

**KINETIC AND MECHANISTIC STUDY ON REACTIVE
OXYGEN SPECIES GENERATION IN PHOTOCATALYSIS
USING ELECTRON PARAMAGNETIC RESONANCE
SPECTROSCOPY**

BY

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Dedicated to my mother, brothers, wife, kid, and especially to my late Father

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LIST OF ABBREVIATIONS

LED	:	Light Emitting Diode
ROS	:	Reactive Oxygen Species
EPR	:	Electron Paramagnetic Resonance
$\cdot\text{OH}$	:	Hydroxyl Radical
$\cdot\text{O}_2^-$	:	Superoxide Anion Radical
$^1\text{O}_2$	:	Singlet Oxygen
H_2O_2	:	Hydrogen Peroxide
eV	:	Electron Volt
UV	:	Ultraviolet
ISO	:	International Standard Organization
MB	:	Methylene Blue
HPLC	:	High Performance Liquid Chromatography
TOC	:	Total Organic Carbon
DMPO	:	5,5-dimethyl-1-pyrroline N-oxide
DEPMPO	:	5-(diethoxyphosphoryl)-5-methyl-1-pyrroline-N-oxide
MNP	:	2-methyl-2-nitrosopropane
EBN	:	N-tert-butyl methanimine N-oxide
TEMPOL	:	2,2,6,6-tetramethylpiperidine-1-oxyl
TEMPO	:	2,2,6,6-Tetramethyl-1-piperidinyloxy
MTSSL	:	1-Oxyl-2,2,5,5-tetramethyl-3-pyrroline-3-methyl) methanethiosulfonate
CTPO	:	3-carbamoyl-(2,2,5,5)-tetraepideuteromethyl-3-

		pyrrolin-1-yloxy
OXANO	:	2-Ethyl-2,4,4-trimethyl-1,3-oxazolidin-3-yl)
		Oxidanyl
DEET	:	<i>N, N</i> -diethyl-meta-toluamide
TALH	:	Titanium (IV) bis (ammonium lactato) dihydroxide
XRD	:	X-Ray Diffraction
SEM	:	Scanning Electron Microscope
IUPAC	:	International Union of Pure and Applied Chemistry
BET	:	Brunauer-Emmett-Teller
NMR	:	Nuclear Magnetic Resonance
MW	:	Microwave
FE-TEM	:	Field Emission-Transmission Electron Microscope
μM	:	Micromolar
TEMPONE	:	4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl
NIEHS	:	National Institute of Environmental Health Sciences
λ (nm)	:	Wavelength
θ	:	The angle at which constructively interfering X-rays leave a crystal
η_{coll}	:	Electron collection efficiency
π	:	Pi (= 22/7)
f	:	Frequency
ω	:	Omega (= $2\pi f$)
W	:	Width
EDXS	:	Energy-dispersive X-ray spectroscopy
XRD	:	X-ray diffraction
XPS	:	X-ray photoelectron spectrometer

q	:	Charge
RF	:	Roughness factor
e ⁻	:	Electron
h ⁺	:	Holes
mol	:	Moles
M	:	Molarity
°C	:	Temperature (degree Celsius)
K	:	Temperature (Kelvin)
B.E	:	Binding Energy
eV	:	Electron Volt
ε	:	Relative dielectric constant
ε_0	:	Permittivity of vacuum
k	:	Boltzmann constant
E	:	Applied potential
E _{coh}	:	Cohesive energy
E _{tot}	:	Total energy
N _O	:	Number of oxygen atom
E _O	:	Energy of oxygen atom
E _{surf}	:	Surface formation energy
P _{light}	:	Light intensity (100 mW cm ⁻²)
k _{tr}	:	Rate of charge transfer
k _{rec}	:	Rate of recombination
SPR	:	Surface plasmon resonance
NPs	:	Nanoparticles
VB	:	Valence band
CB	:	Conduction band

ABSTRACT

Full Name : [Muhammad Kamran]
Dissertation Title : Kinetic and Mechanistic Study on Reactive Oxygen Species Generation in Photocatalysis Using Electron Paramagnetic Resonance Spectroscopy
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Photocatalysis on organic and inorganic semiconductors attract great attention in the last few decades due to its potential uses in the fields of energy and environmental sciences. Despite that, a reliable method for direct photocatalytic activity assessment is still missing. The photocatalytic activity of particulate photocatalyst suspension is commonly evaluated by monitoring the rate of methylene blue bleaching and phenols degradation. For example, de-colorization of methylene blue (organic dye) has been proposed as a standard test method of the photocatalytic activities. Unfortunately, this method suffers from many drawbacks such as dye-self degradation and the need of sample filtration before measurements. Thus, the development of a direct and fast method for monitoring the photocatalytic activity of particulate photocatalyst suspension is urgently needed.

In this research, *in situ* electron paramagnetic resonance spectroscopy (EPR; also known as electron spin resonance, ESR) is used to directly identify the reactive oxygen species (ROS) generated in photocatalytic processes in the presence of an EPR-active reagent. As many types of ROS are usually formed during photocatalysis, the research work is focused on the detection, identification, and quantification of these species with the help of EPR spectroscopy. Among the paramagnetic species, great attention is giving to the hydroxyl radicals ($\cdot\text{OH}$) because of their high oxidizing power as compared to other

species. The work established an EPR method that is further used for the assessment of the activity of different types of photocatalysts based on the detection of the generated ROS.

In the presented method, we investigated the potential use of electron paramagnetic resonance (EPR) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPOL) to directly monitor the photocatalytic activity of TiO₂ suspension without the need for separation and filtration. TEMPOL showed many merits over the currently used model compounds; its aqueous solution is outstandingly stable in the dark and under UV(A) illumination, does not absorb UV(A) and visible light, and has negligible dark adsorption. The influence of TEMPOL concentration, light intensity, and TiO₂ loading on the photocatalytic deactivation rate has been investigated. The mechanisms of the TEMPOL deactivation in the presence and absence of oxygen as well as in the presence of methanol have been discussed. The photocatalytic deactivation products have been analyzed using EPR, ¹H-NMR, and ¹³C-NMR spectroscopies. Two different mechanisms of the deactivation of TEMPOL initiated by OH[•] radicals. First mechanism of the deactivation of TEMPOL is in the presence and absence of saturated oxygen, while the second one is in the presence methanol. A simplifies route of TEMPOL deactivation raises the potential of using the EPR-TEMPOL-Methanol system for direct monitoring of the photocatalytic activities of photocatalyst suspensions. By comparing the photocatalytic deactivation of TEMPOL over different TiO₂ photocatalysts with the photocatalytic oxidation of methanol, the same trends have been observed evincing that the proposed system has a great potential for application as a standard method for assessing the photocatalytic activity of particulate photocatalyst suspensions without the need for filtration or the wait for a long time to establish adsorption equilibrium.

ملخص الرسالة

الاسم الكامل: محمد كامران

عنوان الرسالة : دراسة حركية وآلية توليد أنواع شقوق الأكسجين النشطة خلال عملية التحفيز الضوئي باستخدام مطياف الطيفي الرنين المغناطيسي الإلكتروني

التخصص : كيمياء

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جذب التحفيز الضوئي على أشباه الموصلات العضوية وغير العضوية اهتمامًا كبيرًا في العقود القليلة الماضية نظرًا لاستخداماته المحتملة في مجالات الطاقة والعلوم البيئية، وعلى الرغم من ذلك لم تتواجد طريقة موثوقة لتقييم نشاط التحفيز الضوئي المباشر لمثل هذه المواد، حيث يتم تقييم نشاط التحفيز الضوئي للمحفز الضوئي بشكل شائع من خلال مراقبة معدل التبييض لصبغة الميثيلين الزرقاء أو تدهور مادة الفينولات، على سبيل المثال تم اقتراح إزالة تلوين الميثيلين الأزرق (الصبغة العضوية) كطريقة اختبار قياسية لأنشطة التحفيز الضوئي لمثل هذه المواد، ولسوء الحظ تعاني هذه الطرق من العديد من العيوب مثل التدهور الذاتي للصبغة والحاجة إلى ترشيح العينة قبل القياسات، وبالتالي هناك حاجة ماسة إلى إيجاد طريقة مباشرة وسريعة لرصد نشاط التحفيز الضوئي لمواد المحفز الضوئي.

في هذا البحث، يتم استخدام التحليل الطيفي لرنين المغناطيس الإلكتروني (EPR) والمعروف أيضًا باسم الرنين المغزلي للإلكترون (ESR) للتعرف بشكل مباشر على أنواع مشتقات الأكسجين التفاعلية (ROS) المتولدة في عمليات التحفيز الضوئي ونظرًا لأن العديد من أنواع ROS تتكون أثناء التحفيز الضوئي فإن العمل البحثي يركز على اكتشاف هذه الأنواع وتحديد كمياتها بمساعدة التحليل الطيفي EPR حيث يتم إيلاء اهتمام كبير لجذور الهيدروكسيل (•OH) بسبب قدرتها العالية على الأكسدة مقارنة بالأنواع الأخرى ولقد امتد العمل بطريقة EPR إلى استخدام نفس الطريقة لتقييم نشاط أنواع مختلفة من المحفزات الضوئية.

في الطريقة المقدمة، قمنا بالتحقيق في الاستخدام المحتمل للرنين المغناطيسي الإلكتروني (EPR) و 4-هيدروكسي - 2،6،6،2-رباعي ميثيل بيبيريدين-ن-أوكسيل (TEMPOL) لمراقبة النشاط التحفيزي الضوئي لمستحلب TiO_2 مباشرة دون الحاجة إلى الفصل أو الترشيح، ولقد أظهر استخدام مادة TEMPOL العديد من المزايا مقارنة بالمركبات النموذجية المستخدمة حاليًا، ومنها على سبيل المثال أن محلولها المائي مستقر بشكل واضح في الظلام وتحت إضاءة الأشعة فوق البنفسجية، وأيضًا لا يمتص الأشعة فوق البنفسجية وكذلك الضوء المرئي، ولديه امتصاص ضئيل للظلام، ولقد تم التحقيق في تأثير تركيز TEMPOL وشدة الضوء وتحميل TiO_2 على معدل تعطيل التحفيز الضوئي، وتمت مناقشة آليات قوة تكسير TEMPOL في وجود وغياب الأكسجين وكذلك في وجود الميثانول، وتم تحليل منتجات التحفيز باستخدام مطيافية EPR و H^1 -NMR و C^{13} -NMR، وأوضحت الدراسة وجود آليتين مختلفتين لتكسير TEMPOL بواسطة جذور OH في غياب وجود الميثانول ووجود الميثانول وفي غياب الأكسجين المشبع، ويوضح مسار تكسير TEMPOL إمكانية استخدام نظام EPR-TEMPOL-Methanol لتحديد أنشطة التحفيز الضوئي لمعلقات المحفز الضوئي ومن خلال مقارنة تعطيل التحفيز الضوئي لـ TEMPOL على محفزات TiO_2 الضوئية المختلفة مع أكسدة التحفيز الضوئي للميثانول، لوحظ نفس الاتجاهات مما يدل على أن الطريقة المقترحة لديها إمكانات كبيرة للتطبيق كطريقة قياسية لتقييم النشاط المحفزات الضوئية لمعلقات بدون الحاجة إلى الترشيح أو الانتظار لفترة طويلة لتأسيس توازن الامتزاز.

CHAPTER 1

INTRODUCTION

Nowadays, the use of sunlight as a process on the surface of the photoactive catalyst is highly attractive [1]. The word photocatalysis is the combination of two words, photo means light and catalysis mean active catalyst. Photocatalysis is a photo-activated chemical reaction that is mostly categorized as a free radical mechanism. Photocatalysts is a material which absorb photoirradiation to bring the valence electrons to higher level of energy and then provides such energy to substrates to produce a chemical reaction [2]. In the photocatalysis phenomena, electrons and holes are created upon the material's exposure to light. The photocatalysis process is further divided into two parts. The first is homogenous catalysis in which both catalyst and reactant are in the same phase, while in the second type of heterogeneous catalysis both catalyst and reactant are in different phases [3]. Interestingly, the photocatalysis process is used in every field of research but more importantly in chemistry, material science and chemical engineering (Figure 1.1).

1.1 Applications of photocatalysis

Photocatalysis has been gathering much more attention because it can be used in various environmental and energy applications. Indeed, water organic pollutants and stains can frequently be efficiently photo-decomposed [4]. Many types of semiconductors especially metal oxides are efficiently used for different types of applications such as hydrogen production, water treatment, self-cleaning, and solar cells [5-8]. Furthermore, photocatalysis has been recently involved in many practical applications, including self-

cleaning glass, tent/awning materials, odour-removing paint for indoor applications, NO_x removing paint, concrete and tiles for exterior applications, photo-induced sterile surfaces (ceramics and metals), water and air purification units, and defogging mirrors [9-16]. Henry *et al.*, (2019) explained the use of photocatalysis for several applications (Figure 1.2) [17]. Photocatalysis is considered an important green technology for several applications under ambient conditions [18, 19]. Several types of photocatalysts, e.g. TiO₂ [20, 21], g-C₃N₄ [22-24], SnO₂ [25, 26], Bi₂WO₆ [27], ZnO [28], and WO₃ [29] have been investigated photocatalytic applications. Among them, titanium dioxide (TiO₂), in particular, Evonik P25 showed the highest photocatalytic activity.

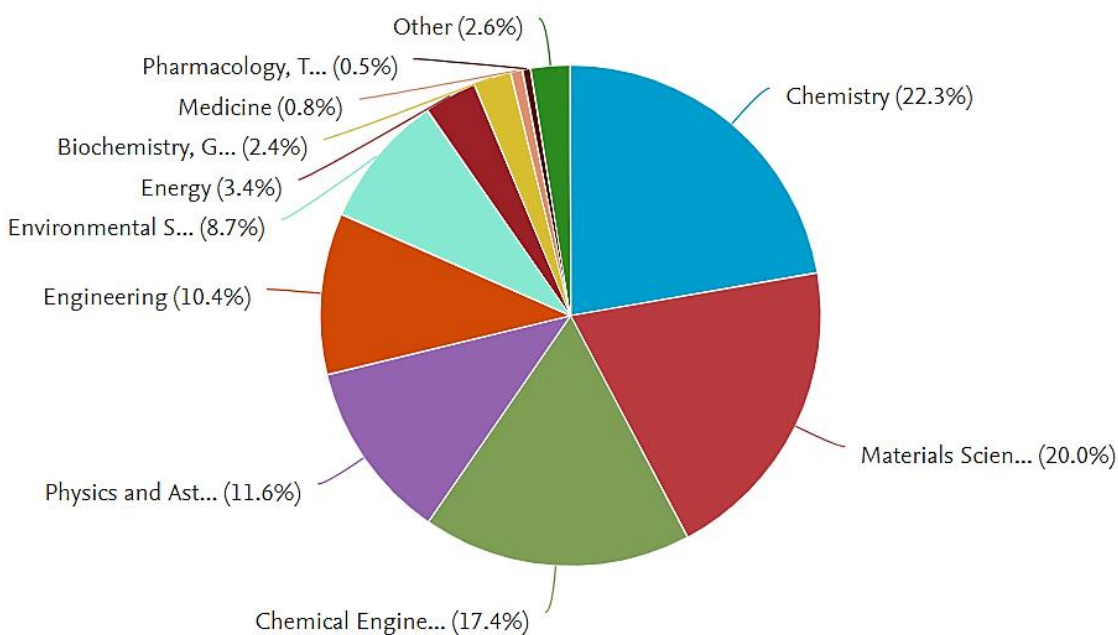


Figure 1. 1. Use of photocatalysis in different subject areas.

TiO₂ is commonly present in three phases (i.e. anatase, rutile, and brookite). With its bandgap of about 3.2 eV (anatase phase), it absorbs approximately 5% of the solar spectrum. Generally, anatase is more thermodynamically stable as compared to rutile and brookite, and thus it is commonly encountered during the synthesis of TiO₂ nanomaterials [30-32]. Due to this reason, TiO₂ in the anatase form has been extensively investigated in photocatalytic applications [33, 34]. The band gap energies and details of crystallography of all three TiO₂ forms are given in Table 1.1 and the crystal structures are present in Figure 1.3 [35, 36].

Table 1. 1. Crystallography of three forms of TiO₂ [35].

Crystal form	Crystallography	Formula unit per elementary cell	Band Gap (eV)
Anatase	Bipyramid tetragonal	4	3.2
Rutile	Tetragonal	2	3.0
Brookite	Orthorhombic	8	3.1-3.4

Traditionally, titanium dioxide (TiO₂), among many semiconductors, has been extensively used in ecological photocatalysis because it is non-toxic, inexpensive, and chemically and biologically inert [37, 38]. However, despite the TiO₂ photocatalysis has been used since 1972, in particular for environment cleaning purposes, the mechanisms of photocatalysis remain mostly unknown [39]. TiO₂ is a well-known photocatalyst for the degradation of organic pollutants in water under UV illumination [40-42]. TiO₂ has many merits, e.g. low cost, biocompatibility, resistance against photo-corrosion, and chemical stability, which make it a good candidate for practical application in photocatalytic processes [20, 21, 43-45].

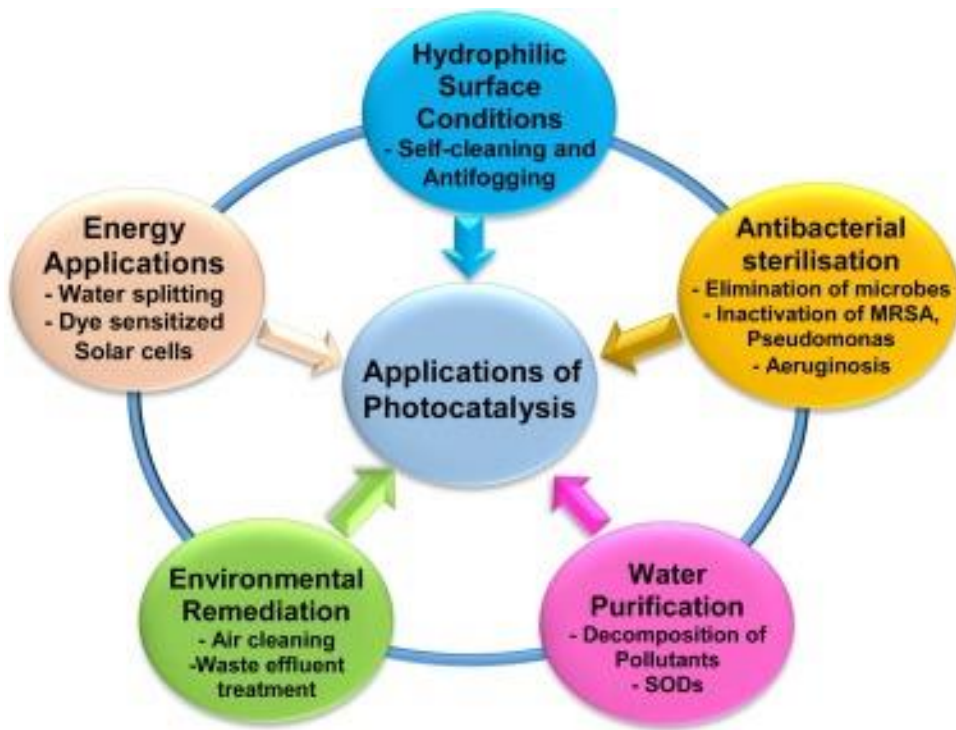


Figure 1. 2. Applications of photocatalysis [17].

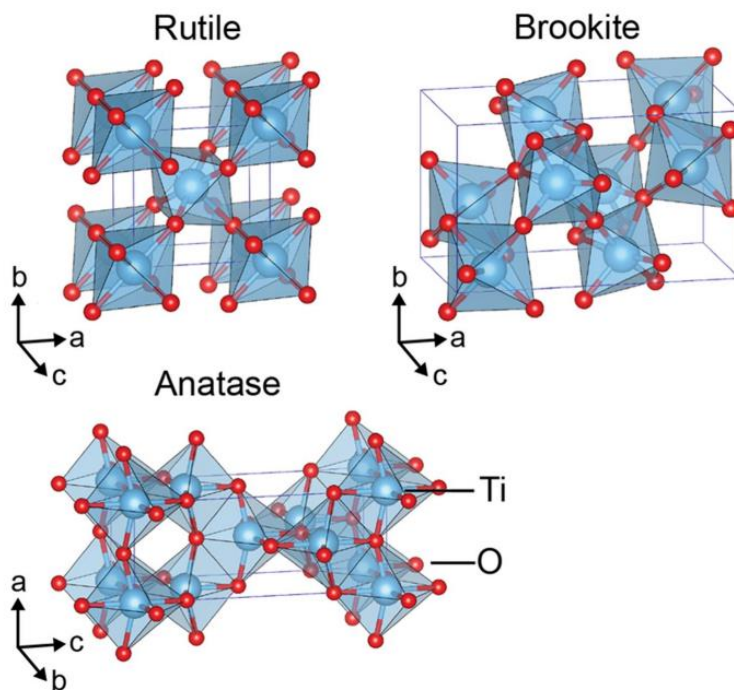


Figure 1. 3. Crystallographic structure of anatase, rutile, and brookite [36].

1.2 Synthesis of TiO₂ and its applications

TiO₂ is a well-known photocatalyst for photocatalytic activity assessment. TiO₂ is commonly present in three phases (i.e., anatase, rutile, and brookite). Generally, anatase is more thermodynamically stable as compared to rutile and brookite, and thus it is commonly encountered during the synthesis of TiO₂ nanomaterials [30-32]. Due to this reason, TiO₂ in the anatase form has been extensively investigated in photocatalytic applications [33, 34]. From the synthesis point of view, TiO₂ brookite is the most difficult phase to synthesize as compared to anatase and rutile, and therefore it has been less studied, however, it has shown a comparable activity to that of anatase or even better in some cases [46-49].

Different methods are used for the synthesis of TiO₂. The physical and chemical methods are the main classification for the synthesis of titania. Physical methods normally follow a top-down approach in which small structures are synthesized from large structures. In comparison, chemical method follows a bottom-up approach, in which the precursors of the molecule reacts to fabricate large structure materials. Physical methods are further classified into two classes of synthesis i.e., flame spray pyrolysis and radio frequent thermal plasma. There are four types of synthesis includes in the chemical synthesis process (hydrothermal, sol-gel, solvothermal and microemulsion) [50]. Physical methods are used for the synthesis of large-scale materials, but the resolution of these prepared materials will be very low. The controllable size, shape and composition of materials are prepared by chemical synthesis. Different forms of nanostructures and complex structural morphologies can also be synthesized by the chemical synthesis process [51].

Among all of these methods for the synthesis of TiO_2 , hydrothermal synthesis is one of the simple, low-cost, and well-known methods which provides maximum purity and maximum dispersibility of the prepared material. In the hydrothermal method, substances are crystallizing at high temperatures and pressure. The hydrothermal process of synthesis is conducted in an autoclave enclosed in a stainless-steel container. This container is kept in an oven at a variable temperature according to the form of the synthesized material. Different forms of TiO_2 can be synthesized by changing the temperature and the concentration materials of the materials [52]. Different forms of TiO_2 nanostructures are shown in Figure 1.4. Nowadays, TiO_2 photocatalysts are used in many photocatalytic applications such as pollutants degradation, water splitting, CO_2 reduction, solar cells, sensors, Li-ion batteries, antibacterial agents and many other biological applications (Figure 1.5) [53-58]. The numbers of publications per year on photocatalysis and especially on TiO_2 are presented in Figures 1.6 and 1.7.

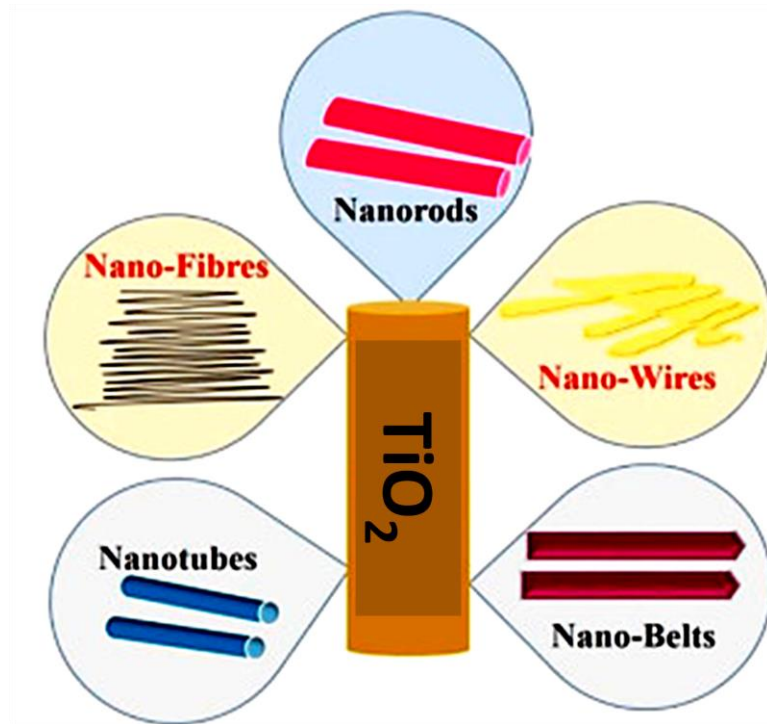


Figure 1. 4. Different forms of TiO_2 nanostructures [52].

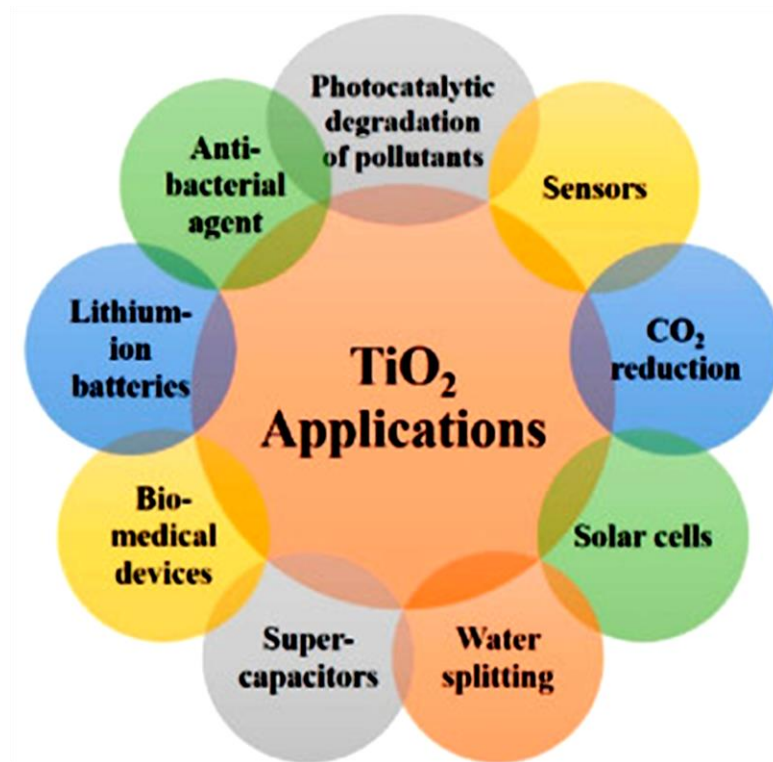


Figure 1. 5. Different applications of TiO_2 nanomaterials [52].

