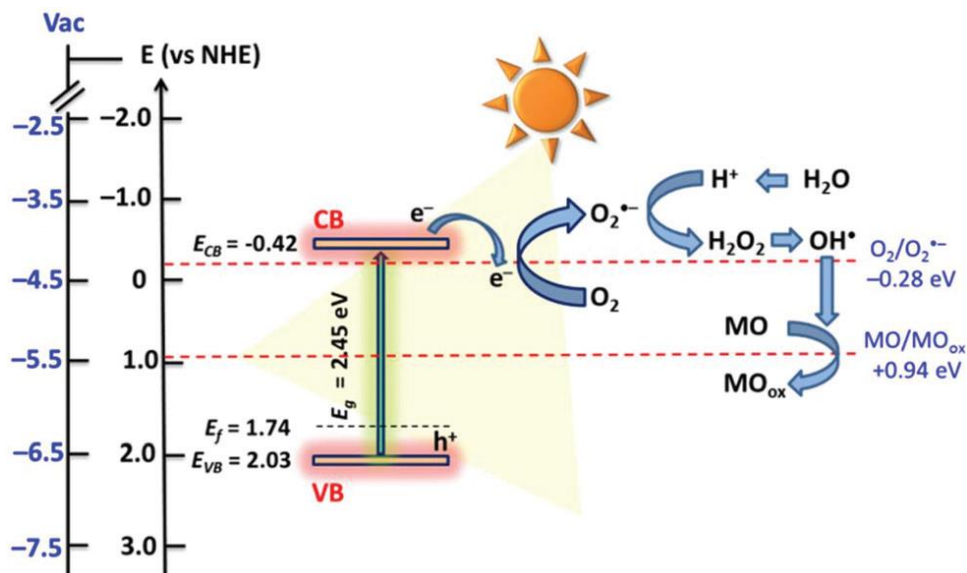


Figure 25, Show the diffractogram of octahedral Cu_2O with some Au deposition on selected facet.

4.7 Photocatalytic Application

The surface engineered hybrid nanoparticles are used for visible light assisted photo-catalysis for the degradation of organic pollutants in water. The size, composition and surface area of nanomaterial plays a crucial role in photocatalytic applications. The energy of the surface site depends on particle size, shape and surface chemistry. The catalytic activity is enhanced when the physical properties of the surfaces are improved by the introduction of novel noble metal to a pristine Cu_2O . The pristine Cu_2O and Au decorated Cu_2O of cube shape and octahedral morphology were evaluated for photocatalytic activities as a photo-degradation of methylene blue (ME) dye under visible-light irradiation. The analysis procedure entails prior to the exposure to visible light radiation, 5×10^{-5} M of the ME dye solution, prepared by adding 2mg of dye in 20ml of H_2O and 2mg of the nanomaterial was added into the ME solution in the absence of light, and left for 30 min to ensure equilibrium is established between the ME and the nanomaterials. The pristine methylene blue (ME) shows a strong absorption peak at 670 nm wavelength, and the photo-degradation on the addition of nanomaterial was monitored by evaluating the decrease in absorbance intensity using ultraviolet-visible spectroscopy at interval of 15 min⁵²⁻⁵⁵. Here in Scheme 10, is the schematic energy representation of band gap diagram of Cu_2O nanoparticles, that illustrate their ability to be photoexcite through the aid of visible light to generate $\text{OH}^\cdot$ radicals which can participate actively in the photo-oxidation ME molecules.



Scheme 10, Represent band gap of Cu_2O

Cube shape pristine Cu_2O with ME analyzed with UV-Vis Spectroscopy, indicate small decrease in absorbance intensity as the measurement time increases from 0 min to 45 min, this is shown in figure 26.