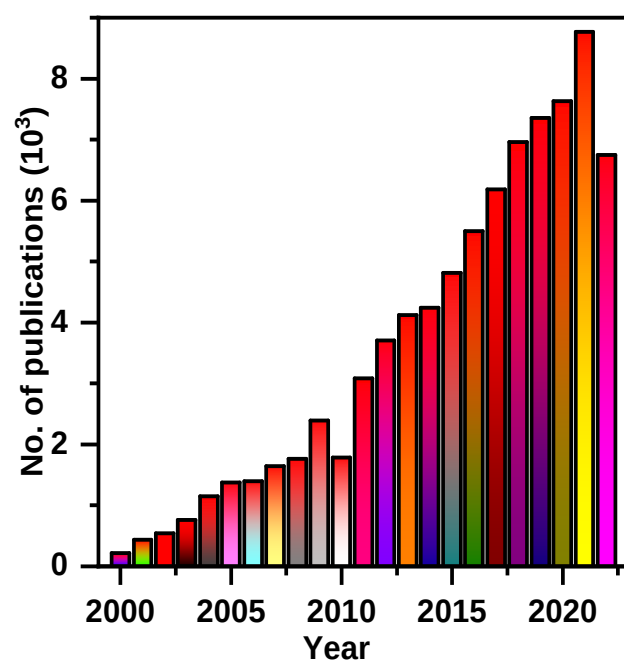


Figure 1. 6. The number of publications per year on photocatalysis.

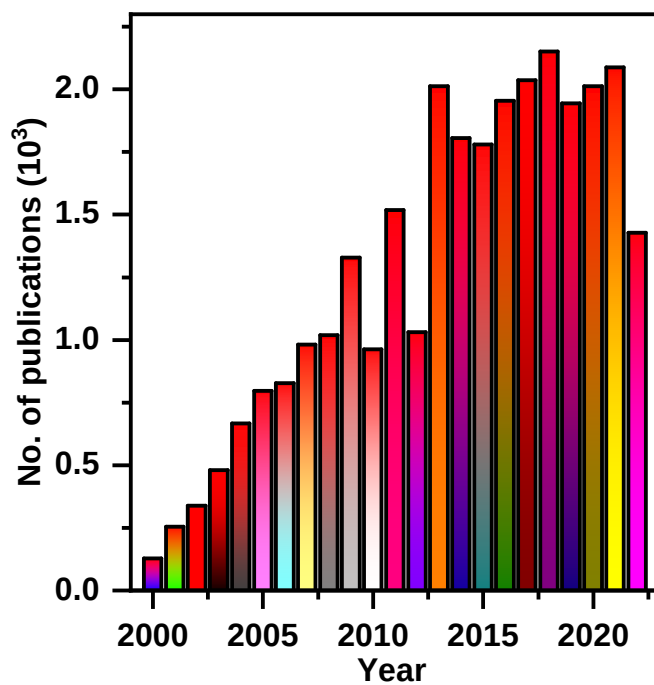
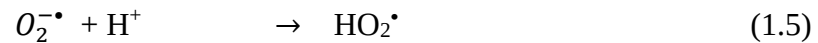
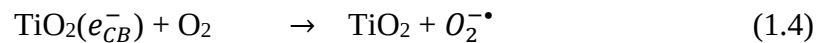
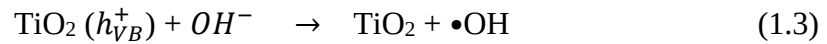
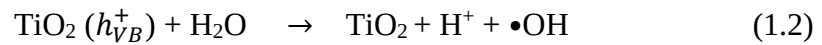
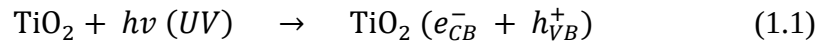


Figure 1. 7. The number of publications per year on photocatalysis by using TiO₂.

1.3 Reactive oxygen species (ROS)

During photocatalysis, many reactive oxygen species (ROS) are usually formed, including the hydroxyl radical ($\bullet\text{OH}$), superoxide anion radical ($\bullet\text{O}_2^-$), singlet oxygen ($^1\text{O}_2$) and hydrogen peroxide (H_2O_2) [59]. Figure 1.8 summarizes the photo-induced processes in a particulate photocatalyst taking place upon absorption of a photon with energy greater than that of the bandgap and indicates the expected photogenerated ROS. The photocatalysis results in redox reactions in which electrons (e^-) and holes (h^+) are generated on the heterogeneous solid surface of the photocatalyst. Several reactive species are then formed with help of these electrons and holes, which actively participate in oxidation and reduction reactions along the photocatalytic processes. Photocatalysis generally starts in the presence of water vapour and an aerobic atmosphere, demonstrating the relevance of both oxygen and water in photocatalysis [59, 60].

Photocatalysis is a multi-step process. For example, the generation of ROS during a photocatalytic process in the presence of TiO_2 is described by the following sequence of steps (equation 1.1-1.5) [7].



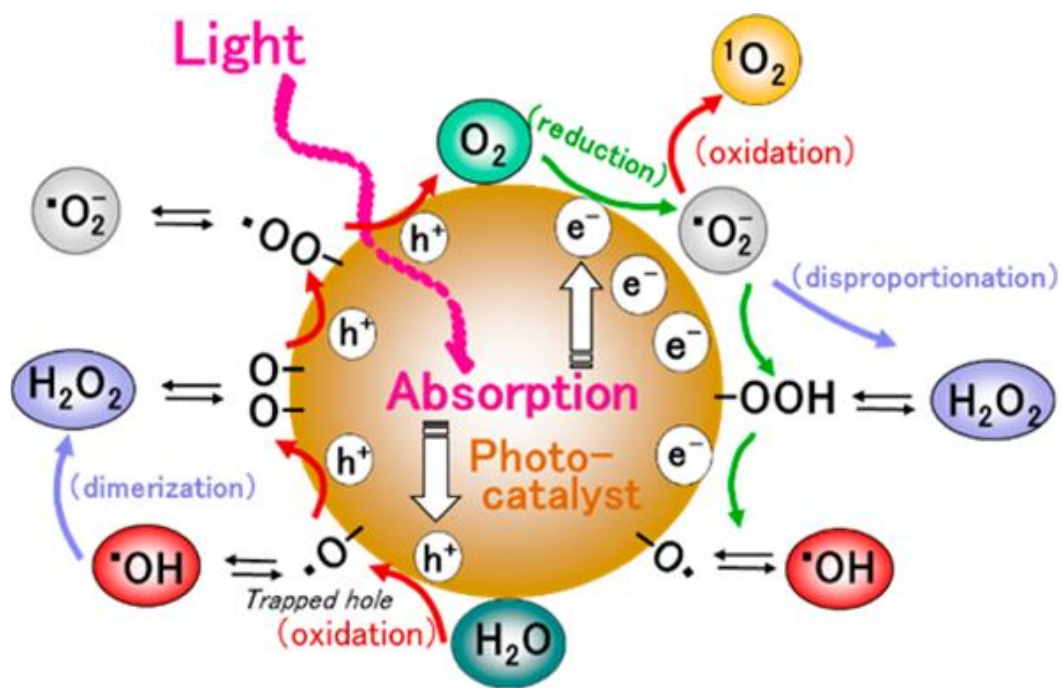


Figure 1. 8. Schematic illustration of the formation of reactive oxygen species during photocatalysis on the surface of a particulate photocatalyst [4].

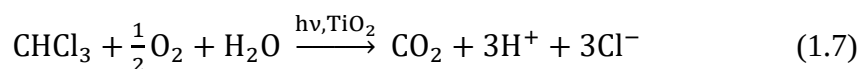
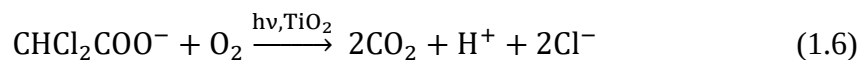
Upon absorption of photons by the photocatalyst, photogenerated holes (h^+) are created on its valence band and photogenerated electrons (e^-) on the conduction band. These holes and electrons diffuse to the surface of the catalyst to start the ROS generation [61]. The species that control the overall efficiency of the photocatalytic processes are still a matter of debate, though it is commonly believed that the hydroxyl radical is the main species responsible for the oxidation of organic compounds during photocatalysis [62]. Recently, eight standard methods have been published by ISO, the world's leading publisher of international standards, and reviewed by Mills et al. [63]. These standard methods focused on; (1) air purification [64-66], (2) water purification [67, 68], (3) self-cleaning surfaces [69], (4) photo sterilization [70], and (5) UV light sources assessments [71]. Three of these standard methods are dedicated to air purification by removing NO [64], acetaldehyde [65], or toluene [66].

For the assessment of the photocatalytic activity towards water purification, the photobleaching of methylene blue (MB) [67] and oxidation of DMSO [68] are used. The use of MB was always questionable, particularly for the slurry reactor due to the high capacity of dark adsorption, dye-self degradation, and photosensitization [64]. Therefore, the MB bleaching test is not recommended for assessing the activity of visible light active-photocatalyst, where a colourless probe is the best. As a better replacement for MB, phenolic compounds were heavily used as substrates for the photocatalytic assessments of water purification [68]. Still, these substrates also suffer from the photosensitization effect due to the surface complexation with some photocatalysts such as TiO_2 [65]. In all of the water purification standard methods [68, 72], samples need to be filtrated before the

analysis either by UV-Vis spectrophotometer, high-performance liquid chromatography (HPLC), or total organic carbon analyzer (TOC).

1.4 Photocatalytic activity assessment

To the best of our knowledge, the only direct test for assessing the photocatalytic activity using a suspension of a photocatalyst is the test developed by Bahnemann's group using (Potentiometric Titration) pH-titration and dichloroacetic acid or chloroform as a model compound [66]. In this test, pH-titration is used to determine the released H^+ -amount from the photocatalytic oxidation of halogenated hydrocarbons in reactions shown in equations 1.6 and 1.7 of dichloroacetic acid and chloroform, respectively.



The usage of a pH sensor in the sticky TiO_2 suspension limits the application and sensitivity of this method, and the titrant NaOH needs to be kept under argon and standardized weekly. Thus, the development of a direct way to assess the photocatalytic activity of photocatalyst suspension remains highly required.

The suspended photocatalytic processes generally start in the water and aerobic atmosphere, demonstrating the relevance of both oxygen and water [59, 60]. Upon photons' absorption by the photocatalyst, electron (e^-)/hole (h^+) pairs are generated in the conduction/valance bands, respectively. The photogenerated holes and electrons are either dissipated as heat or diffused to the surface of the photocatalyst to generate reactive oxygen species (ROS) [73]. The ROSs are primarily in the form of hydroxyl radical ($\cdot OH$),

superoxide anion radical ($\text{O}_2^{\cdot-}$), singlet oxygen ($^1\text{O}_2$), or hydrogen peroxide (H_2O_2) [59]. It is commonly agreed that the photocatalytic degradation of organic pollutants is initiated by a reaction with the hydroxyl radical (either free or trapped) [72]. Thus, the assessment of the activity by the detection of $\cdot\text{OH}$ radical is highly representative.

1.5 Detection of reactive oxygen species using EPR

Although there are several methods for the detection of ROS, the mechanistic details of photocatalysis over TiO_2 are still unknown. Electron paramagnetic resonance (EPR) spectroscopy is a powerful method to detect free radicals [68, 69]. EPR is indeed a powerful and direct method to detect free radicals and reactive oxygen species in biological and chemical environments [68, 69]. EPR spectroscopy with spin trap/probe is one of the best and most simple techniques to detect and quantify ROS [74], and it then appears as a technique of election to tackle the problem under analysis. Detection and characterization of paramagnetic materials are nowadays mostly carried out with help of EPR spectroscopy [75-77], since this spectroscopic technique has several advantages over traditional techniques (in particular chemistry-based methods), thus providing better opportunities to investigate the targeted reactive species and to elucidate the mechanisms of the reactions in which they participate.

Different types of spin traps; 5,5-dimethyl-1-pyrroline N-oxide (DMPO), 5-(diethoxyphosphoryl)-5-methyl-1-pyrroline-N-oxide (DEPMPO), phenyl N-t-butyl nitron (PBN), 2-methyl-2-nitrosopropane (MNP), and N-tert-butylmethanimine N-oxide (EBN) [78-80] and spin probes; 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL), 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO), 1-Oxyl-2,2,5,5-tetramethyl-3-pyrroline-3-methyl)methanethiosulfonate (MTSSL), 3-carbamoyl-(2,2,5,5)-tetra-perdeuteromethyl-3-

pyrrolin-1-yloxy (CTPO), and 2-Ethyl-2,4,4-trimethyl-1,3-oxazolidin-3-yl)oxidanyl (OXANO), [81-84] are using for the detection and quantification of ROS (Fig 1.9 a and b). Commonly, the EPR detects the trapped $\cdot\text{OH}$ radicals using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a conventional spin trapper to form nitroxide radicals [85-87]. Unfortunately, the DMPO is not stable, and it is pretty expensive.

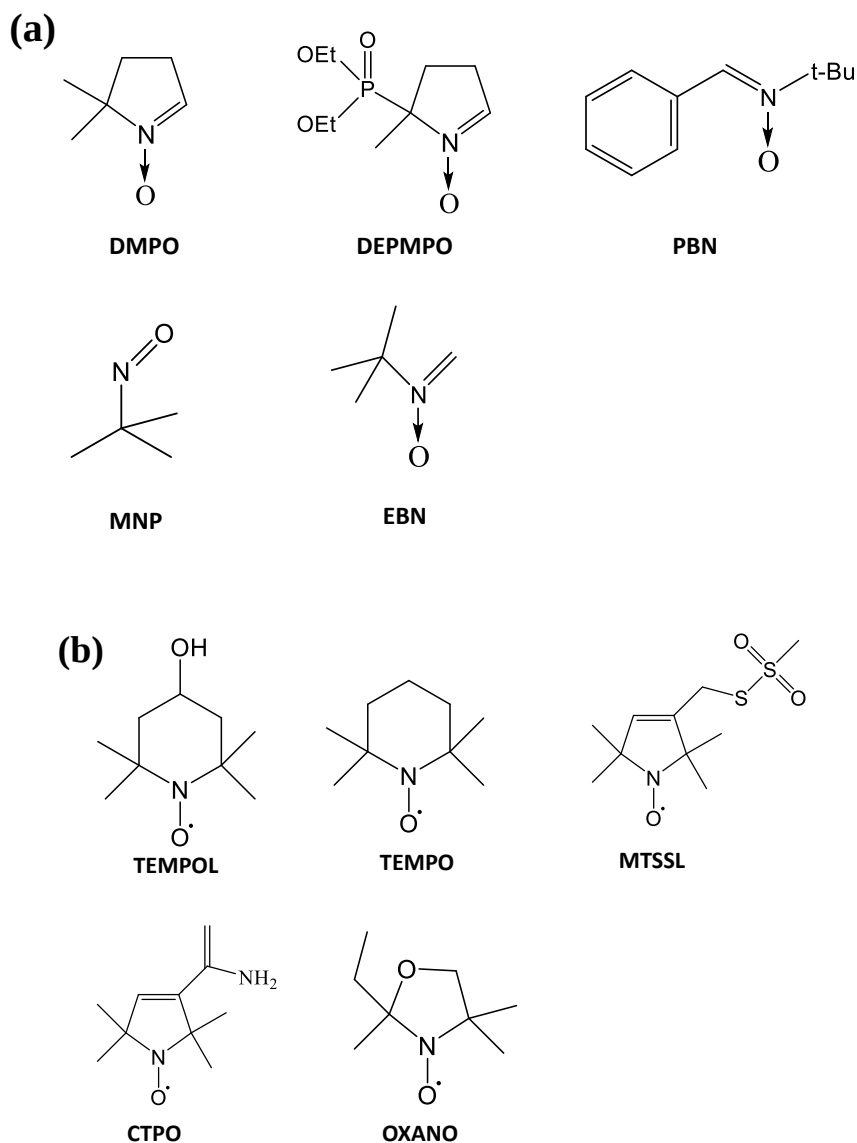


Figure 1. 9. Different types of spin traps (a) and spin probes (b) for the detection of ROS using EPR spectroscopy.

1.6 Significance of TEMPOL for the detection of ROS

2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) is a stable radical and it has been used in many applications in chemistry and biology [9]. Its stability makes it of use for detecting ROS generated in a photocatalytic reaction [88]. The reaction of ROS with TEMPOL shall lead to a decrease of TEMPOL as a function of time that is followed by EPR spectroscopy [89]. This work proposed that most probably the generated $\cdot\text{OH}$ radicals will deactivate TEMPOL molecules as presented in Figure 1.10,

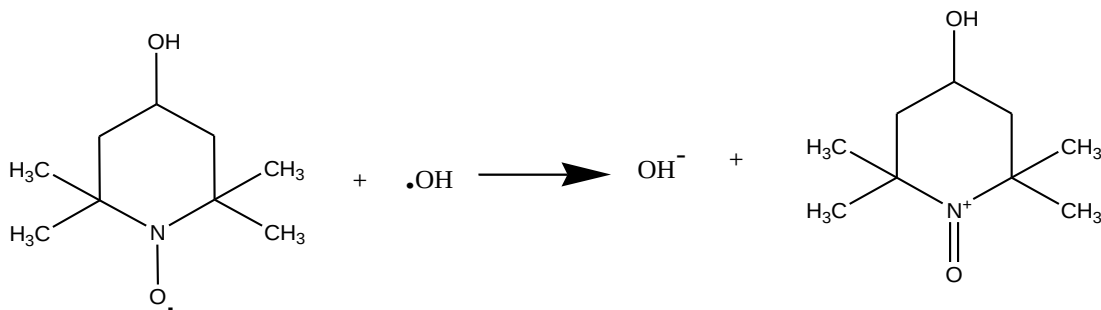


Figure 1. 10. The expected reaction of TEMPOL with $\cdot\text{OH}$ (as a model of ROS species).

1.7 Aims of study

The overall aim of this study is to investigate the kinetics and reaction mechanisms of the generated ROS in photocatalytic processes using EPR spectroscopy. Great attention is paid to exploring an appropriate spin trapper (5,5-dimethyl-1-pyrroline N-oxide (DMPO)) and a much cheaper biocompatible spin probe (4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO radical)) that is ~ 50 times cheaper than DMPO (Sigma Aldrich listed prices), which is an EPR active (stable) radical and can readily react with the photo-catalytically generated ROS, particularly $\cdot\text{OH}$ radicals. In this work, TiO_2 -P25 is considered as a model photocatalyst and then it is extended to investigate other forms of TiO_2 photocatalyst, such as anatase, brookite and rutile. A novel online set-up for the EPR experiments and a new experimental analytical protocol will be developed that includes an integration of the photocatalytic reactor with the EPR instrument as shown in Figure 1.11.

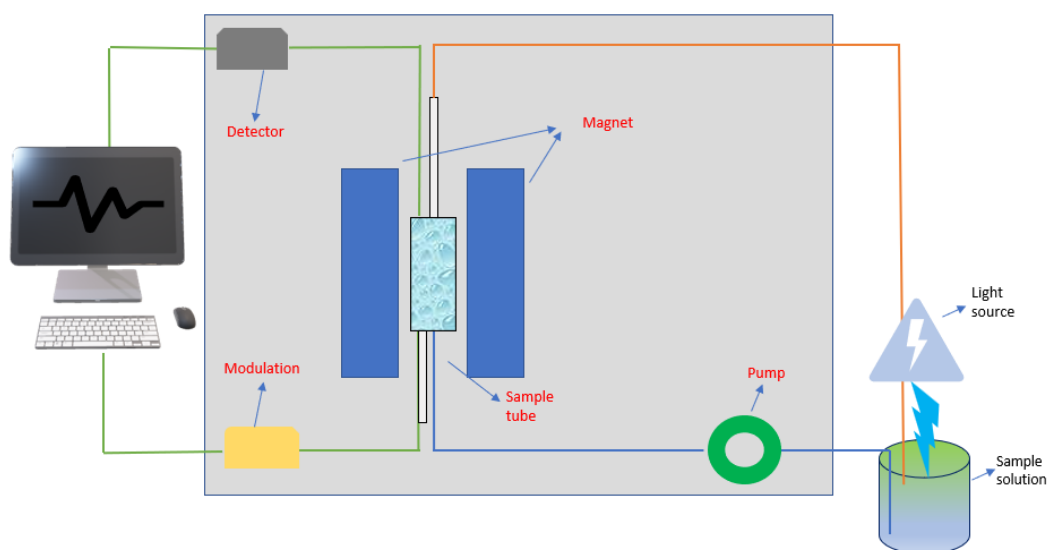


Figure 1. 11. Formation and detection of reactive species in presence of an EPR-propping agent.

The setup shows a simple illustration of a proposed photocatalytic protocol setup that will be used for the kinetics and mechanistic study of reactive oxygen species (ROS) generation using EPR spectroscopy. This will allow the fast detection of the radical species and the optimization of a new method for photocatalytic activity assessment. Different experimental optimization parameters such as light intensity, TEMPOL adsorption, TEMPOL concentration, and TiO₂ loading, on the photocatalytic activity, will be assessed. In turn, this will permit the attainment of a better degree of understanding of the photocatalytic processes and mechanistic study *via* the direct detection and identification of the generated ROS species in the presence of a TiO₂ photocatalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Types of photocatalysts

Photocatalysis is considered an important green technology in different application fields [18, 19]. Several types of photocatalysts (also known as semi-conductors), e.g. TiO_2 [20, 21], g- C_3N_4 [22-24], SnO_2 [25, 26], Bi_2WO_6 [27], ZnO [28], and WO_3 [29] etc., have been investigated for oxidation and reduction reaction in photocatalysis. The bandgap energy of these photocatalysts are given in Figure 2.1 [90].

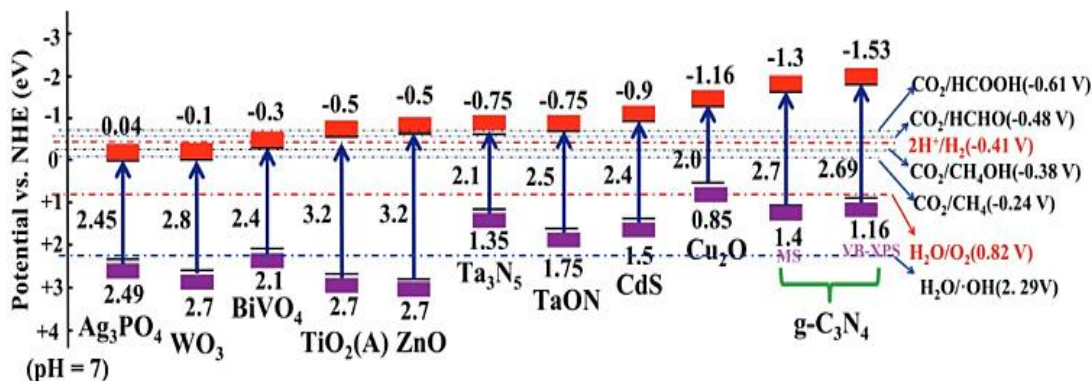


Figure 2. 1. Different photocatalysts (semi-conductors) with bandgap values [90].

Of all these semi-conductors, titania is the most used photocatalyst in the field of photocatalysis. TiO_2 has many merits, e.g., low cost, biocompatibility, resistance against photo-corrosion, and chemical stability, which make it a good candidate for practical applications in photocatalysis [20, 21, 43-45].

2.2 Synthesis and morphological study of TiO₂ photocatalysts

TiO₂ is a well-known photocatalyst for the degradation of organic pollutants in water under UV illumination [40-42]. With its bandgap of about 3.2 eV (anatase phase), it absorbs approximately 5% of the solar spectrum. TiO₂ is commonly present in three phases (i.e. anatase, rutile, and brookite). Generally, anatase is more thermodynamically stable as compared to rutile and brookite, and thus it is commonly encountered during the synthesis of TiO₂ nanomaterials [30-32]. Due to this reason, TiO₂ in the anatase form has been extensively investigated in photocatalytic applications [33, 34]. The specific surface area and the value of enthalpy of all the forms of TiO₂ are given in Figure 2.2. The bold lines in this figure show the energetically stable form of titania as a function of surface area. Different methods for the synthesis of different TiO₂ forms, some of the synthesis methods with structural morphology are given below:

2.2.1 Synthesized single-phase brookite

In 2020, Zou et al., synthesized single-phase brookite through a controllable hydrothermal method by using titanium tetrachloride (TiCl₄), urea, and sodium lactate as a starting material of the reaction. All the characteristics results proved the synthesis of single-phase brookite. They claimed that the amount of urea and sodium lactate affects the morphology of the reaction products. The concluded results of this study proved that a higher concentration of urea and sodium lactate changes the morphology of TiO₂ brookite from spherical to rod-like (Figure 2.3) [91].

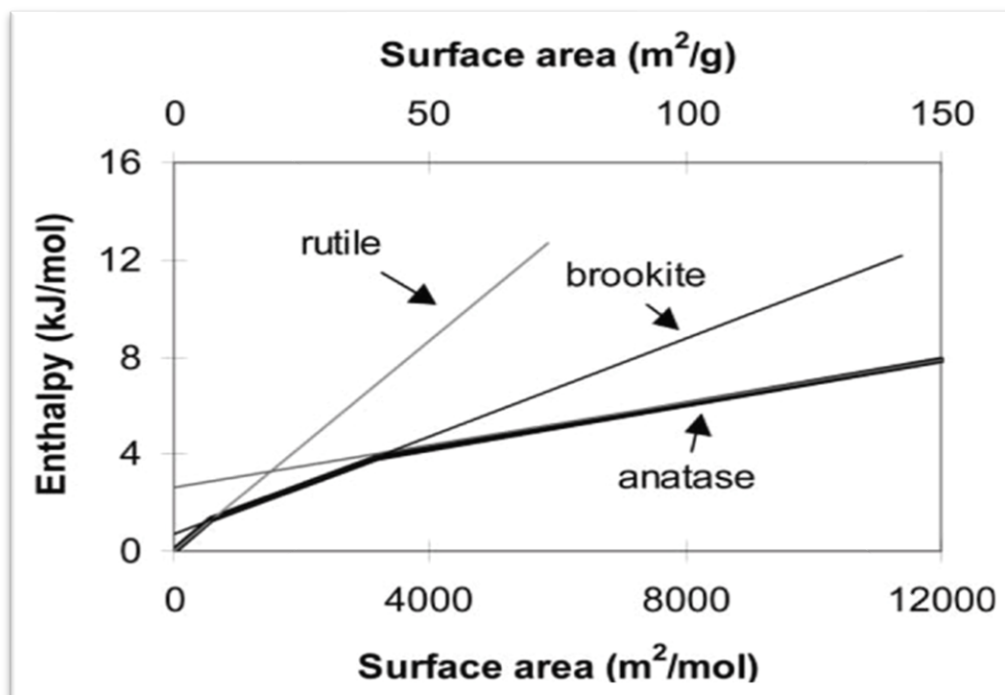


Figure 2. 2. Surface area and enthalpy value of anatase, brookite and rutile [92].