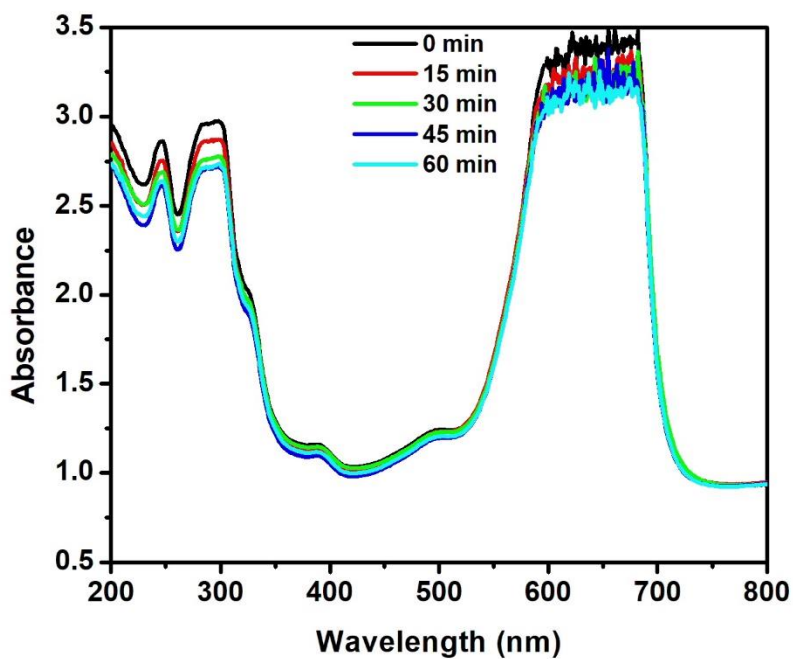


Figure 26, Photo-degradation of methylene blue on Pristine Cu_2O at 15 min interval.

The UV-Vis spectra of the Au decorated Cu_2O with cube morphology, Figure 27, indicate a sharp decrease in the degradation of methylene blue (ME), for much more than when the undecorated Cu_2O were used for the same purpose at the same time interval. At 0 min of taking the UV-Vis measurement, the peak intensity is 3.5 at 670 nm, after 15 min of exposure to the full visible spectrum range the photo-degradation of ME is at an average of 0.4 absorbance decrease.

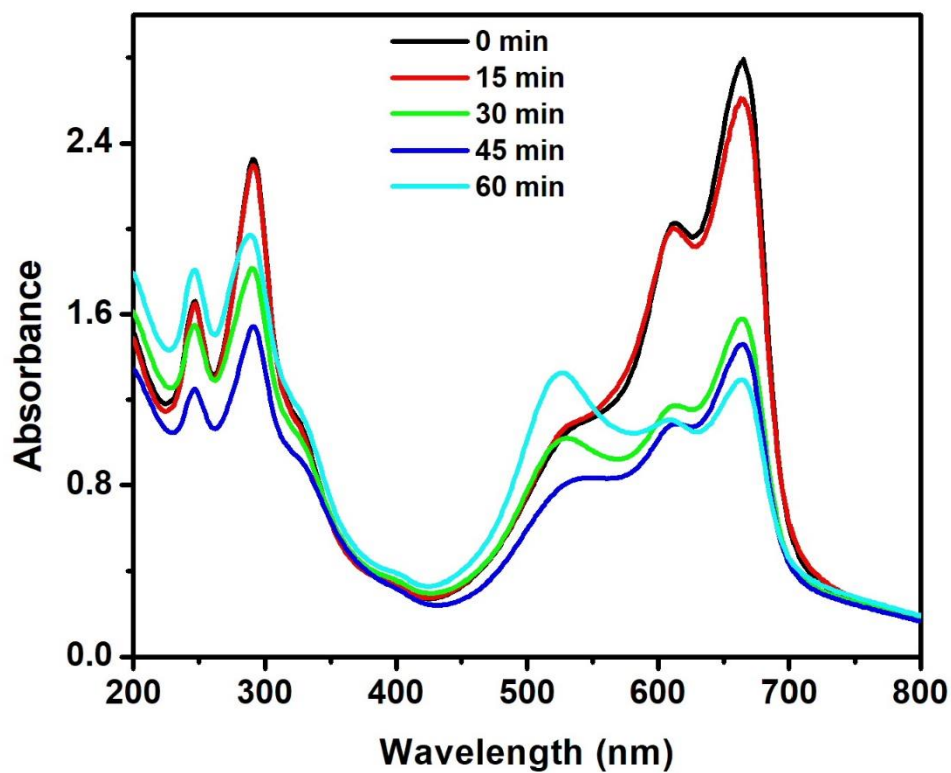


Figure 27, Au- Cu_2O hybrid photo-degradation of ME

In the case of the Cu_2O nanoparticles with octahedron morphology, the UV-Vis spectroscopy measurement for evaluating the photo-degradation of solution of ME, depict an absorbance which does not decrease much with the 15 min time interval set for observing the photo-degradation power of the octahedral Cu_2O morphology, from the graph it can be infer that at every 15 min only about 0.1 absorbance is lost, and this implies that the nanomaterial only degrades ME at a slow rate. In figure 28, ten (10) UV-Vis spectroscopy measurement was taken and the absorbance interval was uniform.

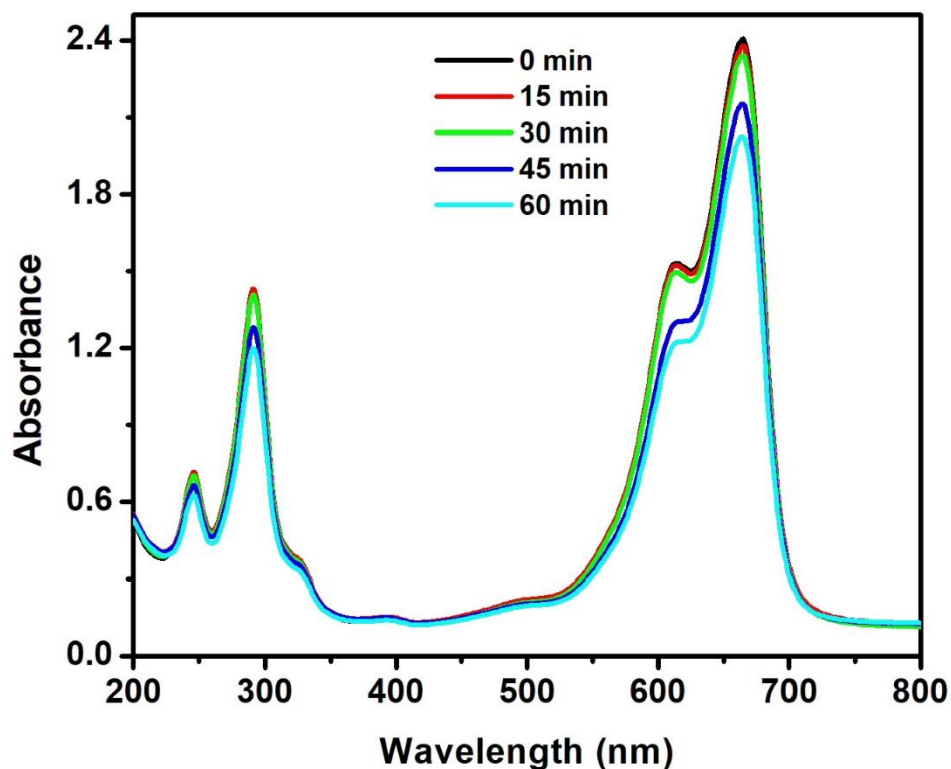


Figure 28, ME degradation by octahedral Cu_2O

There was a great departure in the photo-degradation activity of Cu₂O decorated with Au, as compare to the pristine Cu₂O. here, starting from the measurement at 0 min, and the second measurement at 15 min that absorbance difference was very small, that means that for 15 min only small percentage was degraded, beyond 15 min there was a shape photo-degradation of ME which signifies the contributive effect of the Au to the photocatalytic performance of the nanomaterial and this is shown in figure 29.