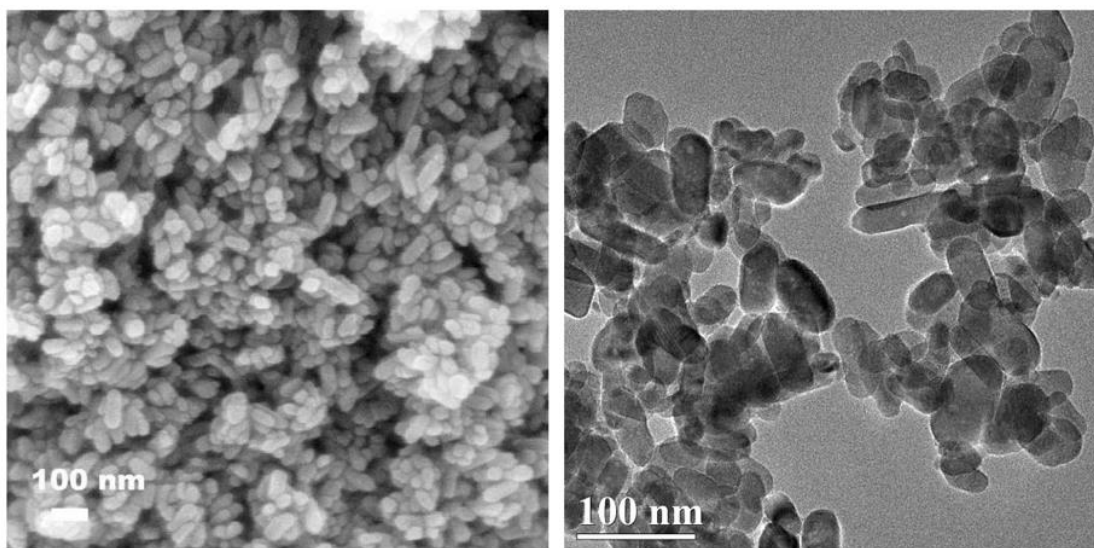


Figure 2. 3. SEM and TEM images of prepared single-phase TiO_2 brookite through the hydrothermal method [91].

2.2.2 Synthesized high-quality TiO₂ brookite rods

In 2012, Kandiel and his coworker prepared high-quality TiO₂ brookite rods by hydrothermal method. They used titanium bis (ammonium lactate) dihydroxide and urea for the synthesis and brookite and other titania forms. XRD, Raman, and morphological results proved the synthesis of high-quality brookite nanorods and form of TiO₂ form (Figure 2.4). They used pure brookite, pure anatase, and a mixture of anatase and brookite for photocatalytic hydrogen evolution activity [93].

2.2.3 Synthesized rutile-mixed anatase nanosheets

Song et al (2016) prepared a photocatalyst called rutile-mixed anatase nanosheets with 001 dominant facets from a hydrothermal method by utilizing Ti(OC₂H₉)₄, NH₄F, HF and water-mixed solution. The crystal morphology and chemical composition were confirmed by different characterization techniques. The experimental results proved that NH₄F not only change the chemical environment, it also transforms the chemical structure from anatase to rutile. Compared with regular nanosheets of anatase and commercial P25 TiO₂, the present form of photocatalysts showed excellent improvement in photocatalytic activity. According to the mechanism, the heterostructure formation of anatase/rutile improved the separation of electrons and holes which helped to improve the photocatalytic activity (Figure 2.5) [94].

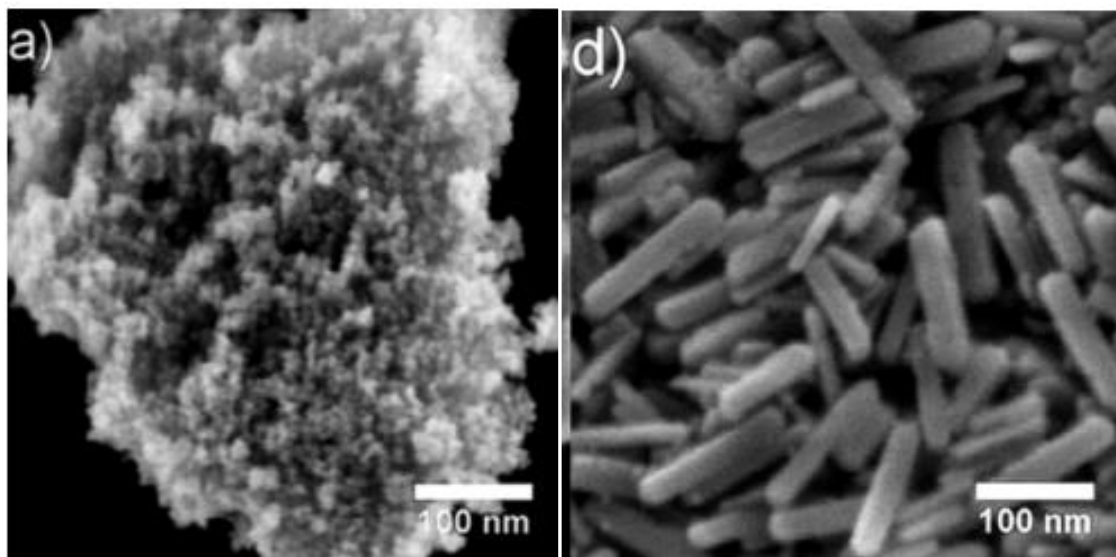


Figure 2. 4. FE-SEM image of TiO₂anatase (a) and brookite (d) prepared by hydrothermal method [93].

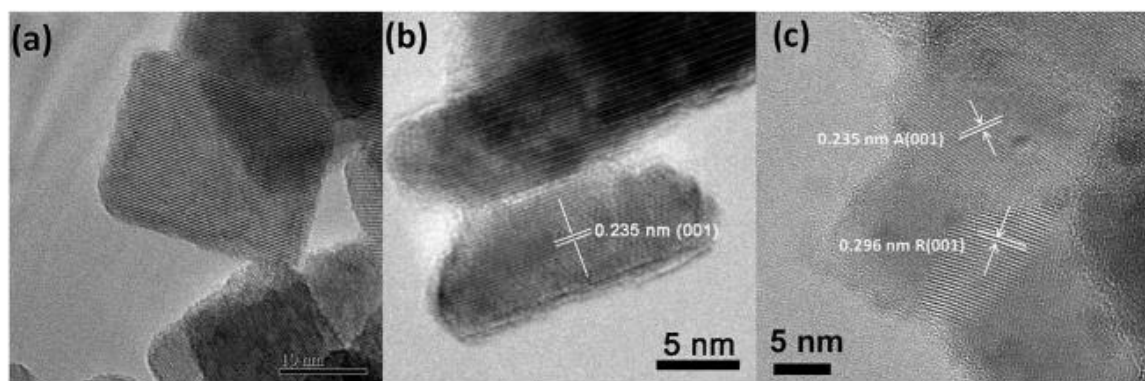


Figure 2. 5. TEM image and HRTEM lattice images of anatase (a and b) and rutile/anatase (c) heterostructures of prepared samples [94].

2.3 Used of EPR in TiO₂ photocatalysis

Different types of catalysts were analyzed by using EPR spectroscopy, but TiO₂ catalysts are the highest studied photocatalyst. Figure 2.6. shows the numbers of published articles in the field of photocatalysis using different types of photocatalysts with EPR spectroscopy, among of them TiO₂ is the most investigated one using EPR spectroscopy. Few research articles have been explained to understand the study of EPR for the analysis of titania paramagnetic form. Different modified forms of TiO₂ also explained the paramagnetic behavior of the TiO₂ photocatalyst.

In 2018, Polliotto and coworkers described the importance of EPR spectroscopy to investigate the fundamental aspects of heterogeneous photocatalysis. They described the behavior of different photoactive oxides with different bandgaps, which show holes and electron stabilization. EPR was demonstrated to allow detailed investigations on the nature of the different stabilization sites for the electrons and holes trapping in terms of O⁻ center's formation (Figure 2.7) [95].

Bouhadoun *et al.* (2017) studied photocatalysis on modified titanium dioxide with gold (Au-TiO₂) and nitrogen (N-TiO₂), which were produced by pyrolysis (Figure 2.8). They have investigated the photodecomposition of acids. They showed that the photocatalytic activity increased in the presence of gold, while it decreases in the presence of nitrogen. They also identified the intermediate products with the help of chromatographic techniques and EPR. The EPR results also confirmed the participation in the studied processes of NO²⁻ paramagnetic center's and also of two novel N-centered paramagnetic species [96].

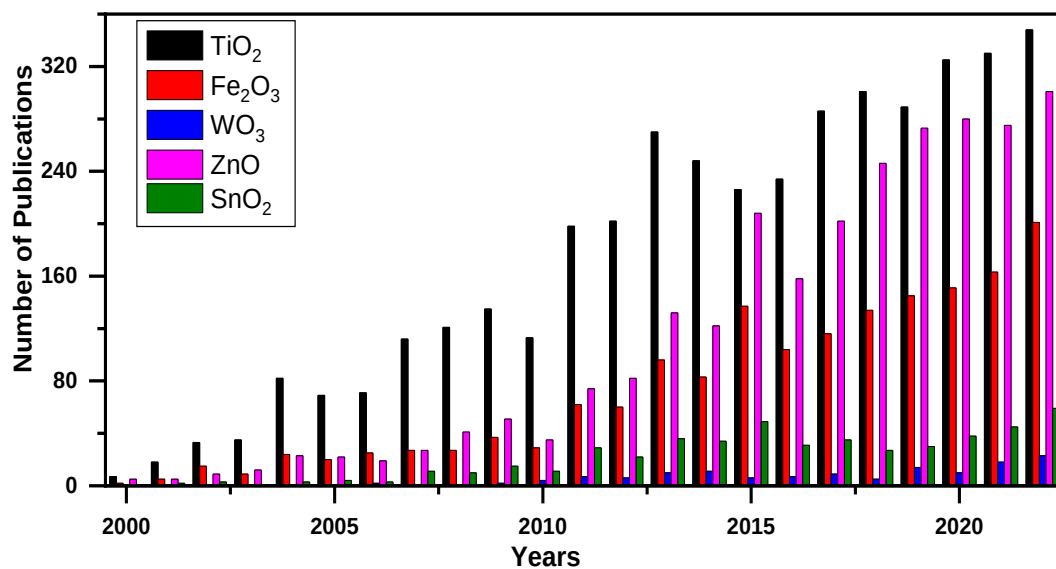


Figure 2. 6. The number of published articles with different types of photocatalysts using EPR spectroscopy.

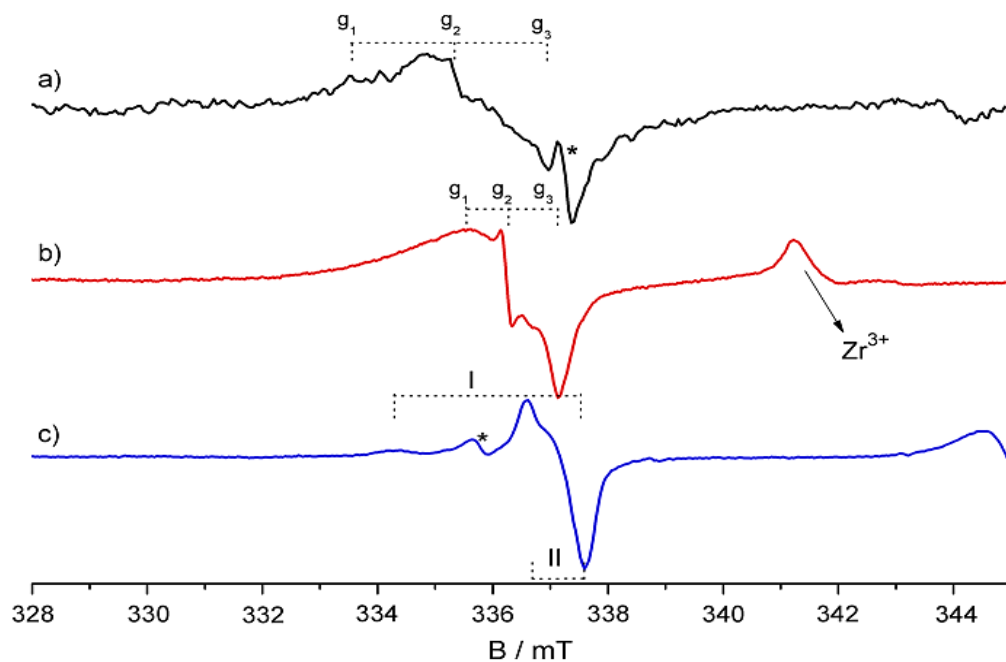


Figure 2. 7. Normalized continuous wave EPR spectra of hole centers of different heterogeneous photocatalysts [95].

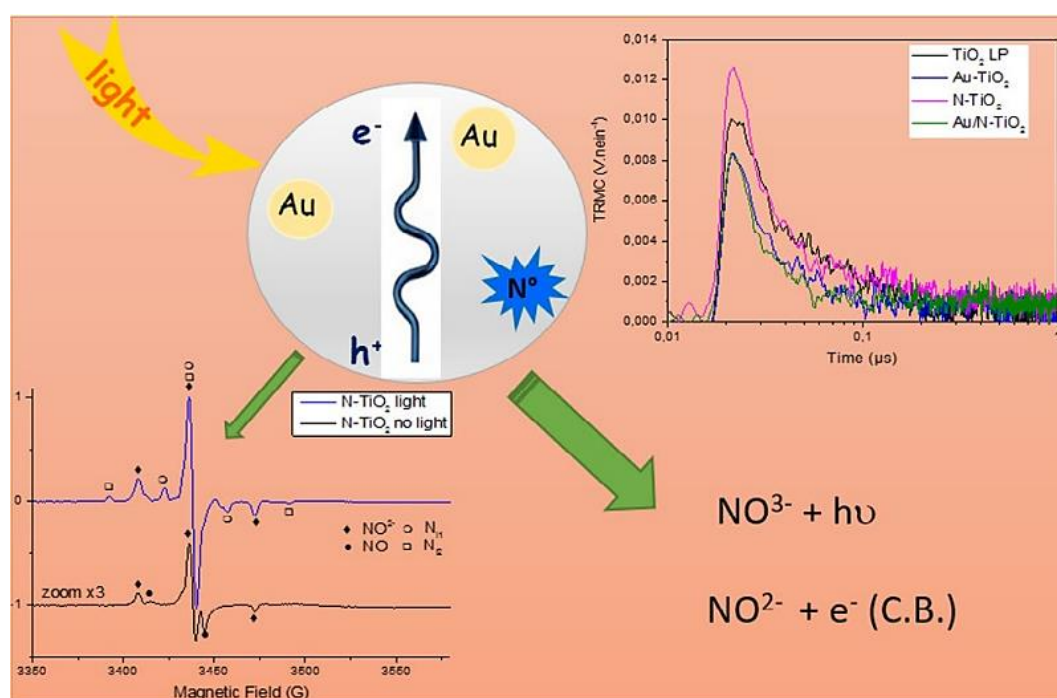


Figure 2. 8. Titania-based nanoparticles and their photocatalytic degradation efficiency for carboxylic acid [96].

Brezova and his co-workers prepared anatase and rutile nanomaterials by the hydrolysis of TiCl_4 using ordinary or ^{17}O enriched water at a different temperature under a vacuum (Figure 2.9). The samples were investigated by EPR spectroscopy under UV light in a 100-160 temperature range. The experimental spectra of anatase revealed the presence of Ti(III) and two kinds of oxygen centers' paramagnetic species.

The peak broadening in the EPR spectra of anatase confirmed the presence of ^{17}O in the crystal lattice. Due to thermal treatment anatase sample produced a variety of paramagnetic signals of Ti(III). The synthesized anatase and rutile produced OH radicals upon the excitation of UV irradiations in the aerated aqueous suspension. The hydroxyl radicals were monitored by the EPR spin-trapping technique by utilizing 5, 5-dimethyl-1-pyrroline, N-oxide (DMPO) as a spin-trapping agent [97].

It is known that paramagnetic species are involved in the photocatalytic reactions that occur during heterogeneous catalysis at the solid-gas phase interface. Morra *et al.* have obtained information about the paramagnetic species formed within the coordination sphere of surface transition metal ions by using EPR (Figure 2.10) [98].

In 2015, Antonopoulou *et al.* investigated the photolytic and photocatalytic degradation mechanisms of *N, N*-diethyl-meta-toluamide (DEET) in the presence of different organic compounds also using EPR spectroscopy. Spin trapping EPR measurements in the presence of TiO_2 showed that the nature of the dissolved organic materials affected the generation of the hydroxyl radical, and demonstrated also that the hydroxyl-DEET radical species that are formed in the initial steps of the photodegradation reaction (Figure 2.11) [99].

Rhydderch and Hwe (in 2015) have investigated, using *in situ* EPR at room temperature, the relevant paramagnetic species that are produced when titania is UV-

irradiated in the presence of reactants that are used in photocatalytic alkylation, like maleimide with *t*-butyl carboxylic or phenoxy acetic acids. It was shown that the phenoxy methyl radical is formed from phenoxy acetic acid, in the presence of maleimide (Figure 2.12a) [100]. Li *et al.* (2015) [21] studied the efficiency of different forms of titanium dioxide in the photocatalysis process for water splitting.

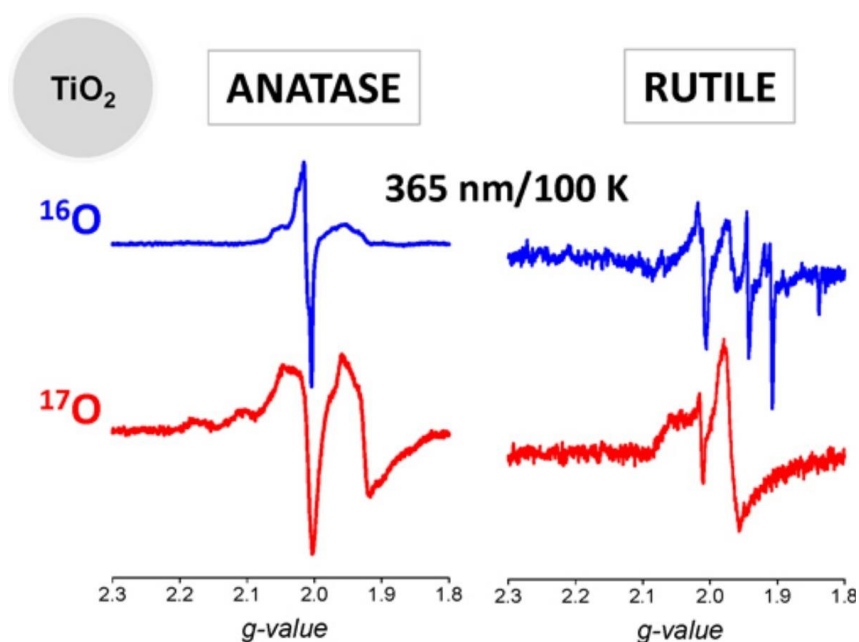


Figure 2. 9. Recorded EPR spectra of TiO₂ anatase and rutile samples synthesized using H₂¹⁷O or ordinary water with 365nm UV irradiation measured at 100k temperature [97].

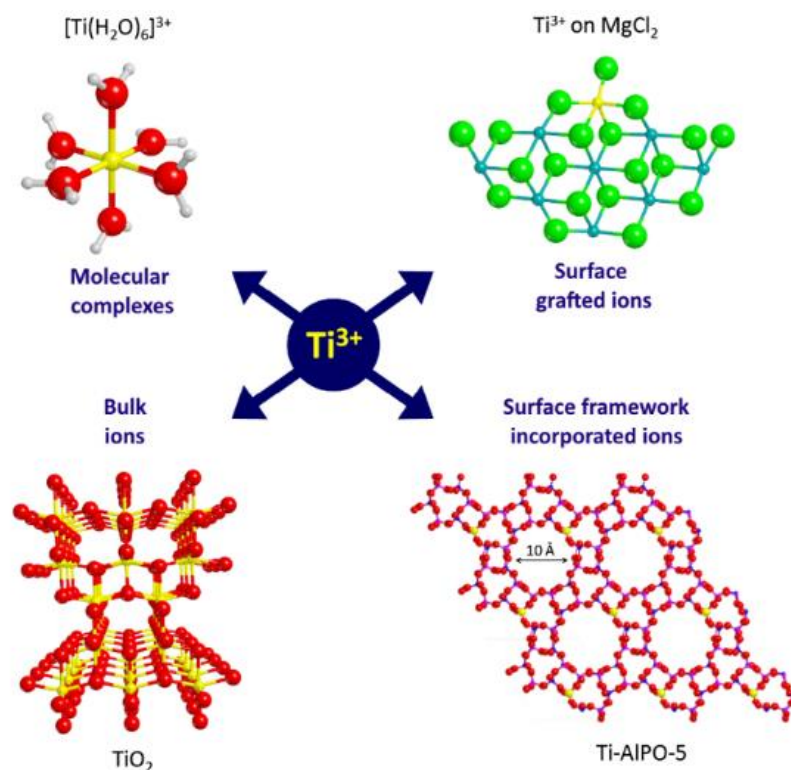


Figure 2. 10. Titania paramagnetic species (Ti^{3+}) formed within the coordination sphere of surface transition metal ions [98].

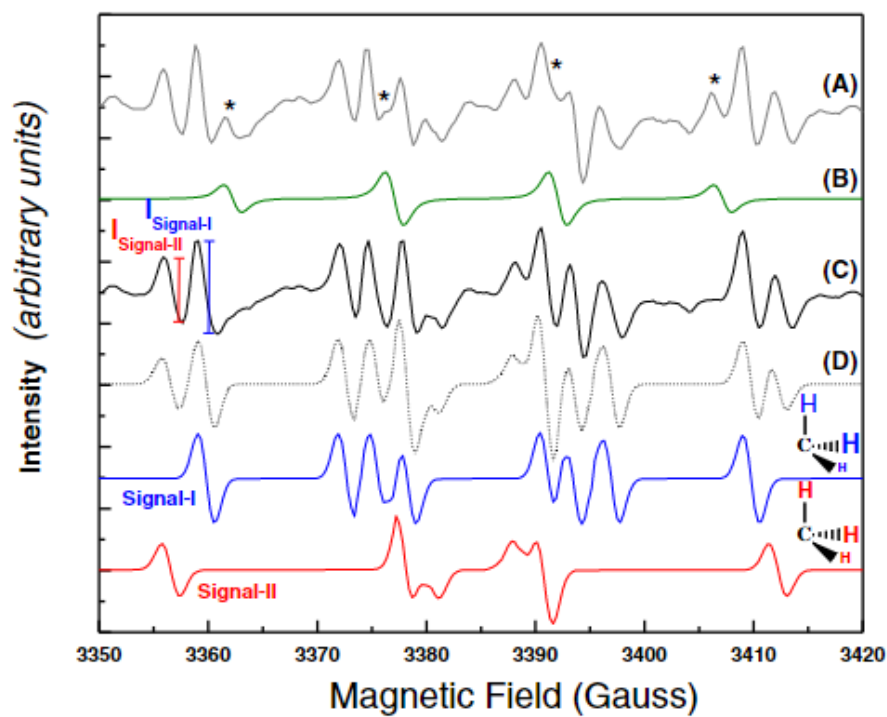


Figure 2. 11. EPR spectrum of the photolytic and photocatalytic degradation of *N*, *N*-diethyl-*m*-toluamide (DEET) in the presence of TiO_2 [99].

EPR was used to investigate the reaction kinetics. The authors observed that the kinetics differ among the different phases of titania investigated and concluded that this behaviour should be ascribed to the formation of different intermediates (Figure 2.12b) [101].

In 2015, Antonopoulou *et al.* investigated the photolytic and photocatalytic degradation mechanisms of *N, N*-diethyl-meta-toluamide (DEET) in the presence of different organic compounds also using EPR spectroscopy. Spin trapping EPR measurements in the presence of TiO₂ showed that the nature of the dissolved organic materials affected the generation of the hydroxyl radical, and demonstrated also that the hydroxyl-DEET radical species that are formed in the initial steps of the photodegradation reaction (Figure 2.11) [99].

Zhao *et al.* (2015) studied the effect of structural defects on the electrochemical properties and photocatalytic properties of TiO₂. They synthesized the TiO₂ by using hydrothermal and post-synthesis chemical reduction processes to improve the oxygen defect implantation. Led was used to form uniformly distributed TiO₂ nanorods. EPR and X-ray photoelectron spectroscopy techniques were used to confirm the presence of oxygen defects (Figure 2.14). The photocatalytic properties of TiO₂ with different types of embedded oxygen defects were investigated, and the results showed that, after the modification, the material exhibits greater photocatalytic activity [102].

Macdonald *et al.* (2012) studied the in situ EPR spectroscopy to analyze the paramagnetic products formed when TiO₂ photocatalyst is irradiated with UV-vis light (Figure 2.15). In the absence of reactants trapped holes (O⁻) and trapped electrons (Ti⁺³) produced a very weak EPR signal. By increasing photon flux and stopping the irradiation the intensities of trapped holes and electrons increase dramatically. On restoring the irradiation, the process is completely reversible.