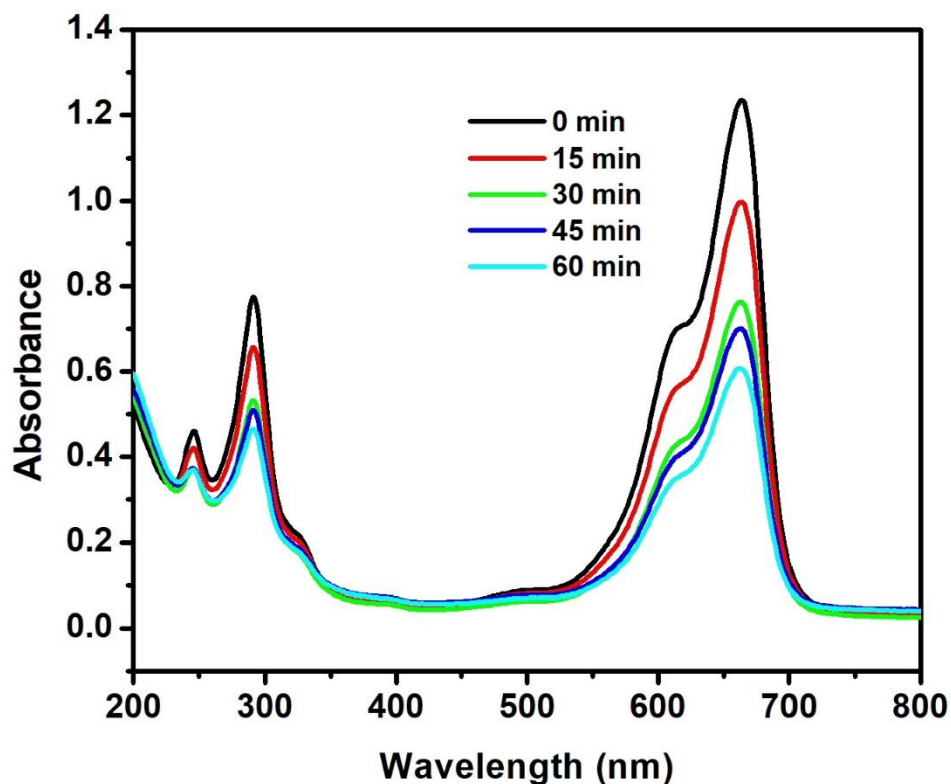


Figure 29, Octahedral Au decorated Cu₂O photo-degradation of ME

In other to understand the kinetic that governs the photocatalytic degradation of organic pollutant in water, the pseudo-first-order model was a suitable model that is generally used to express the photo-degradation process with an initial concentration been low. This is expressed in equation 1.

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (1)$$

Where C_0 is the initial concentration and C is the concentration at time (t), k represents the pseudo-first order rate constant and t stand for time. Figure 30, present the comparative kinetics photocatalytic methylene blue degradation by independent pristine cubic and octahedron Cu_2O morphology as well as their hybridized nanoparticle with gold, $\text{Au@Cu}_2\text{O}$. It becomes more clear that the Au hybrid result in some enhanced photocatalytic properties of the as synthesized nanomaterial. For the pristine cubic Cu_2O only about 10% degradation of methylene blue was achieved at 60 min of degradation time, why for octahedron 12% degradation at same 60 min. The degradation power of the nanomaterial increased to 38% and 45% for cubic and octahedron $\text{Au@Cu}_2\text{O}$ respectively.

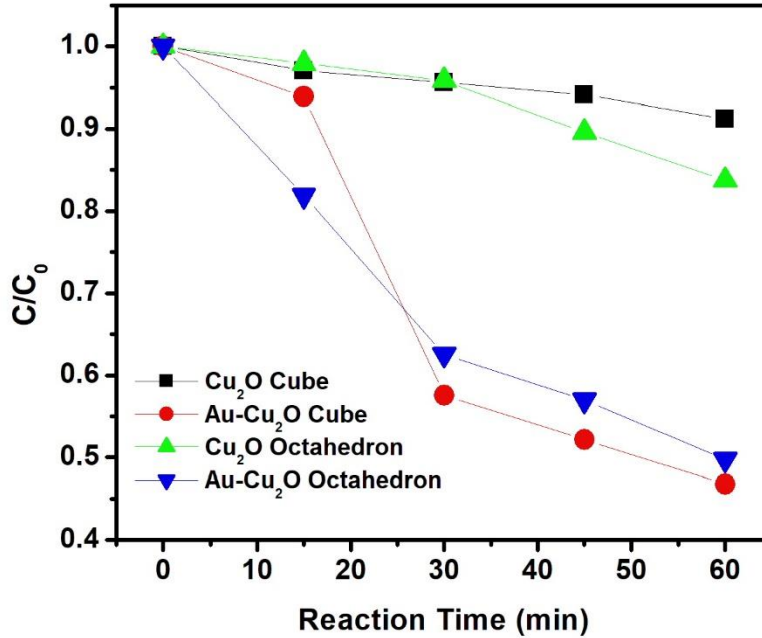


Figure 30, Photocatalytic degradation kinetic of methylene blue in water in two Cu_2O morphology and their hybridized $\text{Au@Cu}_2\text{O}$.