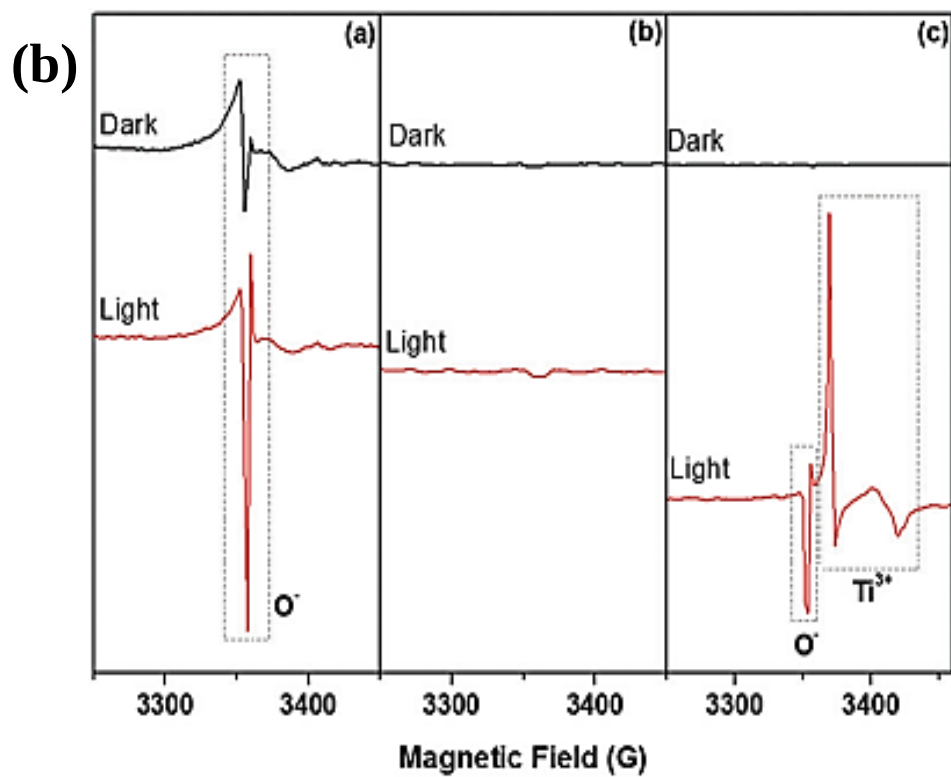
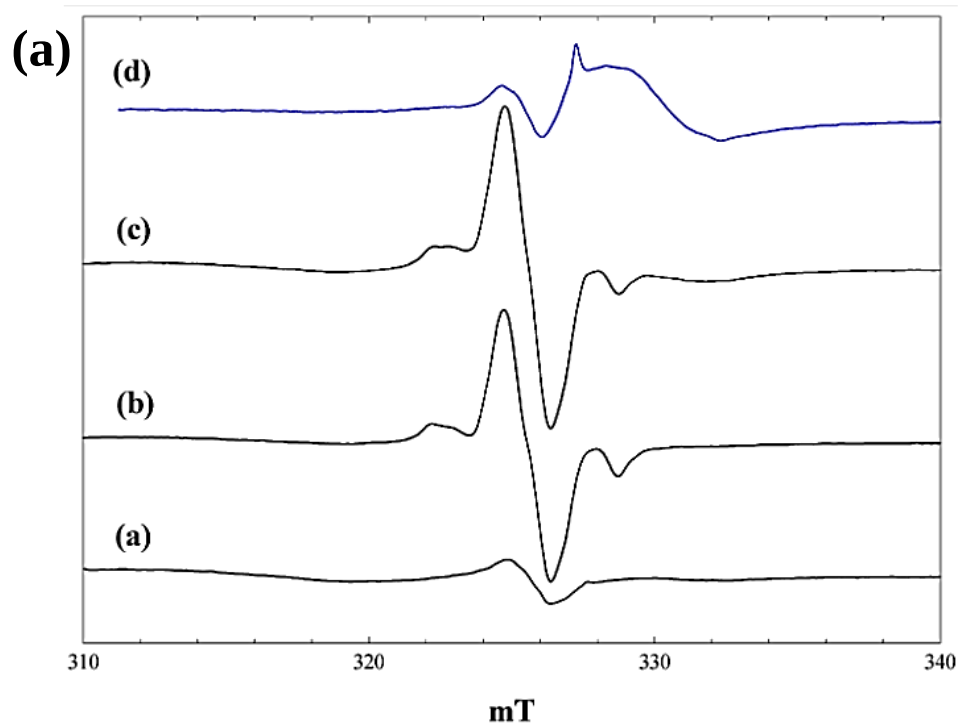


Figure 2. 12. EPR spectra of TiO_2 -P25 in an equimolar ratio of phenoxy acetic acid with maleimide in acetonitrile [100] (a), and photocatalytic oxidation of water on different TiO_2 phases [101] (b).

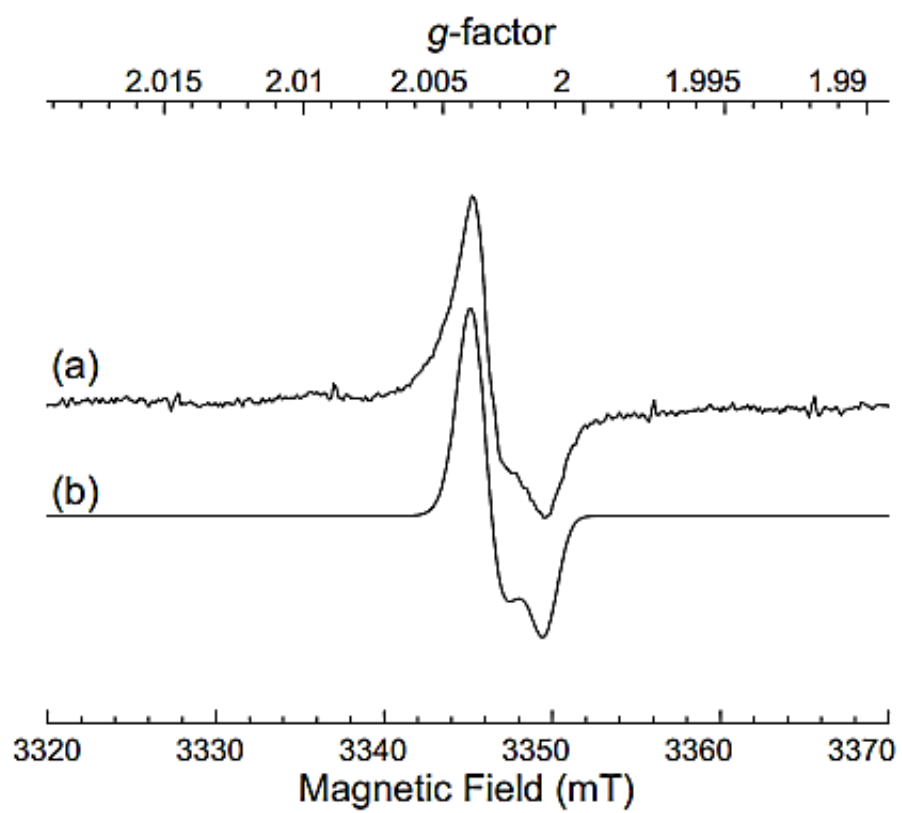


Figure 2. 13. CW-EPR spectrum of plasmon-enhanced photocatalyst (Au-P90) [103].

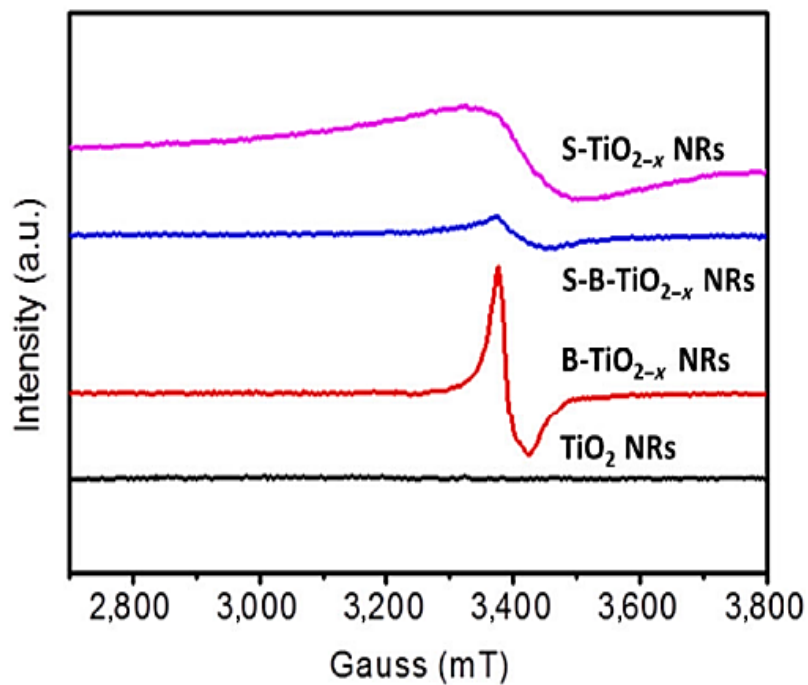


Figure 2. 14. EPR spectra of the TiO₂ sample for the investigation of the valence state and the presence of Ti³⁺ [104].

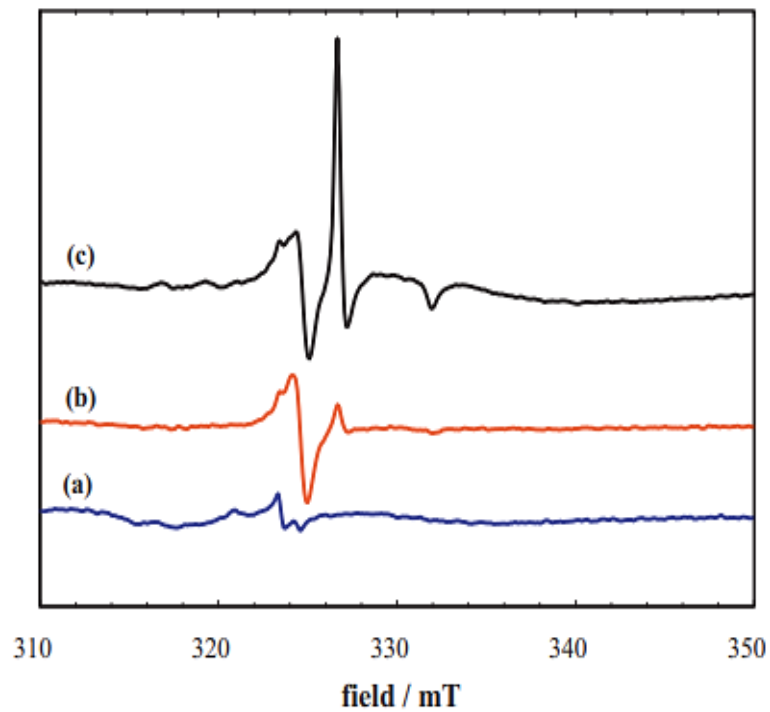


Figure 2. 15. Recorded EPR spectra of rutile (a), anatase-PC500 (b), and anatase-P25 (c) with broad-band irradiation during irradiation [105].

The obtained EPR spectra of TiO₂ samples at low temperature gives significant values of trapped holes and electrons, which very slowly decay in the dark [105].

Dimitrijevic et al (2009) modified the nanoparticles of TiO₂ with dopamine to improve the catalytic activity due to the improved ability of charge separation (Figure 2.16). The formation of reactive oxygen species upon the illumination of modified TiO₂ was studied by using the EPR spin trap and radical-induced fluorescence method. The holes localized on the surface of dopamine suppresses the oxidation of adsorbed H₂O molecule on the surface of the nanoparticles. Furthermore, dopamine does not affect the electronic properties of photogenerated e⁻ and their reaction with dissolved O₂ to produce O₂⁻. O₂⁻ further generates ¹O₂ through a dismutation reaction [89].

2.4 Photocatalytic activity assessment of photocatalysts

Different methods and photocatalysts have been used for the photocatalytic activity assessment. Some of the detailed research works are explained below to understand the phenomena of photocatalytic activity analyses.

Khannyra et al., (2022) synthesized TiO₂/SiO₂ mesoporous materials and used them for outdoor applications (Figure 2.17). They dispersed these synthesized materials on the surface of concrete and analyzed the capability for self-cleaning and air depolluting. The results proved that the photocatalytic activity of the material was increased by increasing the amount of TiO₂. Thus, by the irradiation of UVA light, after the first 60 minutes, the photocatalytic activity of a high amount of TiO₂ catalyst had removed the maximum amount of methylene blue (MB).

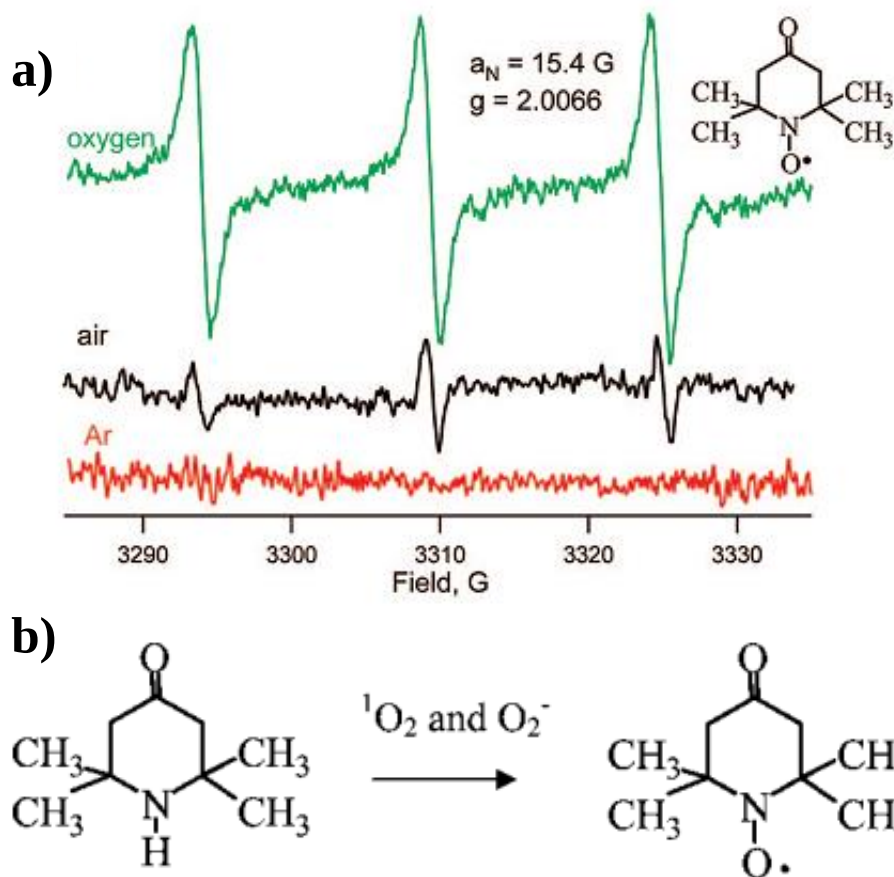


Figure 2. 16. (a) EPR spectra of radical formed after 3 mint light irradiations of 0.1M DA/TiO₂ and 20mM TEMP aqueous solution with O₂ (red), air (black), and Ar (red). (b) the reaction of TEMP with ¹O₂ and the formation of stable nitroxide-type radicals [89].

The surface area plays an important role in the removal of MB, the higher surface area removal the higher amount of MB. They proved that the photocatalytic activity of $\text{TiO}_2/\text{SiO}_2$ remains unchanged after 4 months of dispersing the catalyst on the surface of the concrete. After this outdoor durability test, photocatalytic activity confirms the long-time stability of this synthesized catalyst [106].

In 2016 Driel and his coworkers reports a new method for the photocatalytic activity assessment of TiO_2 photocatalyst (Figure 2.18). They studied the photocatalytic degradation of organic dye (acid blue 9) in TiO_2 present water solution by using UV-vis spectrophotometry. The dye solution loses its concentration with time by the illumination of UVA light. The main idea of this research is the availability of an easy quick test for the qualitative and quantitative photocatalytic activity assessment with TiO_2 photocatalyst [107].

Li et al., (2014) synthesized the different types of brookite and anatase at variable temperatures and confirmed the structural characteristics by XRD and Raman spectroscopy. This synthesized brookite and anatase were used for the oxidation of phenol in an aerated water solution (Figure 2.19). Results proved that the photocatalytic activity of the brookite is higher than anatase at lower and higher temperatures respectively. For the reduction of chromate, anatase activity is higher than the brookite. In the presence of the excess amount of phenol, the O_2 reduction to H_2O_2 , the BET surface area of the brookite is higher than the anatase which is like the oxidation of phenol at the aerated aqueous solution. The overall results proved that brookite has a stronger affinity to oxygen (O_2) in H_2O as compared to anatase [47].

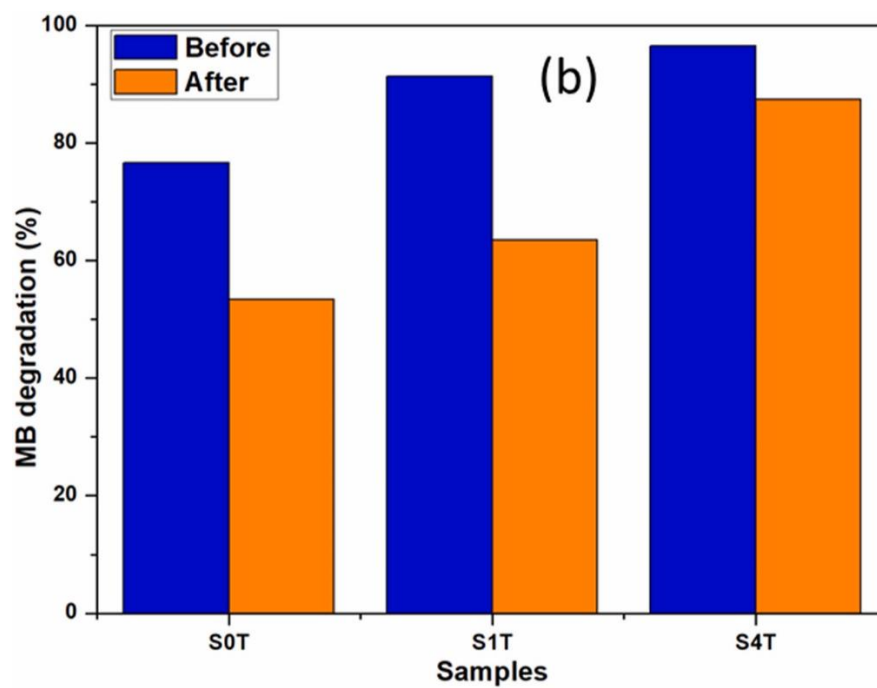
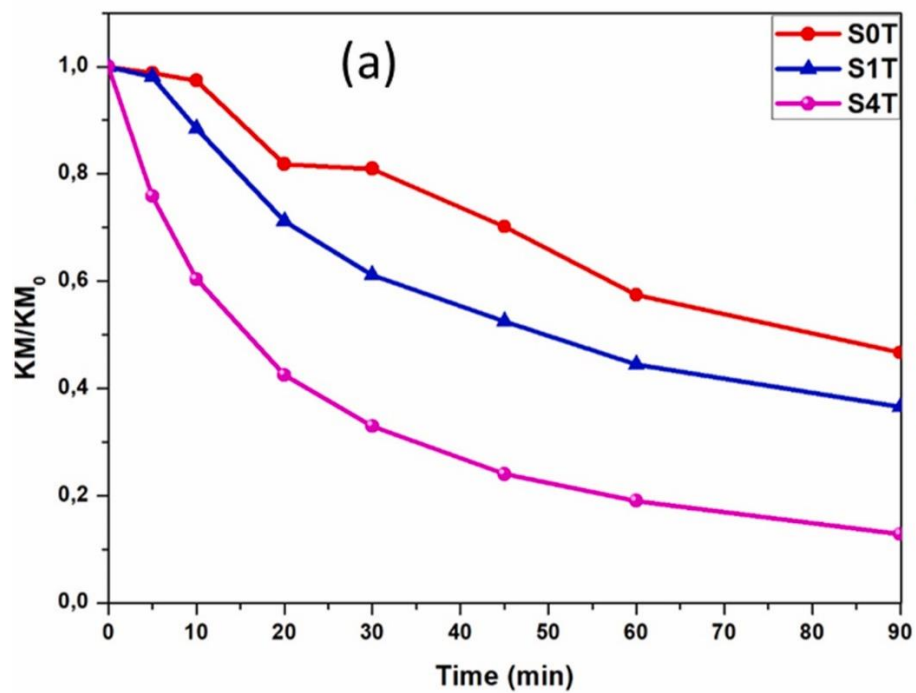


Figure 2. 17. (a) Analysis of MB photodegradation after four months, (b) comparison between before and after the exposure of experiment conditions for the removal of MB.

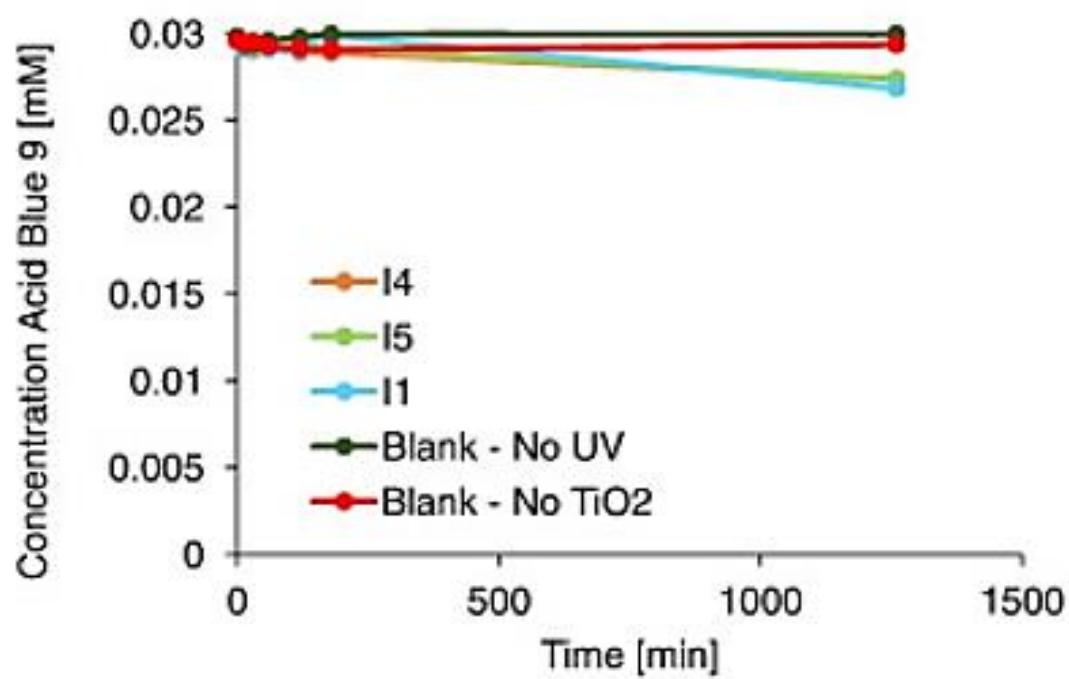


Figure 2. 18. Photocatalytic activity assessment test, degradation of acid blue 6 dye over time.

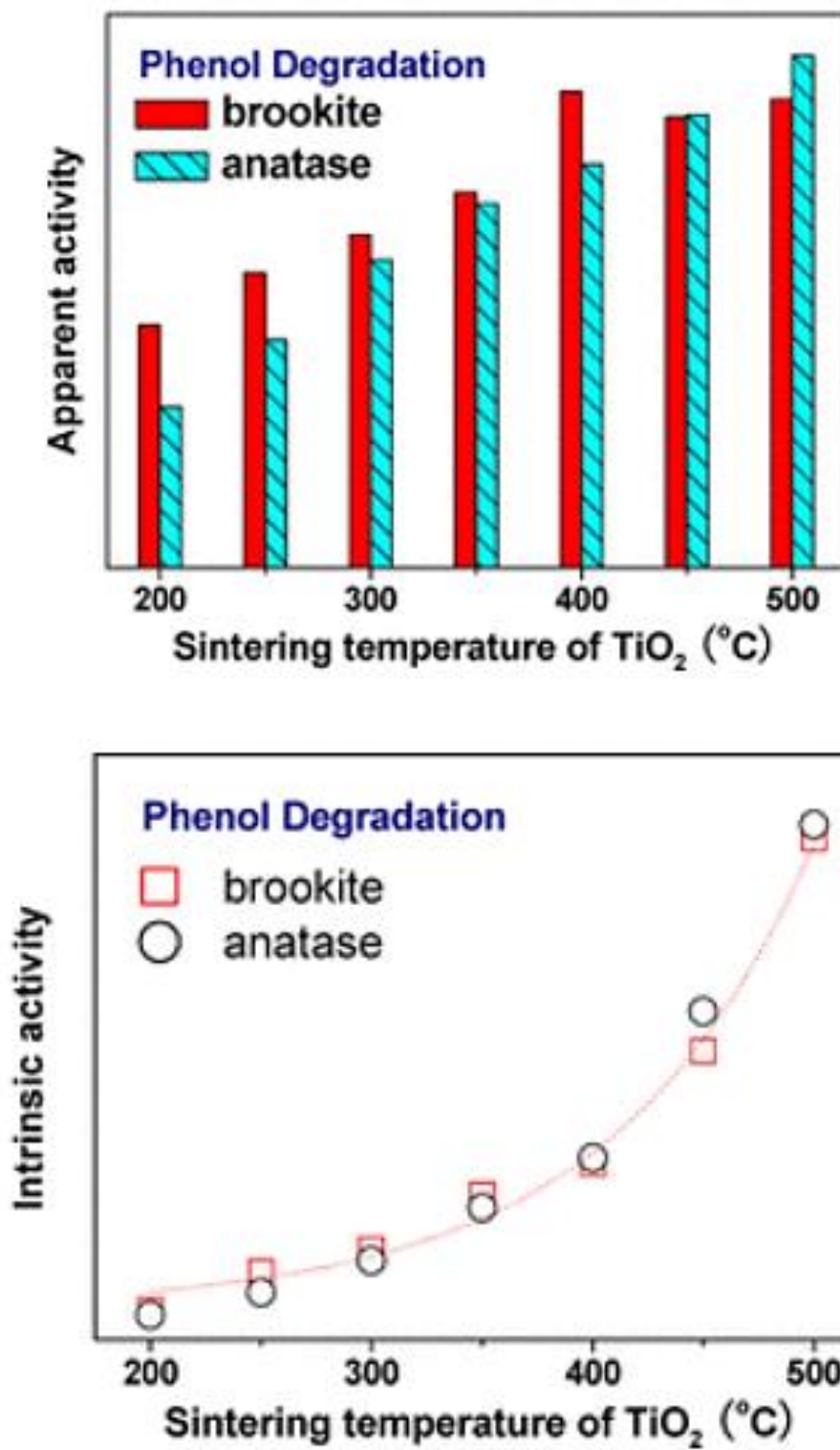


Figure 2. 19. Photocatalytic activity assessment of brookite and anatase at different synthesized temperatures for phenol degradation.

CHAPTER 3

EXPERIMENTAL

In this chapter, firstly the materials used for the study of the photocatalytic test are going to explain. After that, details about the EPR-integrated photocatalytic setup and photocatalytic test are explained. After the mechanistic study, the final products after the deactivation of the reactant were analyzed through NMR characterization. Lastly, the photocatalytic activity of the catalyst was analyzed through different forms of prepared TiO_2 nanomaterials.

3.1 Materials

TiO_2 P25 (which contains a 3:1 ratio of anatase of rutile) was obtained from Evonik, Germany and 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO), titanium (IV) bis (ammonium lactato) dihydroxide (TALH) 50% aqueous precursor, sodium lactate (50% in water), and urea were purchased from Sigma-Aldrich as used same as received (Figure 3.1). Double-distilled water (resistivity $\sim 18.2 \text{ M}\Omega \text{ cm}$) was used during all synthesis and experiments.

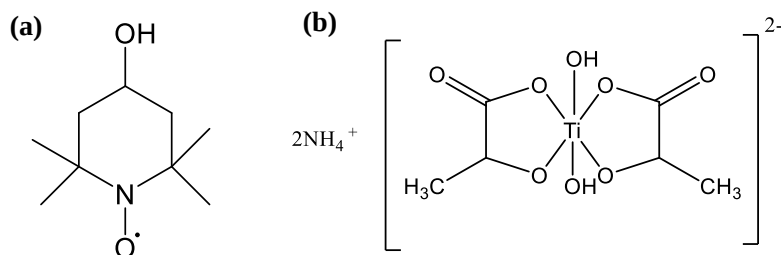


Figure 3. 1. (a) Chemical structure of 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO) and (b) titanium (IV) bis (ammonium lactato) dihydroxide (TALH).

3.2 Synthesis of nanoparticles

The hydrothermal synthesis experiments for TiO_2 brookite, anatase, and rutile were carried out in a 100 mL Teflon cup enclosed in stainless steel autoclave [93]. For the synthesis of pure brookite TiO_2 , 5.0 mL of titanium (IV) bis (ammonium lactato) dihydroxide (TALH) 50% aqueous precursor and 5.0 ml sodium lactate were mixed with urea aqueous solution and the total volume was then adjusted to 50 mL. The final urea concentration was 6.0 M urea. The resulting solution was transferred into the Teflon-lined autoclave. Then the autoclave was tightly closed and put into the oven at 180 °C for 24 hours. After that time, the autoclave was naturally cooled at room temperature. The TiO_2 nanomaterials were centrifuged and washed twice with double distilled water and one time with ethanol and dried in the oven overnight at 70 °C. The complete dried solid was crushed very well with agate mortar and then calcined at 500 °C for 2h to remove the organic compounds adsorbed on the surface and to enhance the crystallinity. For the synthesis of pure anatase, the same procedure for the synthesis of brookite was employed, except that the urea concentrations were adjusted to 0.1M and the TALH precursor was used without the addition of sodium lactate. The rutile was synthesized by the calcination of pure anatase at 800 °C for 2h [108-110]. The scheme of synthesis is given in Figure 3.2.

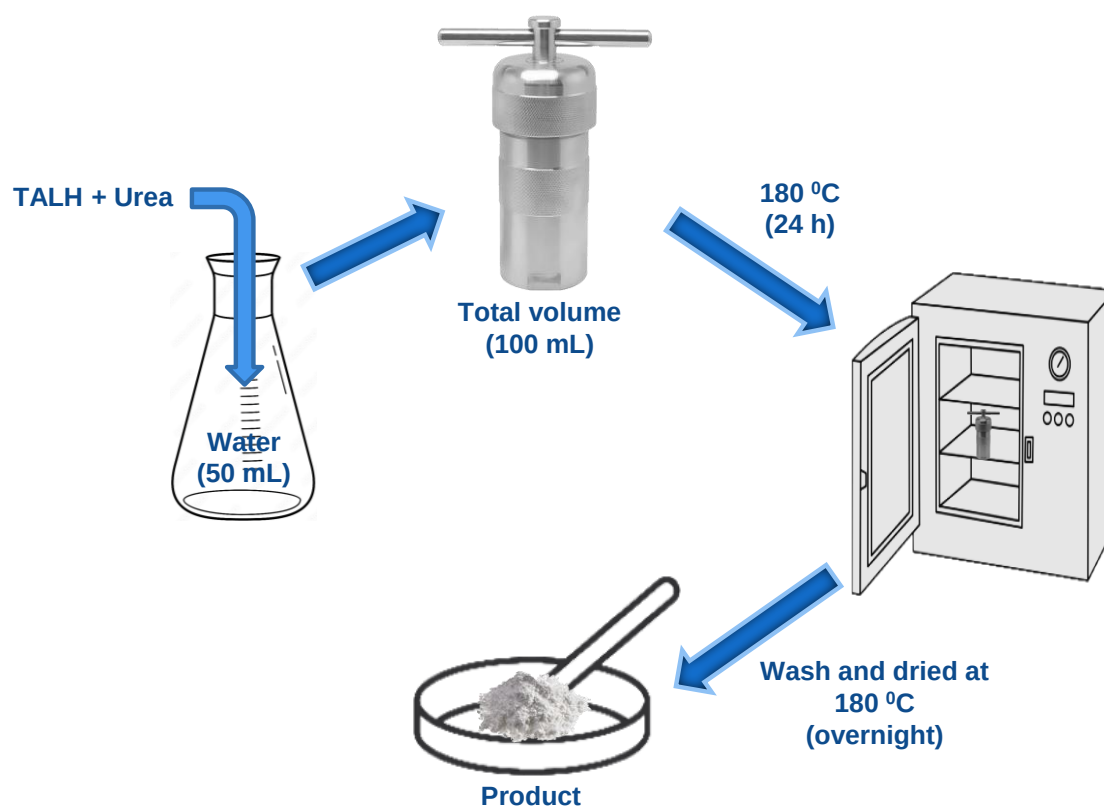


Figure 3. 2. Schematic diagram of the synthesis of titania forms.

3.3 Characterization of materials

The crystal structure of the prepared materials was analyzed by using powder XRD which is operating in a $\text{CuK}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation reflection mode. The angular mode 2θ was recorded from 20 to 80° . Different polymorphs of TiO_2 were evaluated from the relative areas and peak position. Raman spectroscopy was also carried out for the identification of different phases of TiO_2 using the Lab Ram HP Evolution Raman Spectrometer. The laser source was 633 nm wavelength. Each spectrum was collected at 4 number scans for 30 seconds of acquisition time. The structural morphology of TiO_2 polymorphs was analyzed by using field emission-scanning electron microscopy (FE-SEM) at 20 kV acceleration voltage. The Brunauer-Emmett-Teller (BET) surface areas were determined using the N_2 adsorption/desorption isotherm. The details about each used characterization and other techniques are given below.

3.3.1 X-Ray Diffraction (XRD)

In 1895 X-ray was discovered by Roentgen and in 1912 Laue discovered that the crystalline materials showed three-dimensional diffraction grating upon the excitation of X-ray radiations. Most crystalline materials have different diffraction patterns which can be identified through the diffraction pattern database. The present impurities in the crystal structure and lattice parameters of a crystal can also be identified through XRD [111, 112]. XRD is an analytical technique used for the identification of crystalline materials, and can also provide information about the dimensions of the unit cell. When the X-ray light strikes the surface of crystalline materials, it diffracts in a structure characteristics spectrum. The diffraction spectrum plots against intensity (I) vs the angle of diffraction (θ) [113, 114].

XRD is based on the crystalline sample and the constructive interference of X-ray monochromatic light. X-rays in the XRD are generated in a tube of cathode rays, a monochromatic radiation filter which is directed toward the crystalline sample. Multiscattering X-rays pass through the layers of the atoms and the overall diffraction pattern is similar to the grating pattern of the light beam. The analysis of the XRD sample should be crystalline and the atoms layer spacing must be close to the X-ray light. If the X-ray beam passes through different layers of atoms, constructive interference occurs and the peak of diffraction will appear. Furthermore, destructive interference occurs by passing the X-rays through the out phase. The schematic diagram of XRD is shown in Figure 3.3.

XRD consist of three parts; X-ray source, sample holder, and detector. X-ray is produced by heating the cathode ray tube filament to produce electrons, and by applying the voltage the electrons bombarding to the targeted material. When these electrons have enough energy to free the inner shell electrons of the electron, produced characteristic X-ray spectra. In the characteristics, X-ray spectra K_{α} and K_{β} are the main components. The specific value of the wavelength is the characteristics of related targeted materials such as Cu, Cr, Fe, and Mo. etc. Cu is the main targeted material for XRD ($\text{Cu } K_{\alpha}$) with a 1.5418 Å radiation value [115].

The X-ray radiations are directed toward the sample. The intensity of the reflected x-ray was measured by rotating the sample and detector. The detector processes and records the X-ray signal. The signal is further converted into a count rate and sent to data for storage and display.

The intensity of the peaks was observed by the occurrence of constructive interference with the Braggs equation. Brags law was used to calculate the angle where constructive interference from the scattering of X-ray produced a diffraction peak [116].

$$n\lambda = 2d\sin\theta \quad (3.1)$$

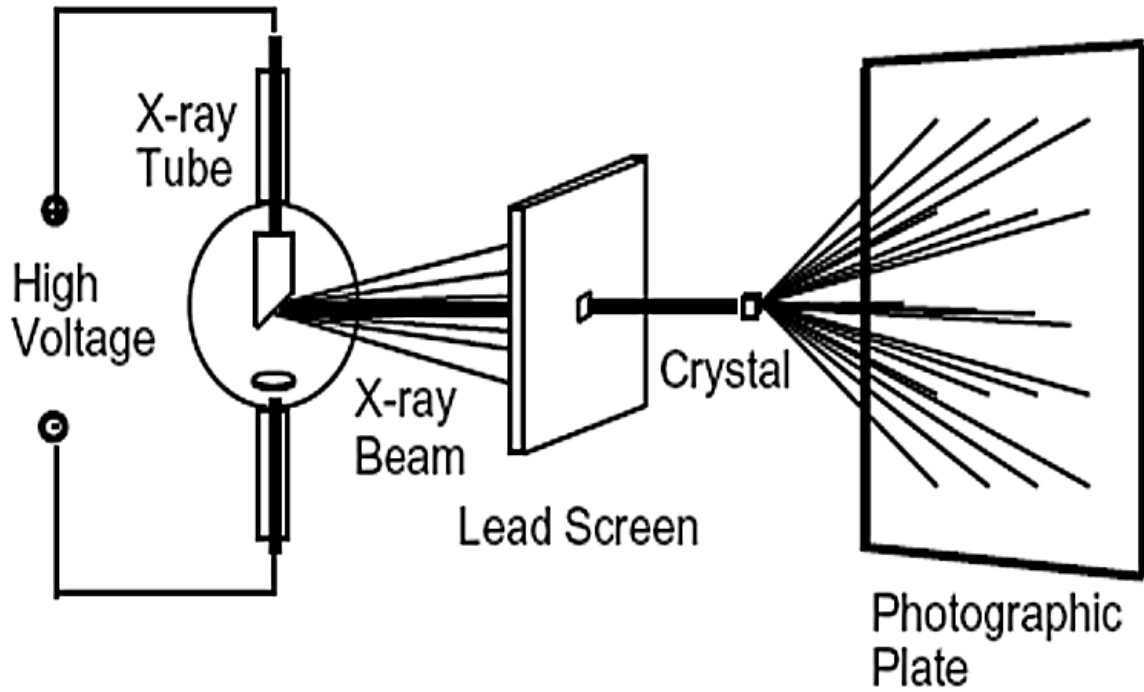


Figure 3. 3. Schematic diagram of powder X-ray diffraction (XRD).

Herein, n is the reflection integer, λ is the wavelength of the X-ray radiation source, d is the spacing between the atom planes, and θ is the angle of the incident in degrees. The particle size of the crystalline sample can be determined by using the Scherrer equation [117].

$$t = \frac{k\lambda}{\beta \cos \theta} \quad (3.2)$$

In the equation, k is a constant value depending on the material, λ is the x-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) after subtracting the instrumental line broadening, θ is the Bragg angle, and t gives the measured size of the particle.

In the present work, the crystal structure of the prepared materials was analyzed by using powder XRD which is operating in a $\text{CuK}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation reflection mode. The angular mode 2θ was recorded from 20 to 80° .

3.3.2 Raman spectroscopy

Raman spectroscopy is an analytical technique used for the detection and quantification of samples by detecting the Raman scattering of light produced by a laser of a particular wavelength. In 1928, Raman spectroscopy is first discovered by an Indian scientist Venkata Raman. The schematic diagram of Raman spectroscopy is given in Figure 3.4. The photons strike the molecule and excite it to the virtual state. The two types of scattering occur in Raman spectroscopy, one is Stokes scattering and the second is anti-Stokes scattering. Stokes scattering is produced when the energy of the scattered light is less than the energy of incident light. On the other hand, anti-Stokes scattering is produced if the energy of scattered photon is greater than the energy of incident photon [118]. The Jablonski diagram for representing the theory is given in Figure 3.5.

Although Raman spectroscopy gives us details about the sample vibrational modes which can be used for the characteristics study of the material. The electric dipole moment (P) is produced when the light interacts with the sample material.

$$P = \alpha E \quad (3.3)$$

Here α is the polarizability and E is the electric field.

In oscillation electric field, an oscillating electric dipole moment is produced. The induced dipole moment will be according to the equation given below.

$$P = \alpha_0 E_0 \cos(2\pi\nu t) + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos(2\pi(\nu + \nu_{vib})t) + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos(2\pi(\nu - \nu_{vib})t) \quad (3.4)$$

$\left(\frac{\partial \alpha}{\partial q} \right)_0$ is the rate of change of α with a change in the value of q at the equilibrium position.

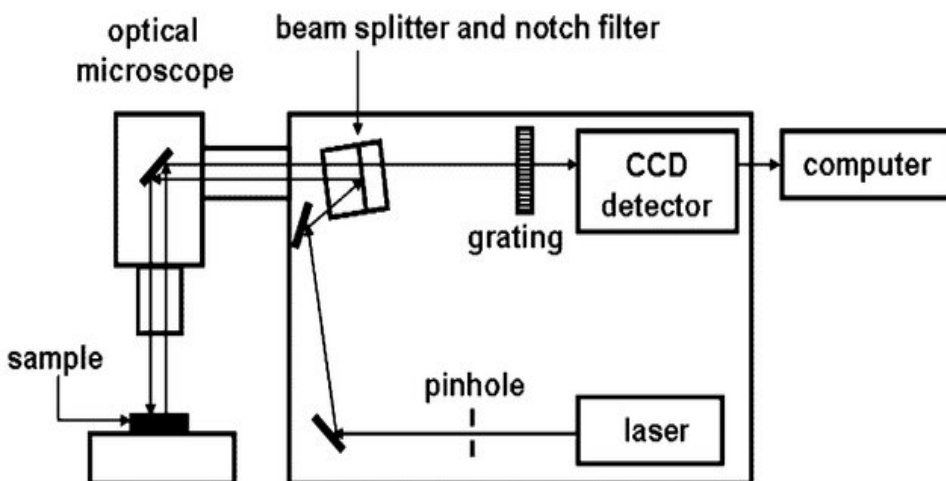


Figure 3. 4. Schematic diagram of Raman spectrophotometer

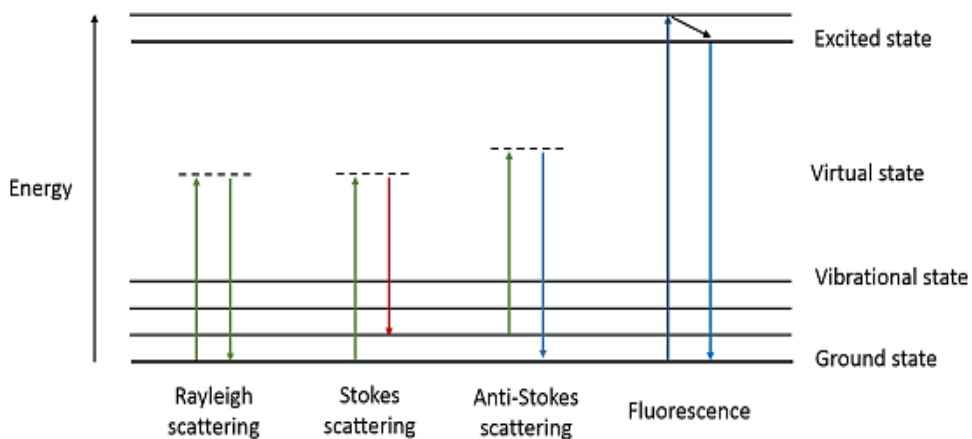


Figure 3. 5. Jablonski's diagram explains the difference between different types of light interaction.

3.3.3 Scanning Electron Microscope (SEM)

The Scanning Electron microscope (SEM) is used to analyze the structural morphology of the samples. SEM uses electrons instead of light for image formation which is used in normal optical microscopes. The beam of the electron is generated from an electron gun with a tungsten filament cathode. The power of electrons can be controlled by controlling the electric and magnetic fields. These fields are used to focus and control the path of the beam to analyze the sample. All the parts of the SEM are working at a high vacuum to enhance the image resolution. The presence of air in the beam path distracted the path of the beam which scattered the beam of electrons [115]. The systematic diagram of the SEM is given in Figure 3.6.

The thermal is generated by passing the electric current through the tungsten filament. The electron is produced by increasing the thermal energy to the work function of the filament. The electrons accelerated with the potential difference towards the anode which forms an electron beam. The charged electrons can affect the electromagnetic lens. The objective and condenser lens are the two types of electromagnetic lenses used in the SEM. The condenser lens controls the size of the beam while the objective lens covers the condenser beam lens and focuses the beam toward the sample [119, 120].

Three types of beams; backscattered beam, secondary electron beam, and characteristics X-ray, produces when the beam of electron interacts with the sample. The backscattering occurs due to the reflection of the electron beam after elastic interaction between the sample and the electron beam. The secondary beam is produced due to the atoms of the sample and the inelastic interaction produced between the surface of the sample and the electron beam.

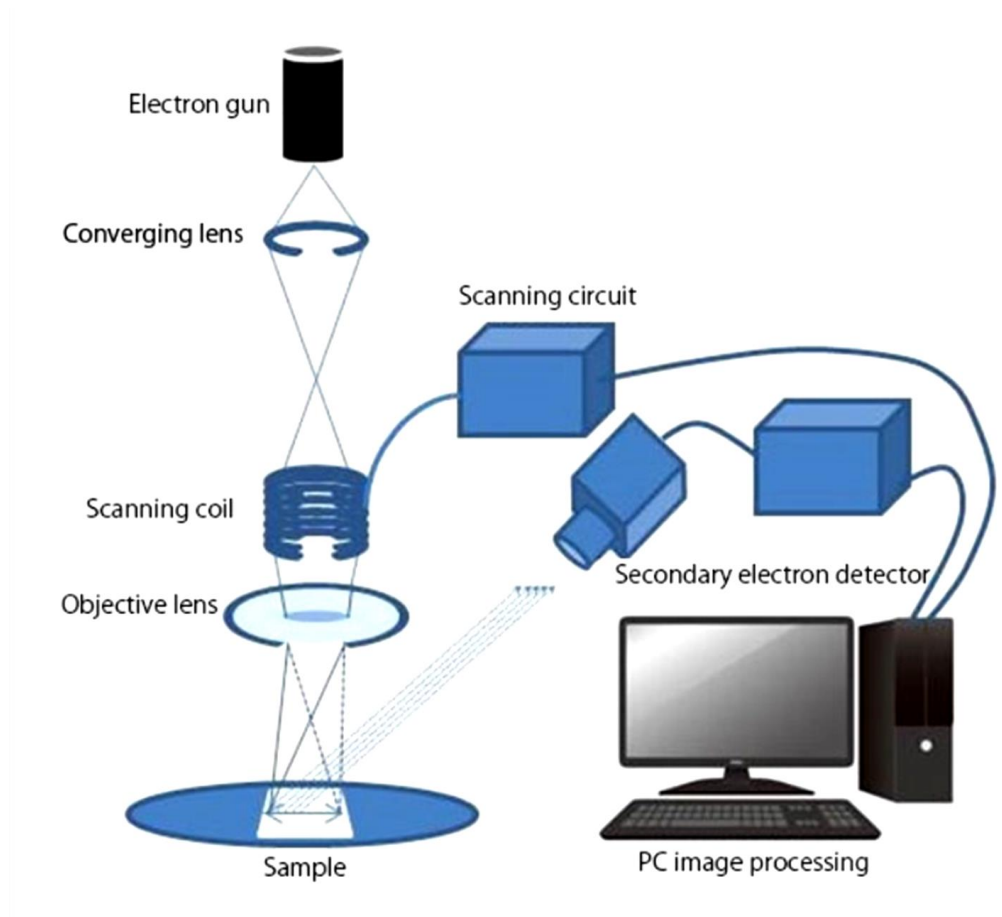


Figure 3. 6. Schematic diagram of powder Scanning Electron microscope (SEM).

This beam produced the surface morphology of the sample materials. The X-ray is produced due to the interaction between the sample and beam and gives us the elemental details of the sample. Every sample has its characteristic X-ray peak which gives us information about the sample [120].

3.3.4 Gas adsorption isotherm

Gas adsorption is a well-known method to analyze the surface area and pore size distribution of a solid porous material. In 1985 International Union of Pure and Applied Chemistry (IUPAC) issued a report for reporting physisorption data for solid and gas samples. This report explains details information about the use of gas adsorption for the measurement of the porosity and surface area of a sample. Specific surface area is defined as the total surface area per unit mass (m^2/g) [121]. Gas adsorption measurement also called BET (three scientists named ‘Brunauer-Emmett-Teller’) is used for the measurement of the surface area [122].

Nanoporous materials have been prepared with different pore sizes and structural morphology such as TiO_2 nanorods and nanospheres [104, 123], carbon nanotubes [124], nanohorns [125], mesoporous molecular sieves [126], and different categorized pore size materials [127]. The gas adsorption method was further developed according to various experimental protocols such as with the presence of nitrogen (N_2) and argon (Ar). The systematic diagram of gas adsorption measurement is given below in Figure 3.7. The gas adsorption method (BET) is based on physical forces such as Van der Waals forces, polarization, filed dipole, attractive dipole and filed gradient quadrupole between adsorbate material to the surface of adsorbent [128].

Langmuir's adsorption isotherm theory [129] is used for the measure of monolayer adsorption. The BET-theory is based on the following points.

1. The formation of a multilayer for the adsorbate on the surface of the adsorbent can go infinitely.
2. The interaction of the adsorbate molecule is in the short range. In another way, the molecular interaction only with the adjacent layer.
3. The Langmuir theory can be applied to each layer. The resulting BET equation is

$$\frac{P}{n_a(P_0 - P)} = \frac{1}{n_m C} + \frac{(C - 1)P}{n_m C P_0} \quad (3.5)$$

Here, P is pressure, P₀ is saturation pressure, n_a is gas total uptake, n_m is monolayer capacity, and C is BET constant. The BET value range should be linear. The value of n_m and C can be calculated from the y-intercept and slope of the plot. The linear range selection is based on the following points.

1. The value of C (BET constant) must be positive, any negative y-intercept showed that the points are outside the BET range.
2. The relative pressure (P/P₀) must be increasing.

The total surface area (S_t) per unit volume can be calculated by using the following equation

$$S_t = \frac{n_m N_A S}{V} \quad (3.6)$$

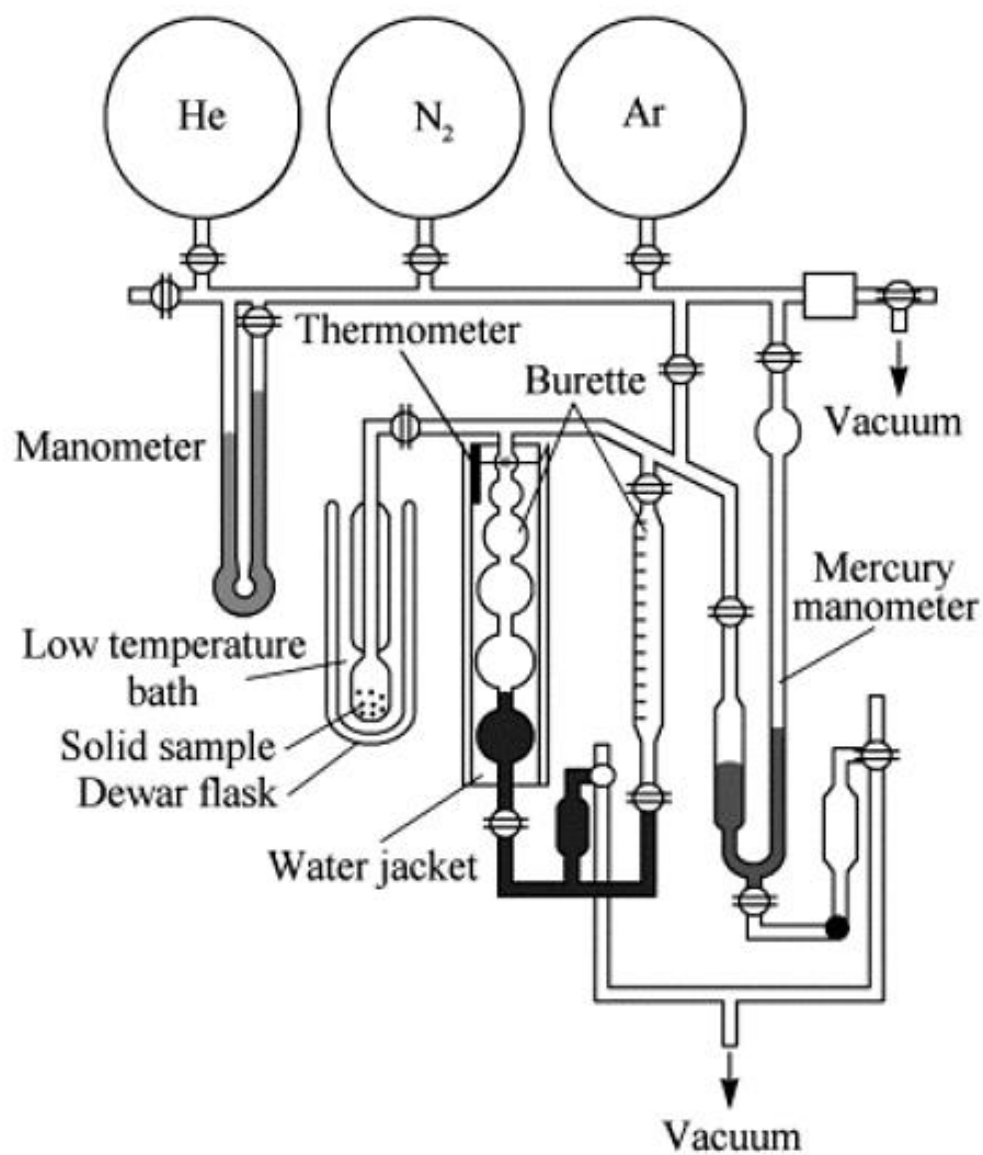


Figure 3. 7. The systematic diagram of gas adsorption measurement.

N_A is Avogadro number, s is the cross-sectional area, and V is the molar volume of the gas adsorbate. BET-specific surface area can be calculated by using the below equation

$$S_{BET} = \frac{S_t}{m} \quad (3.7)$$

Herein, m is the total adsorbent sample mass. Nitrogen (N_2) is mostly used as an adsorbate due to its inert nature and well-known size (0.162 nm^2) [130].

The isotherm is the adsorbed amount of gas in mole per g amount of catalyst (mol/g) as a function of nitrogen relative pressure (P/P_0). According to IUPAC (in 1985), isotherm is classified into six different isotherms which depend on the isotherm behaviour of the sample in the gas adsorption and desorption processes [130]. The six different isotherm behaviour are given in Figure 3.8 [131].

In type I isotherm, the adsorbent showed a significant increase in the adsorption at relatively low pressure and immediately adsorption saturation as the pressure approaches the saturation pressure (P_0). The adsorption shows in type II a small enhancement in the adsorption at low pressure, and then saturation is achieved at saturation pressure. In the isotherm III type, the uptake is increasing with the pressure and no saturation occurred. The isotherm is achieved when the liquefaction energy of the adsorbate is more than the energy of single-layer formation. By increasing the pressure no single layer formation due to the condensation of the adsorbate molecule.