CHAPTER 5

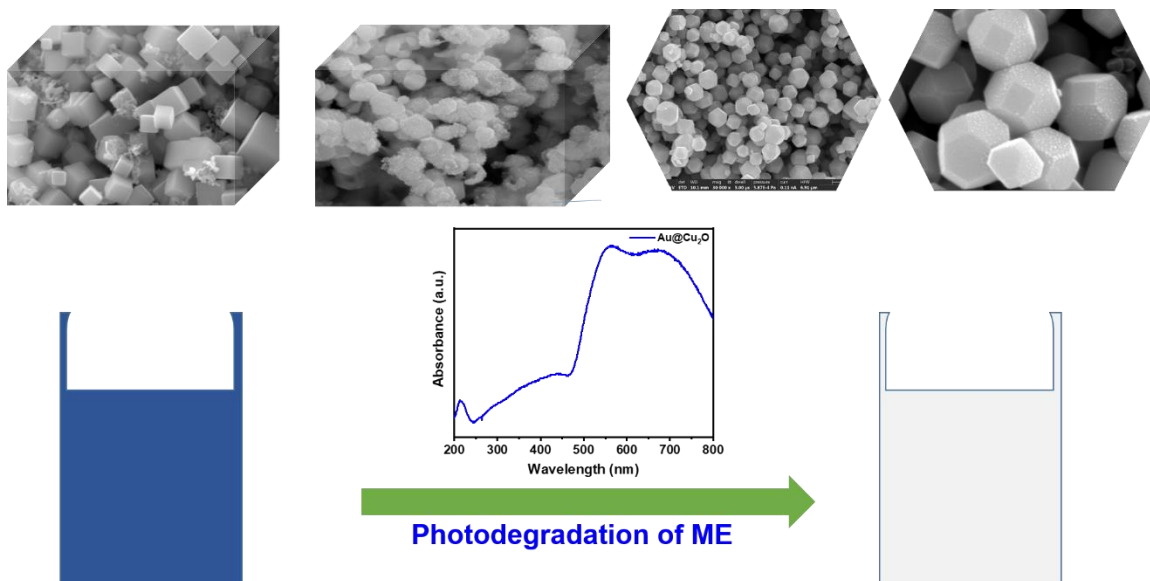
CONCLUSION AND RECOMMENDATIONS

In conclusion, the synthesis of Cu₂O nanomaterials with different morphologies and their corresponding hybridization with Au to synthesize hybrid nanomaterials is successfully carried out. The different pristine as well as hybrid materials were characterized using different analytical techniques. The photocatalytic application result showed enhanced activity for the hybrid nanomaterials. Here the outcome is summarized;

1. Cubic Cu₂O nanoparticle was successfully synthesized using sonication after month of attempt on using non aqueous method to synthesis cubic Cu₂O and then unfold the possibility of making out other morphology from the main cubic target by adjusting the synthesis conditions to actualize the shapes such as rhombic, octahedral etc. In the non-aqueous approach synthesis, ethylene glycol was employed as the reaction medium, copper acetate was use as the precursor salt in the while glucose was used as reducing agent. The non-aqueous approach was jettison as it continues to be so difficult to achieve the end target, judging by the color that is observed as against the expected color of yellow orange, probably due to the inability to mimic the pre-existing synthesis procedural condition.
2. In a novel approach, we were able to synthesis Cu₂O within an aqueous medium and functionalized this semiconductor material for photostability and effective, efficient visible light harvesting which could be used for pollutant degradation, organic synthesis, water splitting and in the reduction of CO₂. Although, we focus the

application of the an-synthesis nanomaterial on water purification with hope to explore it usefulness in the other above stated areas in the future.

3. The visible light harvesting is test for pristine and hybrid Cu_2O reflect the contributive plasmon metal effect on the semiconductor. When the nanomaterial was added into water contaminated with methylene blue (ME), the hybrid nanomaterial for the two morphology investigated show a greater degradation power as compare to the pristine semiconductor.



RECOMMENDATION

The following are recommended for future work

1. The large scale synthesis of Cu_2O for industrial application.
2. Commercialization of gold decorated Cu_2O hybrid nanomaterial.
3. Application of the Cu_2O nanoparticle for anti-bacterial infection

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