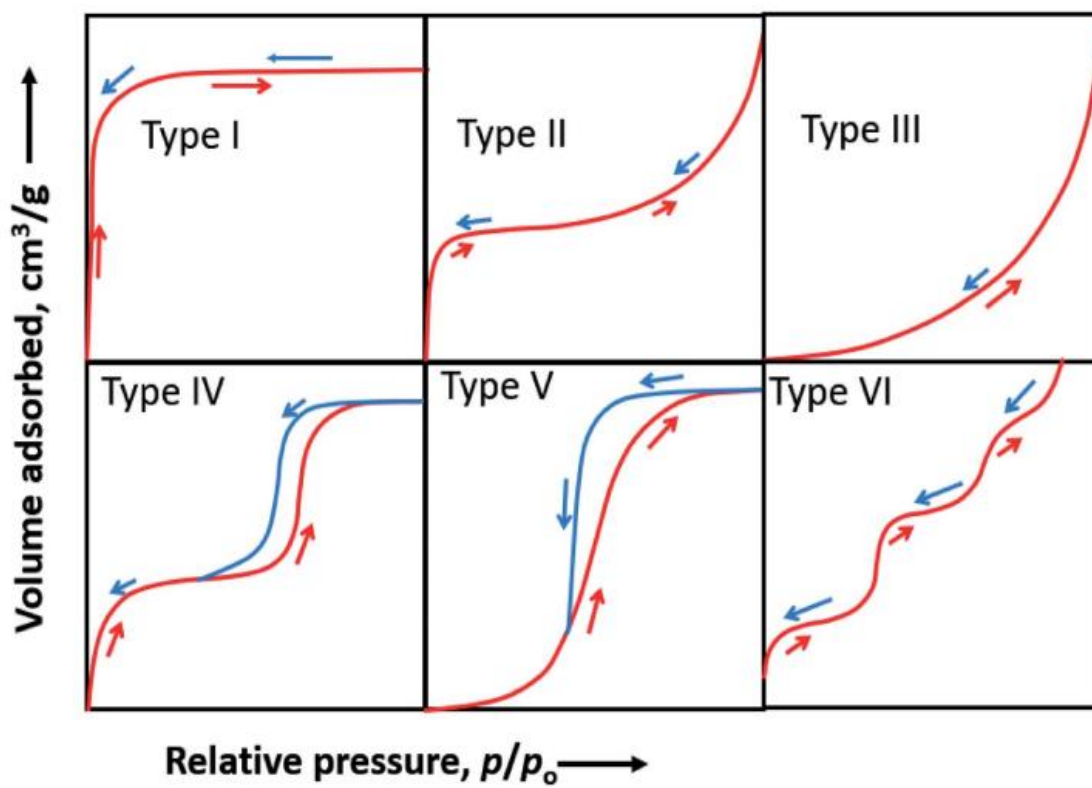


Figure 3. 8. Six different types of isotherms behaviours [131].

Type IV isotherm is obtained when the present adsorbent material has porous morphology. At low-pressure values, the isotherm shows similar behaviour as type II isotherm. By increasing the pressure value, when the pressure reached the saturation value the uptake approaches the saturation region. The change like isotherm is due to the condensation process in the capillary tube. At the start of the isotherm, the first layer forms then take place the adsorption condensation. The nature of type V is somehow like the type IV adsorption isotherm. In type V, at low pressure, it shows the behaviour of type III isotherm. Lastly, type IV adsorption isotherm explained the layer-to-layer adsorption on nanoporous materials. The capacity of each layer shows the step height while step sharpness represents the system temperature [130, 131].

3.3.5 Nuclear Magnetic Resonance (NMR) spectroscopy

Nuclear magnetic resonance (NMR) is a technique used when the nuclei of any atom are immersed in a constant magnetic field and shown to other oscillating magnetic fields. The occurrence of this phenomenon depends on the property of spin. Most of the materials which have a proper spin can be detected using NMR. The presence of atoms in the molecules can be assumed as a small value of the magnetic field will help the nuclei to show the spectra of NMR [132, 133]. The schematic block diagram of the NMR spectrometer is shown in Figure 3.9.

Some of the nuclei have different elemental isotopes which show different characteristics of spin. NMR active nuclei must have a nuclear magnetic movement ($\bar{\mu}$). Protons (+1 charge) and neutrons (no charge) are the parts of the nuclei. The atomic mass number (A) of an atom is the sum of the number of protons (Z) and neutrons (N). Only those nuclei will retain the magnetic field if they have an odd number of protons and

neutrons. Some nuclei have fractional spin values (for example 1/2, 3/2, 5/2,.... etc), and some others have integral spin values (for example 1, 2, 3,..... etc) while some of the nuclei have without any value of spin means zero value of I (for example ^{12}C , ^{16}O , ^{32}S ,.... etc). Most of the researchers focus on ^1H , ^{13}C , ^{19}F , and ^{31}P NMR measurement due to their high applicability in the field of research and all of these has spin $I=1/2$ [134, 135].

The angular momentum of the nucleus of an atom ($\bar{P}$) depends on the spin quantum number (I).

$$\bar{P} = \hbar \bar{I} \quad (3.8)$$

Here, $\hbar = \frac{h}{2\pi}$ and h is the Plank's constant. The P magnitude is given in the equation below [136].

$$P = \hbar \sqrt{I(I + 1)} \quad (3.9)$$

Herein, I is the spin quantum number.

The angular momentum direction depends on other quantum numbers. The angular momentum components are along the z-axis direction (P_z).

$$P_z = m\hbar \quad (3.10)$$

m is fixed to the separate values such as I, I-1, I-2,..... -I for the I value.

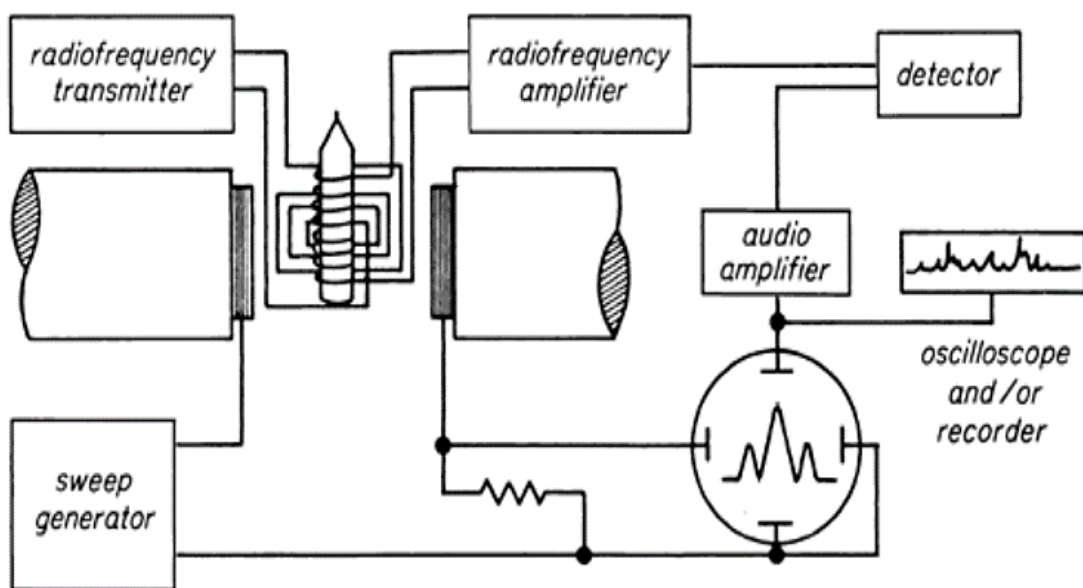


Figure 3. 9. The schematic block diagram of the NMR spectrometer.

The relationship between angular momentum ($\vec{P}$) and magnetic moment ($\vec{\mu}$) is given in this equation.

$$\vec{\mu} = \gamma \vec{P} \quad (3.11)$$

Herein, γ is the nucleus gyromagnetic ratio. The interaction between the magnetic field applied along the z-axis direction ($\vec{B}_0$) with the magnetic moment is explained in the equation below.

$$E = -\vec{\mu} \cdot \vec{B}_0 \quad (3.12)$$

The two states of energy are related to parallel or anti-parallel spin to an applied magnetic field are shown in Figure 3.10.

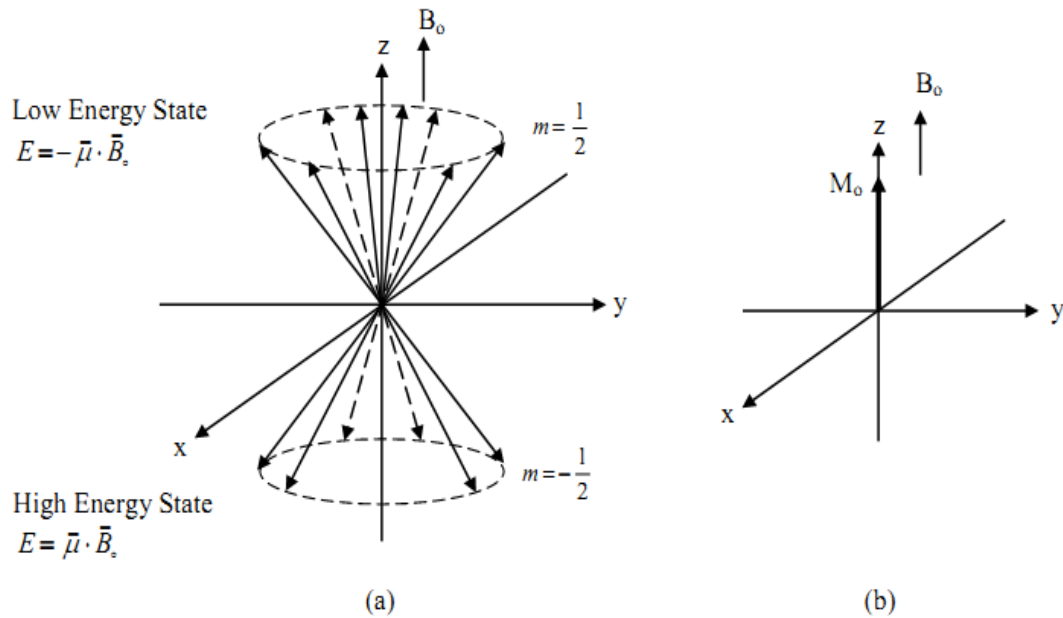


Figure 3. 10. (a) The two possibilities of nucleus spin state of spin parallel and anti-parallel to the applied magnetic field in the z-axis direction (b) the overall vector of spin magnetism (M_o) is equivalent to the overall magnetic moment z component.

3.3.6 Electron Paramagnetic Resonance (EPR) Spectroscopy

Electron paramagnetic resonance (EPR) also called electron spin resonance (ESR) spectroscopy is a unique technique which is used to study the unpaired electron chemical species on the base of an electron's angular momentum. In 1896, the first evidence for electron angular momentum was examined when Zeeman (a Dutch physicist) observed the splitting of lines in optical spectra in a constant magnetic field [137]. In the 1980s, the first commercial EPR spectrometer was launched in the market which was comprehensively used in the medical and biological areas of research. These days, the EPR technique is one of the best and standard tools for research.

The electrons (e^-) in an atom is a negatively charged particle that orbits around the nucleus and has a quantum spin. The orbital angular momentum (L) generates due to the rotation of the e^- around the nucleus. The electron spin generates angular momentum [138].

The direction of the spin angular momentum is on the z-axis

$$S_z = \frac{h}{2\pi} m_s \quad (3.13)$$

Where (h) is the plank's constant and m_s is the spin angular quantum number and it has $2S+1$ values. For the unpaired electrons, the values will be $S = 1/2$, $m_s = +1/2$ and $-1/2$. The magnetic moment (μ_e) is directly proportional to the spin angular momentum (S)

$$\mu_e = -g_e \mu_B S \quad (3.14)$$

Here g_e is the g-factor of free electron (2.0023) while μ_B is the Bohr magneton

$$\mu_B = \frac{e h}{4\pi m_e} \quad (3.15)$$

Herein, e and m_e are the charge of the electron and the mass of the electron. When an atom is placed in the magnetic field, it interacts with the magnetic moment of the electron. This energy interaction could be written as follow

$$E = -\mu \cdot B \quad (3.16)$$

When no external magnetic field (B) is applied to the system, the energy value will be one only. After applying the B , the energy state will split into two different energy states.

$$E_{+\frac{1}{2}} = -\frac{1}{2} g\mu_B B \quad (3.17)$$

$$E_{-\frac{1}{2}} = \frac{1}{2} g\mu_B B \quad (3.18)$$

So, the difference in energy will be equal to

$$\Delta E = g\mu_B B \quad (3.19)$$

A specific value of energy ($h\nu = \Delta E$) is required to move the electron from the ground state to the excited state which will be equal to

$$h\nu = g\mu_B B \quad (3.20)$$

The magnetic field and microwave frequency can be varied to achieve the best parameters, but g is a proportionality constant whose value depends on the environment of the electron.

$$g_e = \left(\frac{h}{\mu_B}\right) \left(\frac{\nu}{B}\right) \quad (3.21)$$

The g-value for a free electron is constant ($g = g_e$), but in metal ion complexes the nuclei produced a second magnetic field. The related equation is given below

$$\frac{1}{g} = \left(\frac{\mu_B}{h} \right) \left(\frac{B + \Delta B}{\nu} \right) \quad (3.22)$$

The resonance magnetic field is not fixed because needs a different range of microwave frequencies [139]. The change in g value (Δg) contains the chemical interaction information between electron and molecular electronic structure. For organic radical structure, the value of g is near to the g value of electron (g_e), and the g-value of methyl radical is ~ 2.0026 [140]. The g-value range for the transition metal complexes is in the range of 1.4-3.0, which depends on the geometry of the metal complexes [141]. A block diagram of the EPR spectrometer is given below (Figure 3.11)

EPR spectroscopy can be conducted by changing the magnetic field or frequency. The EPR spectrometers normally work in the range of 8-10 GHz (x-band), while some of the spectrometers work in the low (1-2GHz (L-band), 2-4 GHz (S-band)), or high field 35 GHz (Q-band), and 95 GHz (W-band) [142]. EPR samples can be gases, liquids, powders, or frozen solutions. The solvents that have a high dielectric constant value are not good because they will absorb MW radiations. By increasing the applied magnetic field, the energy difference between the energy level increase until it matches the MW radiations and results in photon absorption. The photon absorption signal passes through the phase-sensitive detector which converts the absorption signal to the first derivative spectrum. The centre of the absorption spectrum peak help to find the value of g. EPR spectra normally present the first derivate of the absorbance spectra for easy interpretation (Figure 3.12). The value of the magnetic field is generally described in Gauss or mTesla units [143, 144].

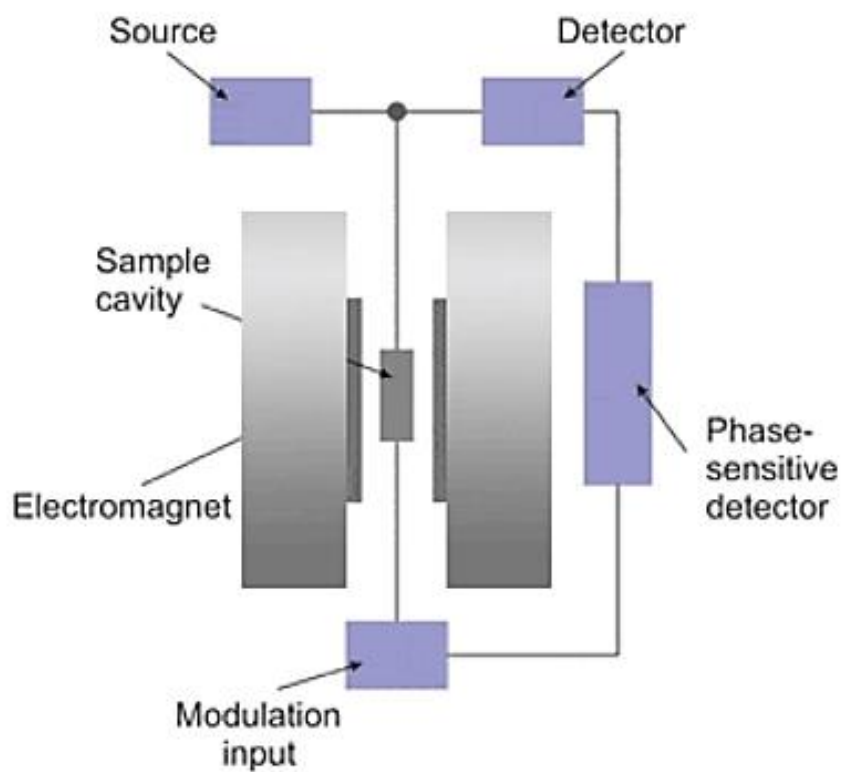


Figure 3. 11. Block diagram of a typical EPR spectrometer.

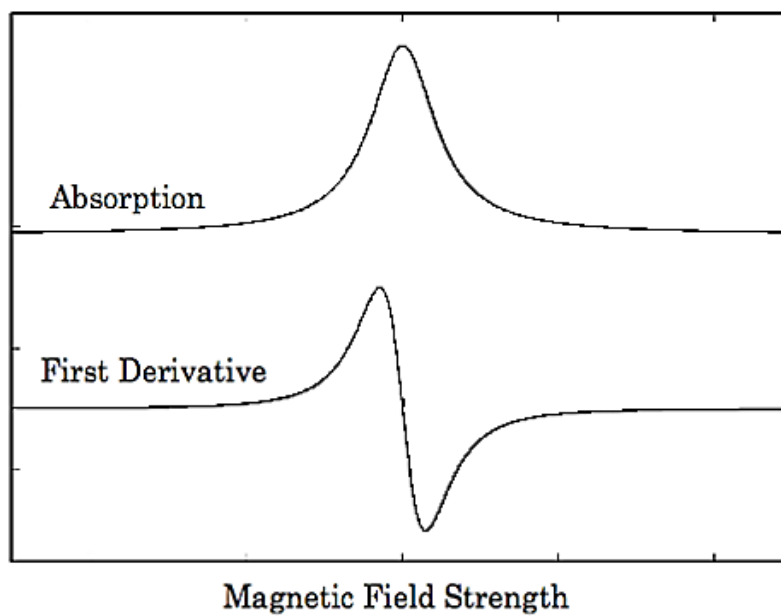


Figure 3. 12. An EPR spectrum of absorption and first derivative spectra.

3.4 EPR-integrated Photocatalytic Setup and Photocatalytic Test

A customized X-band benchtop-EPR spectrometer from ADANI, known as ADANI-XLab, equipped with a built-in multi-capillary flow cell and a peristaltic pump, was used to record the EPR signal. The EPR signals were collected at a modulation frequency of 100 kHz. The sweep time and width were 10 s and 10 mT, respectively. The attenuation and modulation amplitudes were 3.16 mW and 200 μ T, respectively. Sixty EPR scans were collected per photocatalytic test at a time interval of 1.0 min. In this setup, a 25 mL photo-reactor having a Thorlab LED light source is attached to the EPR spectrometer having a capillary flow cell as schematically shown in Figure 3.13.

In a typical photocatalytic test, 5 mg of TiO₂ P25 has been dispersed in 10 mL of 100 μ M TEMPOL aqueous solution by sonication in a 25 mL cylindrical photoreactor (inner diameter 30 mm). A smaller volume (within the range 10-2 mL) can be analyzed with this method based on the used photoreactor inner diameter. The suspension is then kept under stirring and purging with air in the dark for 15 min. The photoreaction is connected to the EPR system, and the flow rate of the TiO₂ suspension into the EPR cell was controlled using the integrated peristaltic pump. It was adjusted to be 10 mL min⁻¹ and kept constant. After 180 s from starting the recording of the EPR signal, the light is turned on, and the photoreactor is illuminated from the top using a collimated UV(A) light using a high-power Thorlab LED as a light source. The distance between the photoreactor and the LED was kept constant, and the light intensity was varied by controlling the LED current. The light intensity was measured by a calibrated Si-photodiode (FDS100-CAL, Thorlabs).

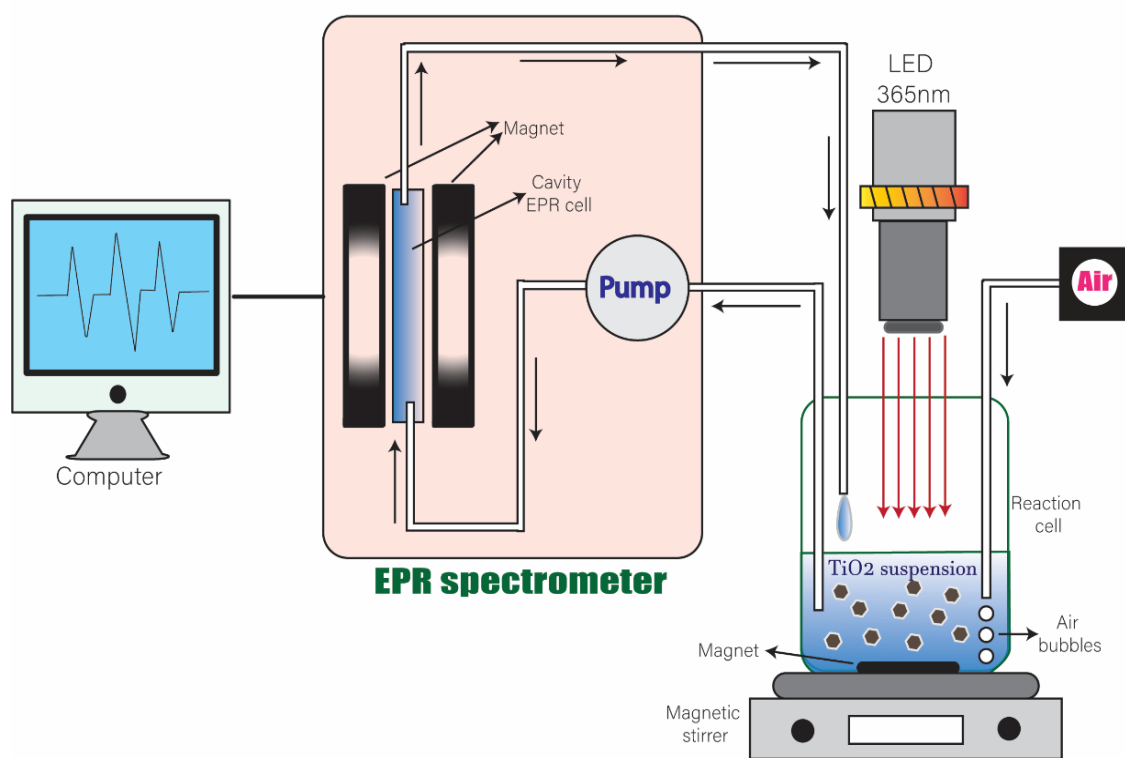


Figure 3. 13. Schematic illustration of the EPR-photocatalyst setup.

3.5 Computational methodology and programs

The density functional theory (DFT) calculations were performed using Gaussian 09 program with the agreement of the Becke 3-parameters, Lee, Yang, and Parr (B3LYP) method which was introduced by Becke and Lee with his coworkers [145-147]. The structures were optimized by using 6-31+ which is normally used for non-metallic atoms. This basis set was selected due to its ability to produce accurate results that matched the result of the experiments of normal size organic molecules at a reasonable cost.

For the data analysis, the ratio of the paramagnetic species at the end of the reaction is achieved by simulating the EPR spectra of the reaction mixture with the help of available free software from the National Institute of Environmental Health Sciences (NIEHS) [148] called WinSim. The simulating EPR spectrum were generated by using the estimated hyperfine values from the optimized molecular models of the radical species using Gaussian 09 Becke 3-parameters, Lee, Yang, and Parr (B3LYP) density functional method of calculations.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Structure analysis

Figure 4.1 shows the XRD patterns of the synthesized TiO_2 materials. In agreement with the previous report [93, 149], at low urea concentration, the hydrothermal decomposition of the TALH precursors resulted in the formation of TiO_2 anatase. At a urea concentration of 6.0 M and in presence of sodium lactate, pure TiO_2 brookite was obtained. Using TALH and urea to produce TiO_2 brookite leads to the formation of rod-like particles [150]. Rutile was synthesized by the calcination of the anatase at 800 °C for 2h.

Raman spectra of the different forms of TiO_2 are present in Figure 4.2. Generally, the TiO_2 brookite form has complex vibrational modes as compared to other forms of TiO_2 [151, 152]. In the Raman spectrum of TiO_2 anatase, the main peaks of anatase located at 138.7, 392.3, 510.3, and 635.3 cm^{-1} (dashed line) can be observed. The little shifting of the anatase peak from 138.7 to 147.8 cm^{-1} (short dot line) and the appearance of other extra peaks in the spectra of brookite are in agreement with the XRD results [150]. A clear extra and sharp modes at 207.8, 240.3, 279.9, 317.7, and 362.1 cm^{-1} can be observed in the Raman spectra which indicates the presence of pure brookite [93]. In the case of rutile one prominent peak appears at $\sim 138 \text{ cm}^{-1}$.

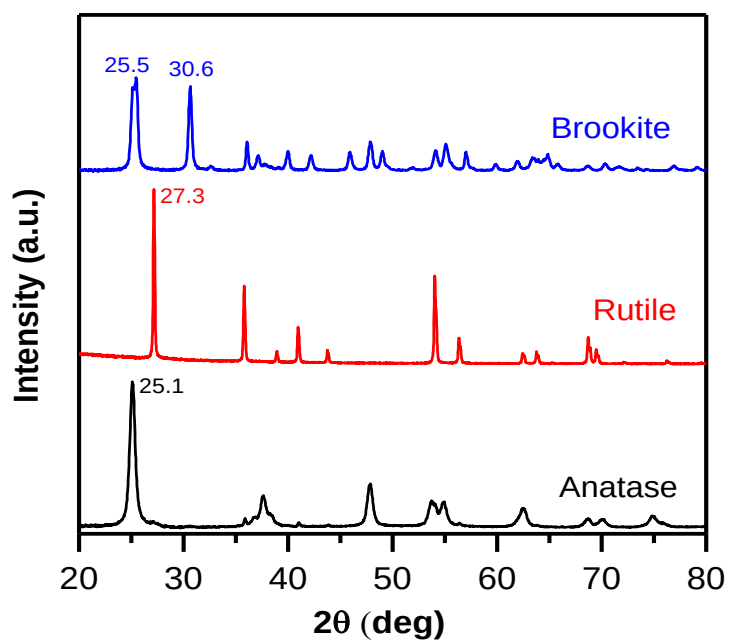


Figure 4. 1. XRD patterns of TiO_2 anatase, brookite and rutile.

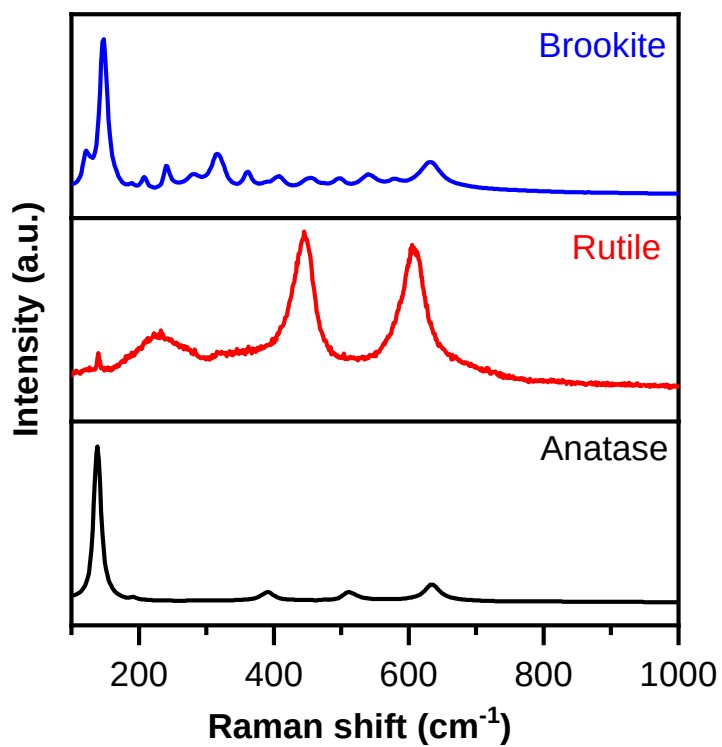


Figure 4. 2. Raman spectra of TiO_2 and pure brookite.

The morphology of the different forms of TiO_2 was investigated with the help of a field emission-transmission electron microscope (FE-TEM) as shown in Figure 4.3. The TEM micrographs indicated that the TiO_2 anatase powder consists of aggregates from nanosized particles (Figure 4.3a). The latter particles belong to the brookite form as can be concluded from the comparison with the morphology of pure brookite presented in Figure 4.3b. The formation of the rod-like morphology is mainly due to selective adsorption and preferential growth in the presence of lactate ions in an alkaline medium [153]. The morphology of the rutile is shown in Figure 4.3c. The captured image of rutile material do not show a proper size of rutile particles compared to other TiO_2 in figures 4.3a and b due to its particles agglomeration.

Figure 4.4 (a, b, and c) shows the N_2 adsorption-desorption isotherms of the synthesized TiO_2 samples. It is clear from the isotherms presented in the figure that all the TiO_2 samples exhibit to some extent the character of mesoporous materials (isotherm type IV) due to the voids between the aggregated particles [154]. Figure 4.4d shows the calculated BET surface area. It is found that anatase powder has a higher surface area (i.e., $66.92 \text{ m}^2 \text{ g}^{-1}$) as compared to pure brookite and rutile. This is mainly attributed to the increased sizes of the brookite particles as compared to that of anatase

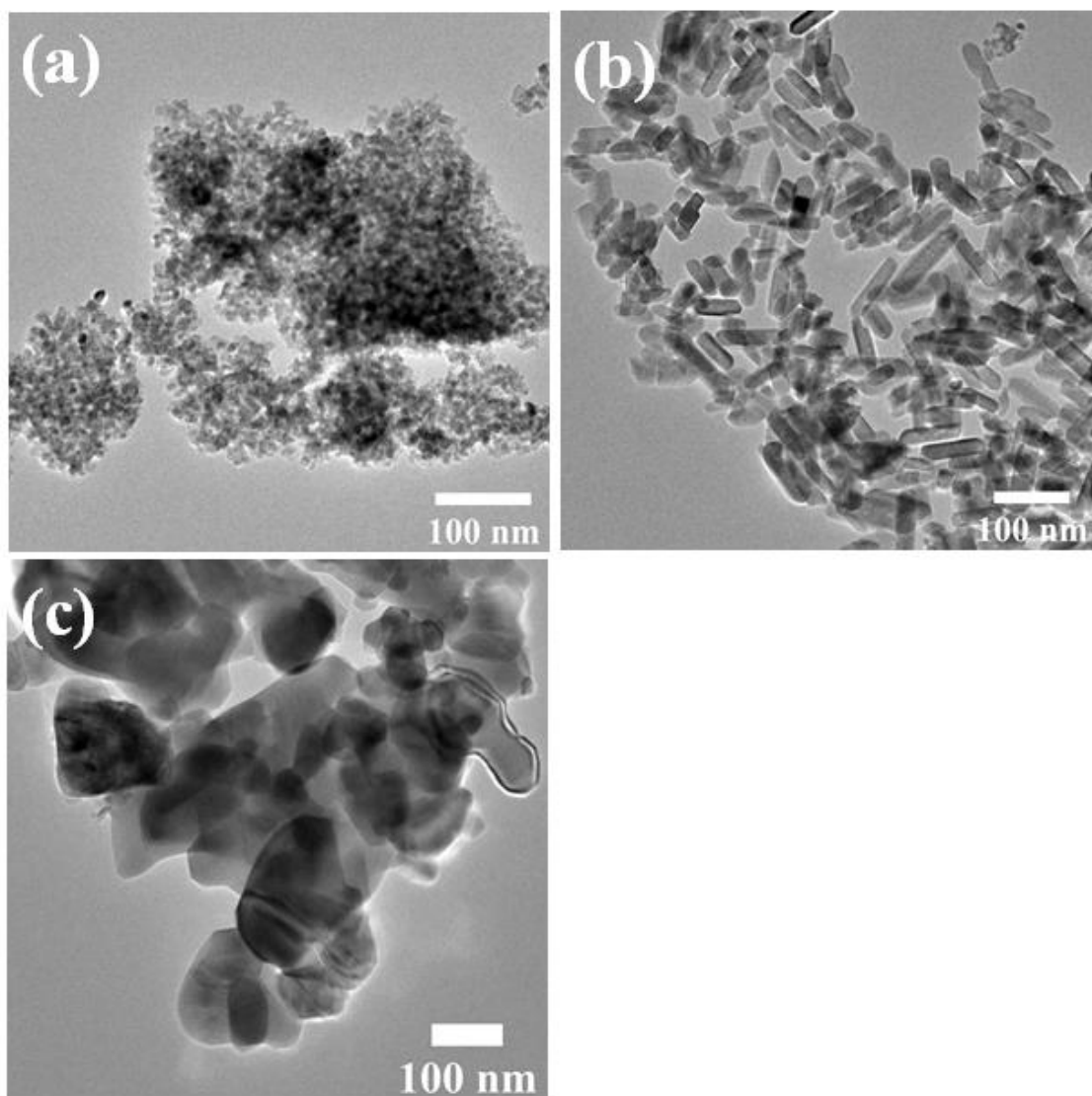


Figure 4. 3. TEM images of TiO₂ anatase (a), brookite (b), and rutile (c).

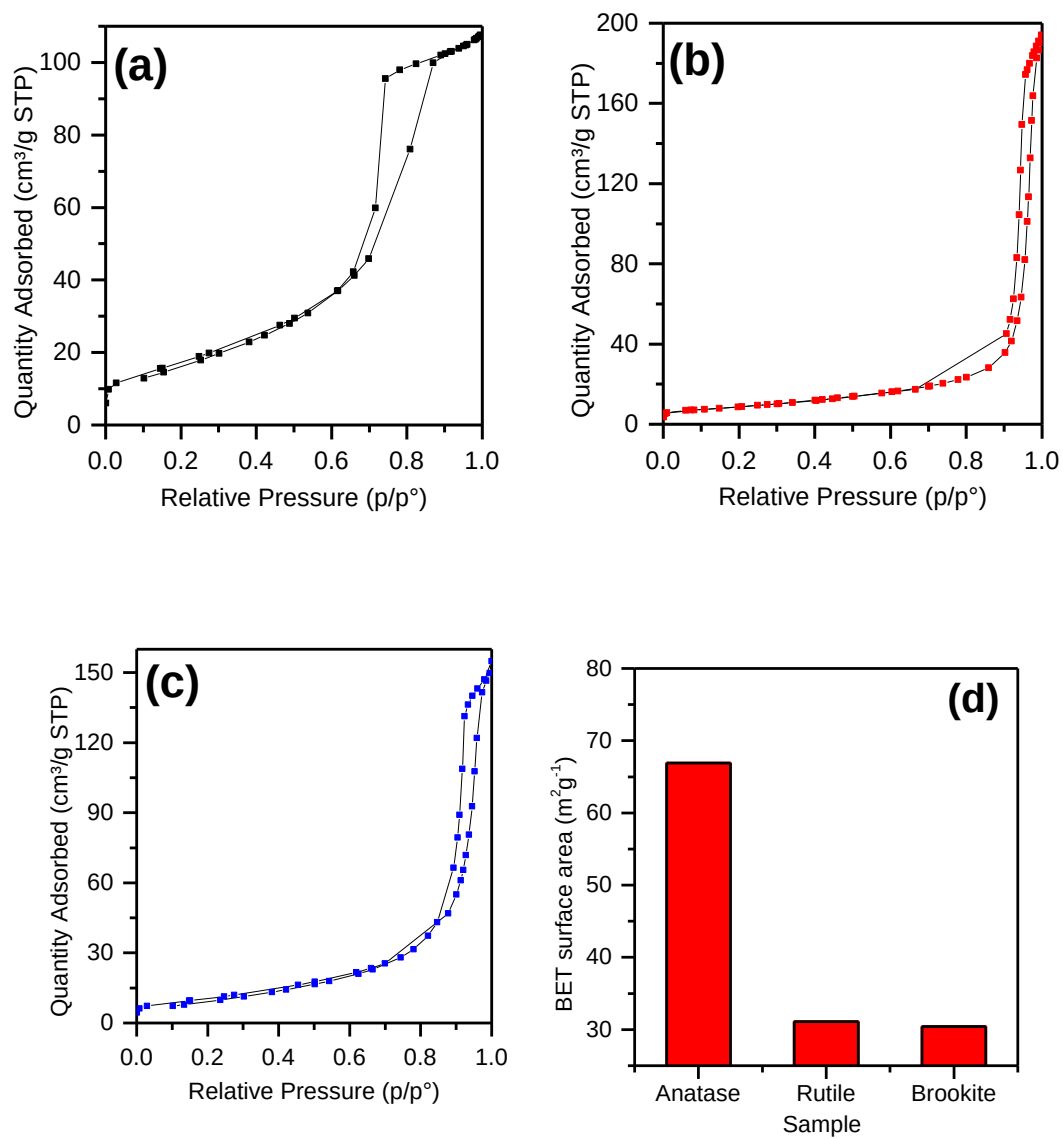


Figure 4. (a-c) N₂ adsorption-desorption isotherms and (d) BET surface areas of TiO₂ anatase, brookite, and rutile.

4.2 TEMPOL Stability Testing

Figure 4.5 shows a typical EPR signal of TEMPOL with a g-factor equal to 2.005554. TEMPOL's stability in water at ambient conditions was investigated by following the intensity of the EPR central signal of a field of 335 mT over 30 days (Figure 4.6). Almost the same intensities have been observed; however, the aqueous solution of TEMPOL was left on the top of the bench during this period evincing that TEMPOL exhibits excellent stability in water under ambient conditions. The influence of UV(A) light on TEMPOL aqueous stability has also been checked. As shown in Figure 4.7, considerable stability has also been observed, indicating that TEMPOL has great potential to be applied as a model compound to monitor photocatalytic activity. To assure that there is no dark reaction in the presence of TiO_2 photocatalyst, the EPR signal of TEMPOL in an aqueous suspension of TiO_2 is measured during a period of 1 h. The central peak intensity values are compared to the clear TEMPOL solution, as shown in Figure 4.7. Again, a stable signal is observed, indicating that no reaction occurs in the dark. In addition to the high stability of TEMPOL, it does not absorb UV(A) and visible light (Figure 4.8). Thus, photosensitization associated with the dyes (e.g., MB) and phenolic compounds is avoided, and hence the photo-induced catalysis can be readily assured [64, 65].

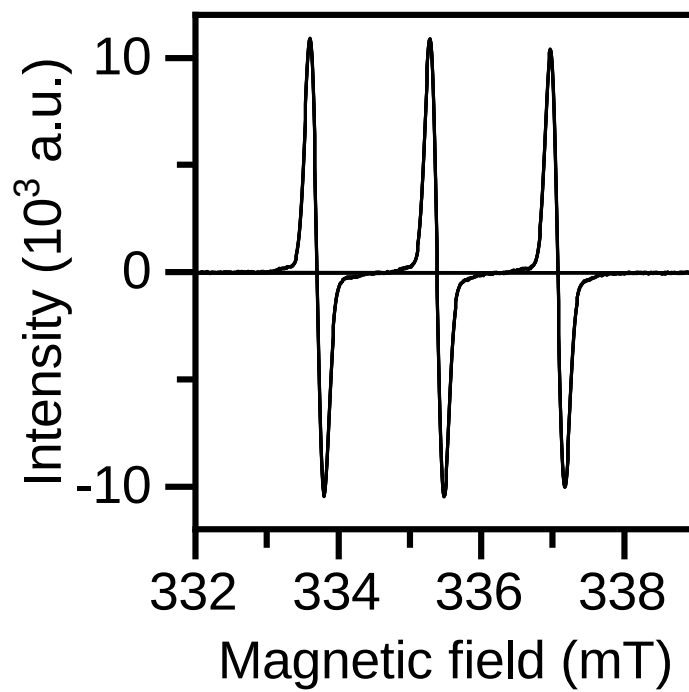


Figure 4. 5. Typical EPR signals of 100 μM TEMPOL aqueous solution.

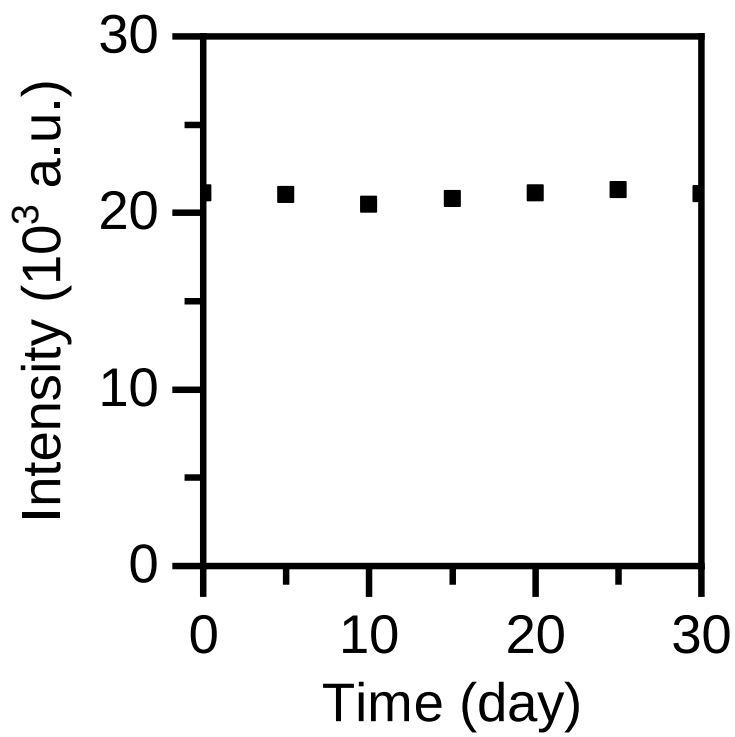


Figure 4. 6. Long-term stability test of TEMPOL aqueous solution at ambient temperature.

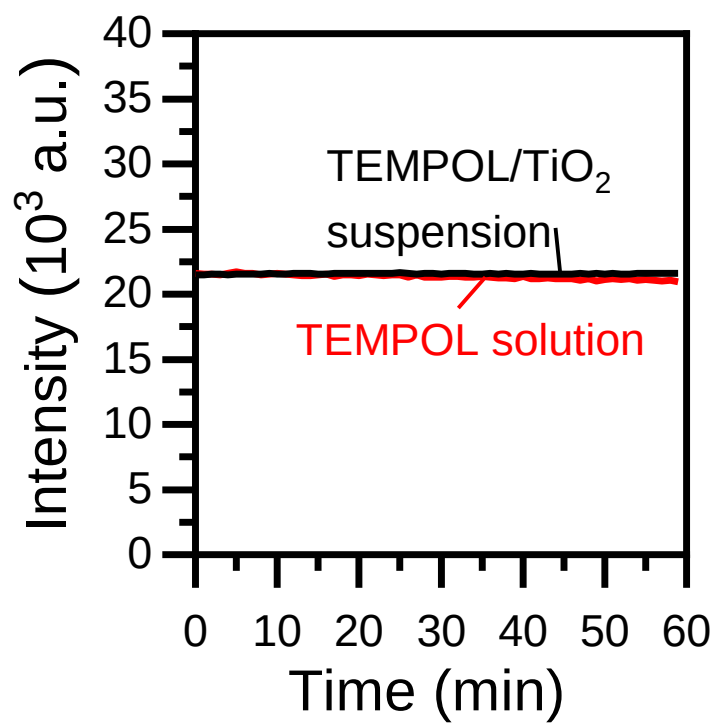


Figure 4. 7. Stability test for TEMPOL in water under UV(A) light (7 mW cm^{-2}) and in the dark in an aqueous suspension of TiO_2 .

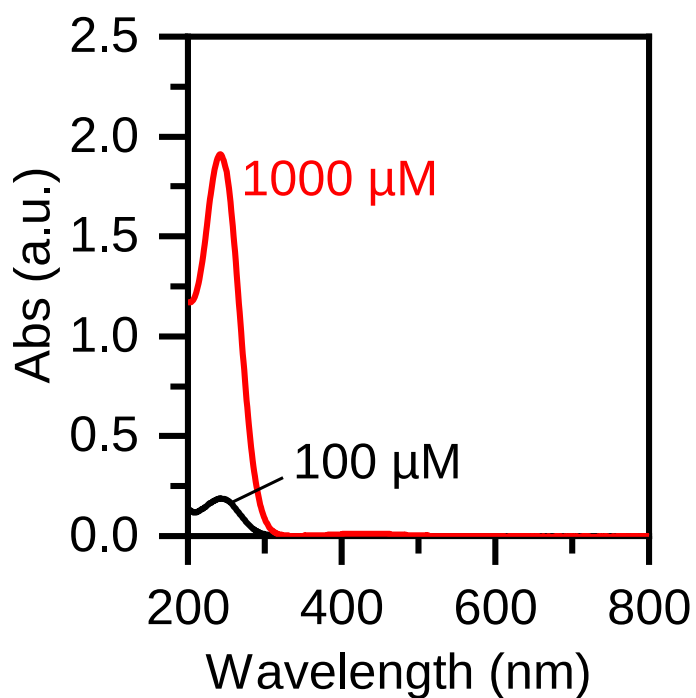


Figure 4. 8. UV-Vis spectra of TEMPOL aqueous solution.

4.3 Dark Adsorption of TEMPOL on TiO₂

For dark adsorption measurements, 5 mg of TiO₂ P25 was dispersed in 10 mL aqueous solutions of TEMPOL with different concentrations (namely, 25, 50, 75, 100, 125, 150, 200, and 250 μ M). The concentration of TEMPOL at each test was verified by using a calibration curve obtained from the EPR spectra of TEMPOL aqueous solutions measured under identified conditions. The prepared suspensions were kept under shaking at a speed of 200 rpm in the dark for 12 h at 25 °C. The small portions of the suspensions were then filtrated at specific time intervals, and then the EPR signals of each filtrate were recorded. Concentrations of TEMPOL in the different suspensions were verified by comparing the intensity of the EPR spectra with that of the standard TEMPOL solutions, as shown in Figure 4.9. Interestingly, no significant changes in the EPR signals have been observed even after 12 h of shaking compared to the blank samples, indicating that dark adsorption of TEMPOL on TiO₂ is negligible. According to the MB standard method, at least 12 hours are recommended to ensure the negligible influence of dark adsorption on the rate of the photocatalytic reaction [63]. Thus, unlike MB, the TEMPOL can be directly used without spending a long time performing the photocatalytic test.

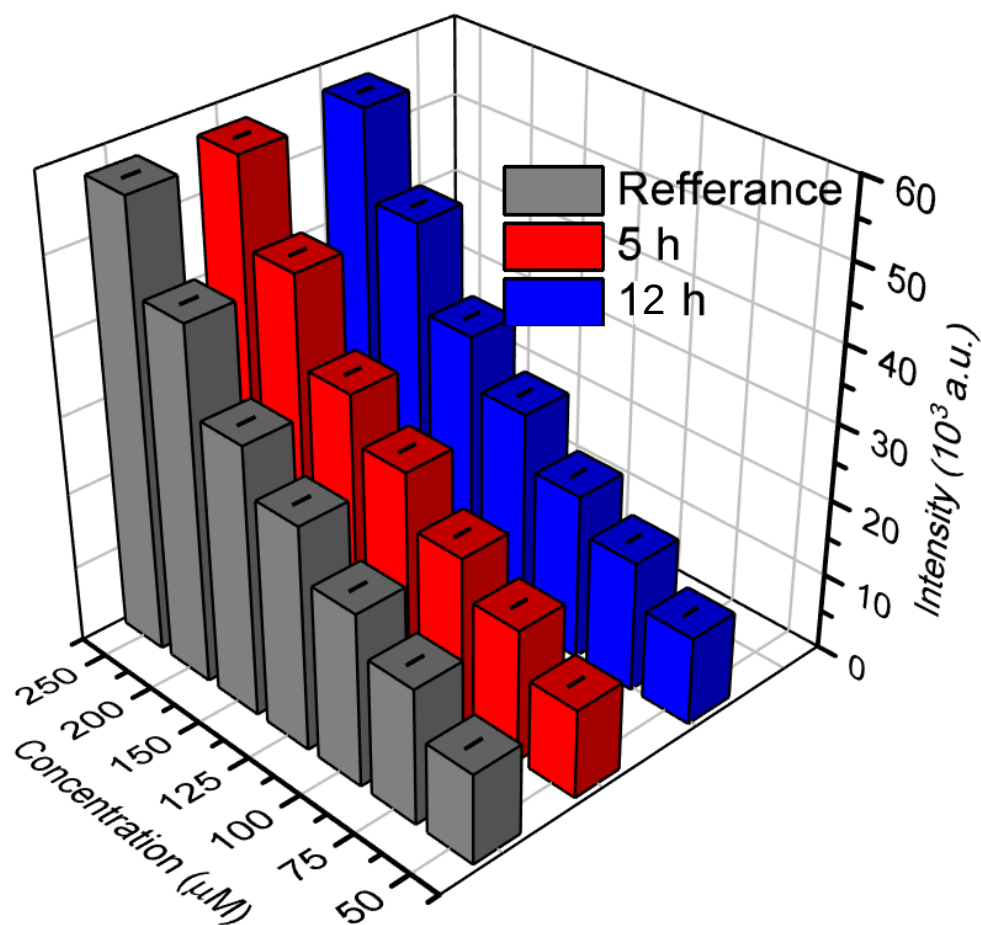
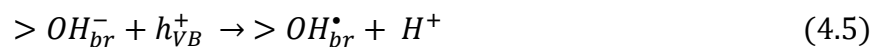


Figure 4. 9. Intensities of EPR signals were recorded for the filtrated TEMPOL aqueous suspensions after shaking for 5 and 11 h in the dark. The intensity of blank TEMPOL aqueous solutions, i.e., without adding titania, is also presented.

4.4 Photocatalytic Deactivation of TEMPOL over TiO₂ suspension

4.4.1 Typical EPR response

In photocatalysis, reactive oxygen species (ROS) are generally generated upon the illumination of the TiO₂ photocatalyst suspension with photons that have higher energy than its bandgap [70-72]. Upon the light absorption by the TiO₂ photocatalyst (Equation 4.1), electron/hole pairs are generated. The conduction band electrons (e_{CB}^-) diffuse to the surface and react with the molecular oxygen, leading to oxygen anion radicals ($O_2^{\bullet-}$, Equation 4.2). The latter can further react to form $HO_2^{\bullet}$ and H_2O_2 species, as shown in Equations 4.3 and 4.4, respectively. Whereas the valance band holes (h_{VB}^+) can be trapped either at the bridging oxygen anions or react with the surface adsorbed water leading to the formation of $>OH_{br}^{\bullet}$ or $\bullet OH$ radicals, as shown in Equation 4.5 and 4.6, respectively [71].



Distinguishing between the different types of $\bullet OH$ radicals is usually not possible, and hereafter the ' $\bullet OH$ radicals' term will be used to describe the $\bullet OH$ radicals formed through the different pathways. It is strongly believed that $OH^{\bullet}$ radicals are the main species

accountable for the photocatalytic oxidation of organic compounds. It is thus essential to find a model compound for assessing the photocatalytic activity based on the detection of the $\text{OH}^\bullet$ radicals. Interestingly, we found in this study that TEMPOL can react with the generated ROS species leading to the formation of an EPR silent compound. The proper employment of an EPR technique to directly measure the intensity without the need for sample filtration added essential advantages of using TEMPOL. Figure 4.10 shows the overlaid EPR signals of TEMPOL/ TiO_2 suspension measured under UV(A) illumination. 60 EPR spectra are recorded at a time interval of 1.0 min, but few of them are shown for clarity.

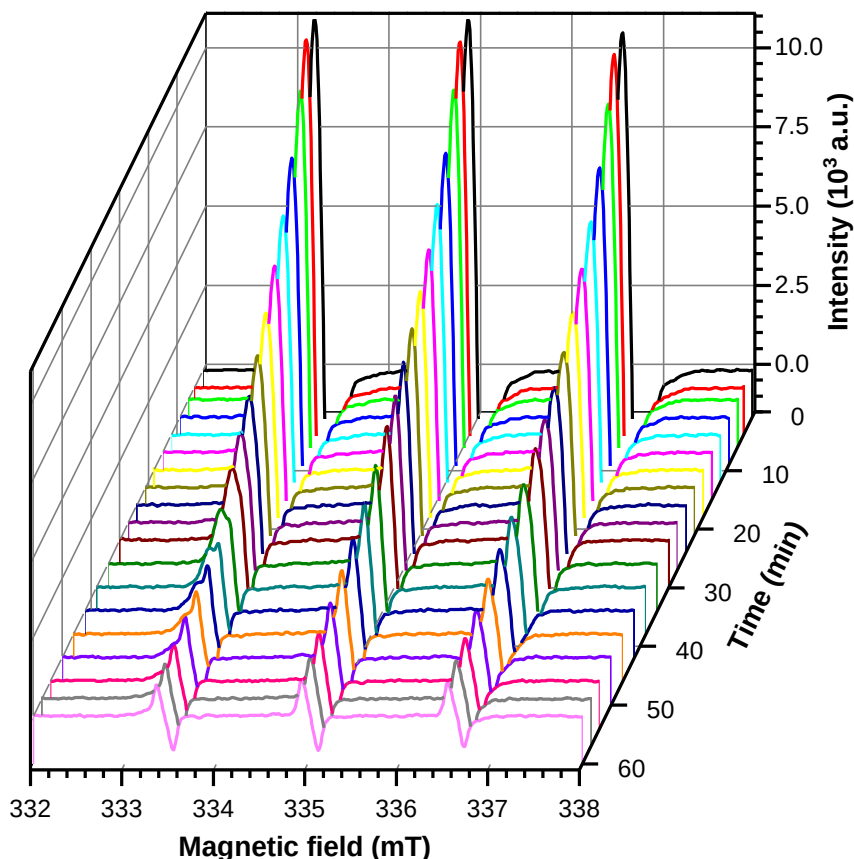


Figure 4. 10. Overlaid EPR signals for the photocatalytic deactivation of TEMPOL in presence of TiO_2 P25 under UV(A) light illumination. TEMPOL concentration was $100\ \mu\text{M}$, and Light intensity was $7\ \text{mW cm}^{-2}$.

4.4.2 Influence of TEMPOL Concentration and TiO₂ loading

According to the literature, TEMPOL reacts with the $\cdot\text{OH}$ leading to EPR silent products [89]. Consequently, the amount of the photo-catalytically generated $\cdot\text{OH}$ can be correlated to the TEMPOL-deactivated products. Figure 4.11 shows the profile of the photocatalytic deactivation of TEMPOL at different initial concentrations. Figure 4.12 shows the plot of $\ln(S_0/S_t)$ vs. time, where S_0 and S_t are the intensity of the EPR signal at $t = 0$ and t min, respectively. Linear plots have been observed within the early stage of the reaction for all investigated concentrations of TEMPOL.

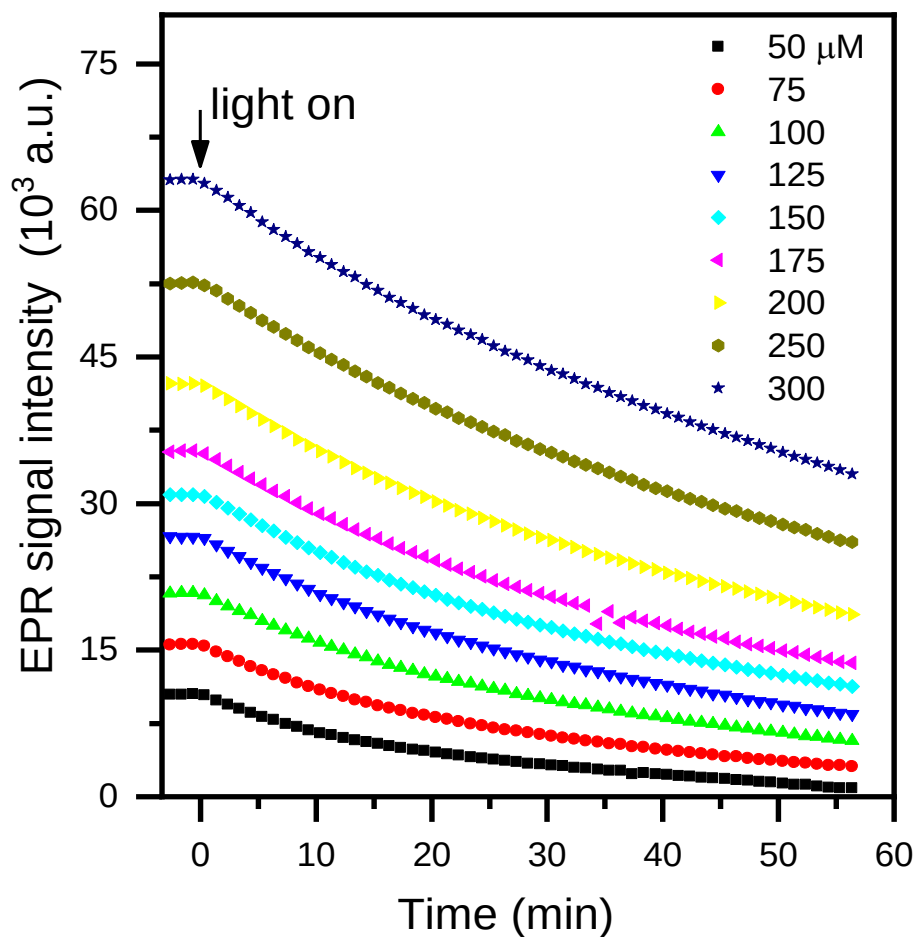


Figure 4. 11. Time course of photocatalytic deactivation of TEMPOL in the presence of TiO₂ P25 under UV(A) light illumination. TEMPOL concentration was 0-300 μM , Light intensity was 7 mW cm^{-2} .

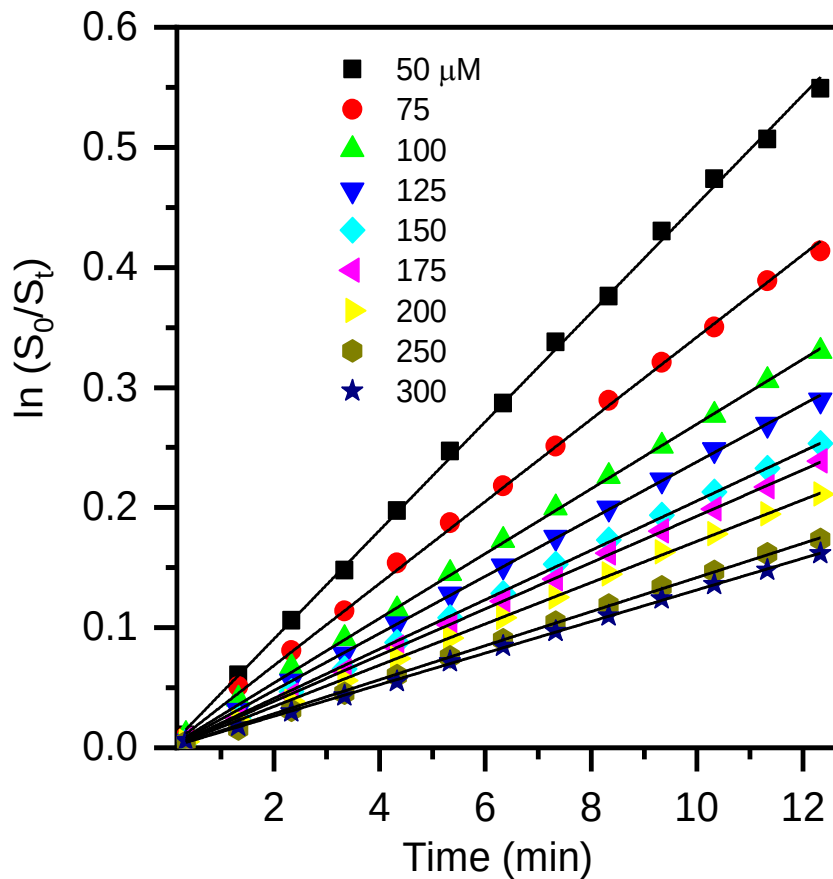


Figure 4. 12. kinetics of photocatalytic deactivation of TEMPOL in the presence of TiO₂ P25 under UV(A) light illumination. TEMPOL concentration was 050-300 μM , Light intensity was 7 mW cm^{-2} .

The initial rate of the photocatalytic deactivation of TEMPOL has been measured assuming first-order kinetic. The initial rate (R_0) of photocatalytic deactivation of TEMPOL has been calculated using Equation 4.7 and listed in Table 4.1,

$$R_o = k_{obs}[C_o] \quad (4.7)$$

where k_{obs} is the observed first-order rate constant derived from the slope of Figure 4.12, and C_0 is the initial concentration of TEMPOL in μM . It is observed that the initial rate increases with increasing the initial concentration of the TEMPOL up to 200 μM as shown in Figure 4.13. Then it levels off and reaches almost a saturation level.

Table 4. 1. Observed first order rate constants and initial rates (R₀) of the photocatalytic deactivation of TEMPOL under UV(A) light illumination using different initial concentration of TEMPOL

TEMPOL concentration (μM)	Slopes of $(\ln(S_0/S_t))$ vs time ($\text{s}^{-1} \times 10^4$)	R₀ ($\text{M.s}^{-1} \times 10^8$)
50.0	7.55	3.54
75.0	5.70	3.84
100	4.49	4.51
125	3.97	4.78
150	3.43	5.15
175	3.21	5.63
200	2.87	5.85
250	2.36	6.06
300	2.19	6.39

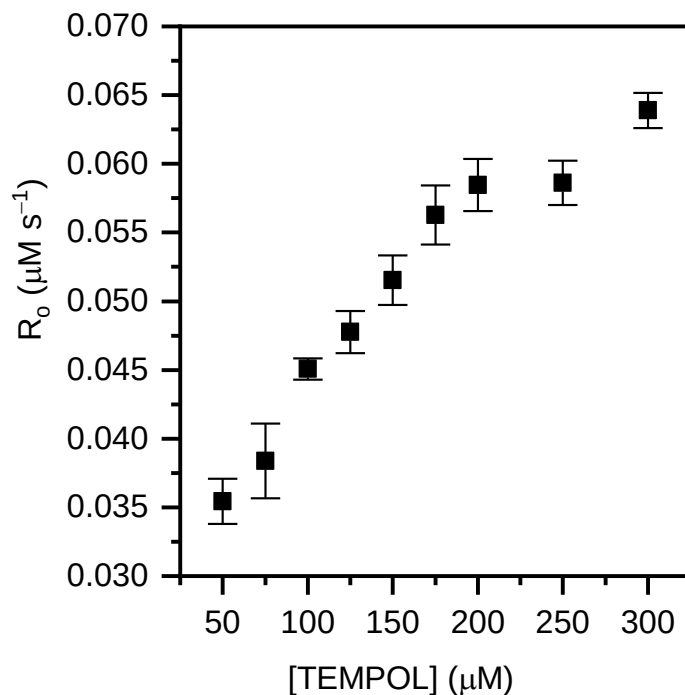


Figure 4. 13. Influence of TEMPOL concentration on the initial rate (R₀) of photocatalytic deactivation of TEMPOL under UV(A) light illumination by using TiO₂ P25 loading was 0.5 mg mL⁻¹ and different initial concentration of TEMPOL with a Light intensity 7 mW cm⁻².

As proven by the dark adsorption measurement, the adsorption of TEMPOL on the surface of TiO₂-P25 is negligible. Thus, the rate of the photocatalytic deactivation of TEMPOL is limited by the diffusion of TEMPOL toward the surface of the photocatalyst and/or by the availability of the $\cdot\text{OH}$ radicals on the surface. With increasing the concentration of the TEMPOL the flux of TEMPOL molecules diffusion towards the surface will increase, and thus the rate of the photocatalytic reaction increases. Beyond a specific limit ($\sim 200 \mu\text{M}$), the initial photocatalytic rate will be dominated by the availability of the surface $\cdot\text{OH}$ radicals, and thus the rate of TEMPOL deactivation starts to level off.

In a similar way, the influence of TiO₂-P25 loading on photocatalytic deactivation was also investigated and presented in Figure 4.14 (a and b) and the results data are listed in Table 4.2. The initial rate was found to increase with increasing the loading, and 0.5 g L⁻¹ was sufficient to reach the highest activity. The same trend has been previously reported for TiO₂-P25 with other model compounds [155].

Table 4. 2. Observed first order rate constants and initial rates (R_0) of the photocatalytic deactivation of TEMPOL under UV(A) light illumination using different TiO₂ loading.

TiO₂ loading (mg mL⁻¹)	Slopes of (ln(S₀/S_t)) vs time (s⁻¹ × 10⁴)	R₀ (M.s⁻¹ × 10⁸)
0.1	3.04	3.04
0.2	6.71	6.51
0.3	7.29	7.79
0.5	9.42	9.42
0.7	10.4	10.4
0.9	10.9	10.9

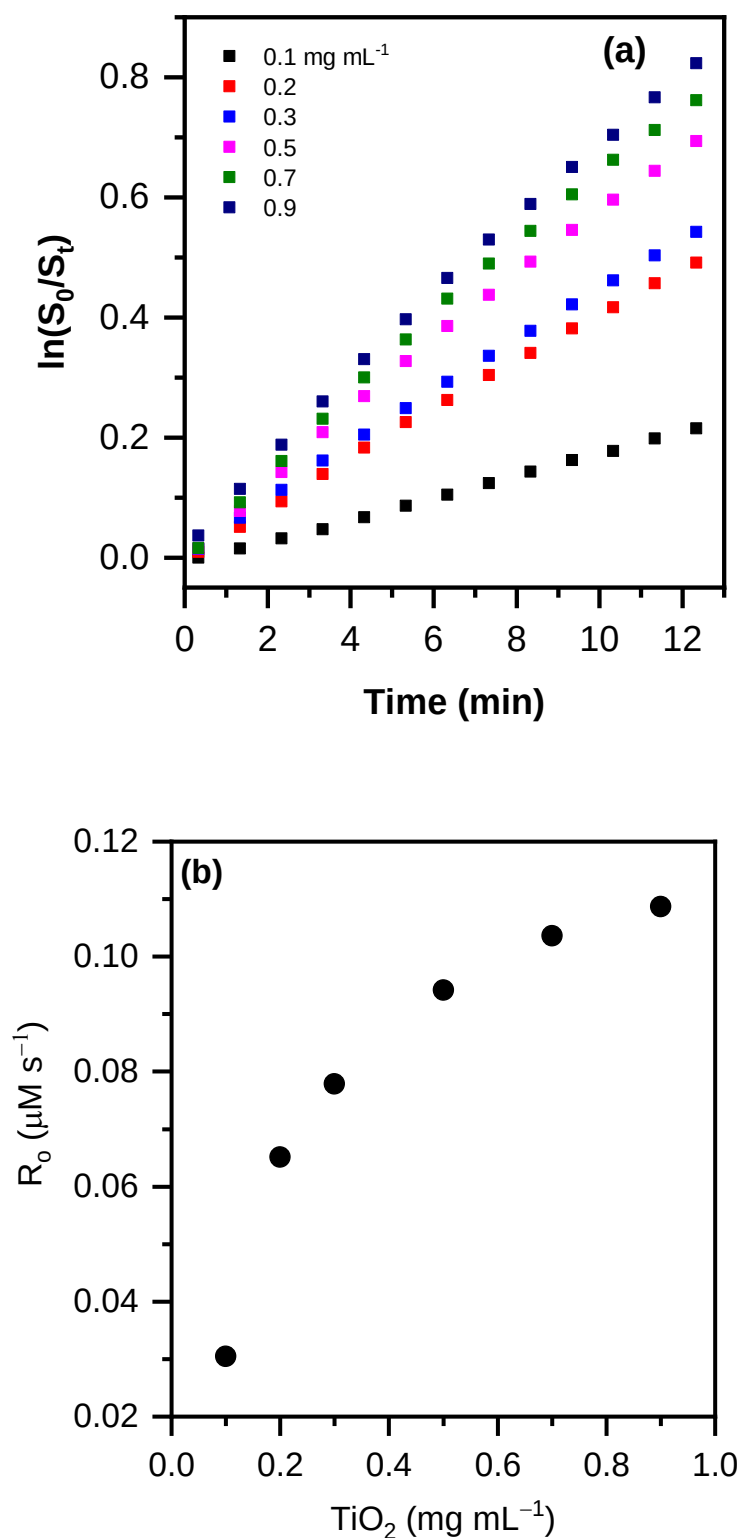


Figure 4. 14. Influence of TiO_2 P25 loading on the photocatalytic deactivation of TEMPOL processes under UV(A) light illumination. Part (a) Rate law of the TiO_2 P25 loading; and Part (b) The initial rate (R_0) of the deactivation of TEMPOL having concentration 100 μM , Light intensity was 7 mW cm^{-2} .

4.4.3 Influence of Light Intensity

The influence of light intensity on the rate of photocatalytic reaction is a crucial parameter. Figure 4.15 shows the profile of TEMPOL deactivation measured in the presence of TiO₂-P25 at different light intensities ranging from 2.0 to 45 mW cm⁻². The corresponding plot of $\ln(S_0/S_t)$ versus time is presented in Figure 4.16 and the estimated rate constants as well as the initial rates values are reported in Table 4.3.

Table 4. 3. Observed first order rate constants and initial rates (R_0) of the photocatalytic deactivation of TEMPOL under UV(A) light illumination using light intensity.

Light Intensity (mW cm⁻²)	Slopes of ($\ln(S_0/S_t)$) vs time (s⁻¹ × 10⁴)	R_0 (M.s⁻¹ × 10⁸)
1.90	2.12	2.07
7.60	4.99	4.88
13.2	6.49	6.47
19.9	8.56	8.32
27.4	9.64	9.39
32.2	10.8	10.3
37.8	11.6	11.0
45.4	11.8	11.4

It is found that the initial rate of TEMPOL deactivation increases with increasing the light intensity due to the expected increase of photogenerated [•]OH concentration by increasing the light intensity. At very high light intensity, the rate starts to level off, which can be attributed to the saturation of the photocatalyst active sites with surface-bound [•]OH radicals. Thus, any further increase in light intensity will lead to complete recombination for the photogenerated electron/hole pairs. It can also be attributed to the limited availability of TEMPOL at the surface of the photocatalyst.

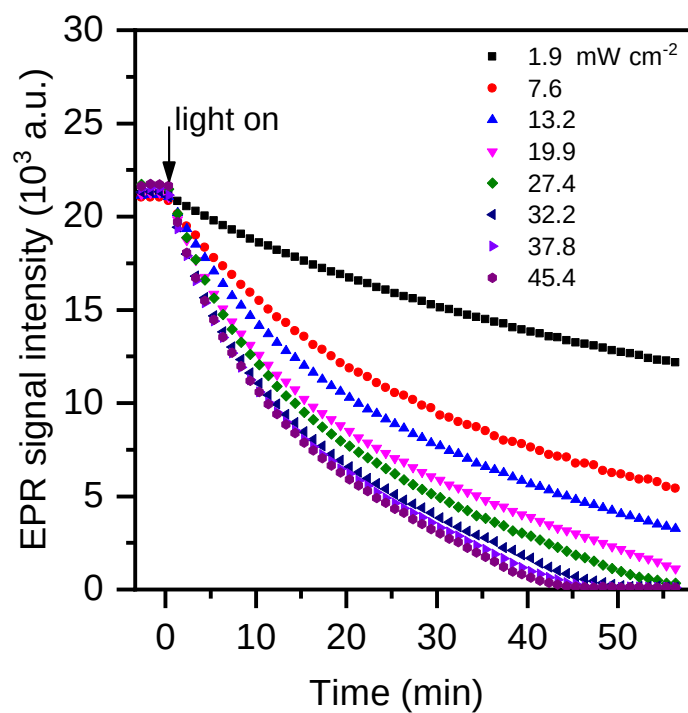


Figure 4. 15. Time course of photocatalytic deactivation of TEMPOL in presence of TiO₂ P25 under UV(A) light illumination at different intensities. TEMPOL concentration was 100 μ M.

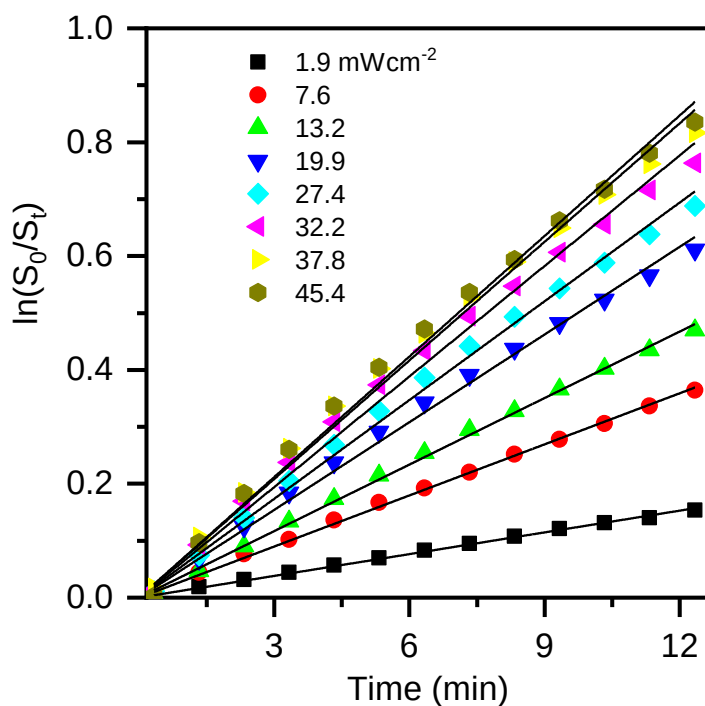


Figure 4. 16. Kinetics of photocatalytic deactivation of TEMPOL in presence of TiO₂ P25 under UV(A) light illumination at different intensities. TEMPOL concentration was 100 μ M.

Figure 4.17 shows the relation between the initial rates of TEMPOL deactivation initial photonic efficiency (ξ_0) versus the photon flux. The initial photonic efficiency deactivation relation with the photon flux (I_{hv}) described by an empirical kinetic expression shown in Equation 4.88 and by using its linearized form (Equation 4.9), as shown in Figure 4.18, produced the slope value of $(\beta - 1)$ [156].

$$\xi_0 = V k_r \frac{K C_0}{1 + K C_0} \eta (I_{hv})^{\beta-1} \quad (4.8)$$

$$\log (\xi_0) = \log \left(V k_r \frac{K C_0}{1 + K C_0} \eta \right) + (\beta - 1) \log (I_{hv}) \quad (4.9)$$

Figure 4.17 shows the relation between the initial rates of TEMPOL deactivation initial photonic efficiency (ξ_0) versus the photon flux. The initial photonic efficiency deactivation relation with the photon flux (I_{hv}) described by an empirical kinetic expression shown in Equation 4.10 and by using its linearized form (Equation 4.11), as shown in Figure 4.18, produced the slope value of $(\beta - 1)$ [156].

$$\xi_0 = V k_r \frac{K C_0}{1 + K C_0} \eta (I_{hv})^{\beta-1} \quad (4.10)$$

$$\log (\xi_0) = \log \left(V k_r \frac{K C_0}{1 + K C_0} \eta \right) + (\beta - 1) \log (I_{hv}) \quad (4.11)$$

where A is the illuminated area, I is the incident light intensity, λ is the wavelength of the incident light, N_A is Avogadro's number, h is the plank's constant, and c is the velocity of light.

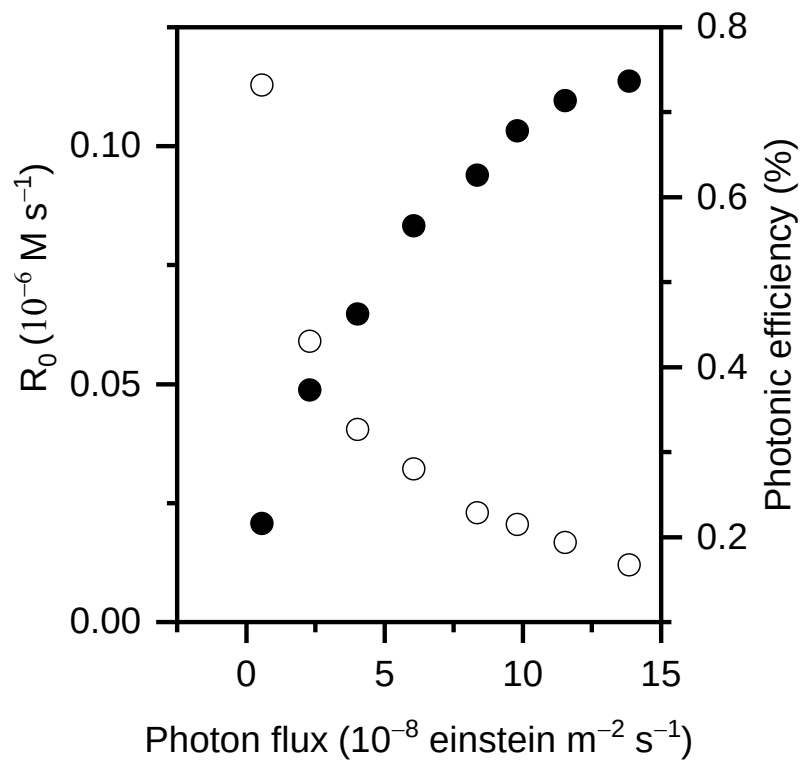


Figure 4. 17. Plot of initial rate (R_0) and photonic efficiency (ξ_0) versus photon flux, TEMPOL concentration was 100 μ M.

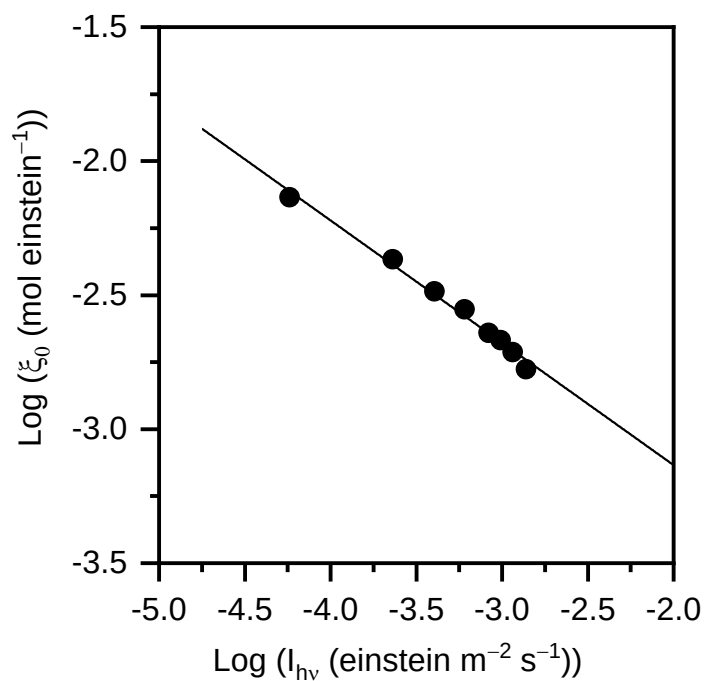


Figure 4. 18. Plot of $\log(\xi_0)$ versus the photon flux $\log(I_{hv})$. TEMPOL concentration was 100 μ M.

Figure 4.17 shows a non-linear relation having a plateau at high photon flux, whereas the photonic efficiency shows a non-linear decrease with increasing photon flux. In Figure 4.18 the plot of $\log(\xi_0)$ versus the photon flux gives a straight line with a slope equal to $(\beta - 1)$, where β value was found to be 0.54. The β is an empirical constant related to the ratio between interfacial charge transfer and recombination of the charge carriers that depends on the photocatalytic materials. The obtained β is comparable to the reported value (0.5) of many photocatalytic systems as concluded from the linear dependence between the square root of the absorbed light intensity and the photonic efficiency of TiO₂-aqueous suspension [70, 155].

4.5 Proposed mechanisms of the Photocatalytic Deactivation of TEMPOL

It is more likely that the deactivation of TEMPOL occurs through oxidation by the photogenerated $\cdot\text{OH}$ radicals [89]. Generally, in photocatalysis, molecular oxygen is used as an electron acceptor that reacts very fast with the photogenerated electrons (within 100 ns to 100 μs), leading to the formation of $\text{O}_2^{\cdot-}$ [71]. The produced oxygen radical molecule might further react to form $\cdot\text{OH}$ radicals; however, the primary $\cdot\text{OH}$ radicals are produced via the valance band holes. To identify the non-radical final products resulting from the photocatalytic deactivation of TEMPOL, sets of photocatalytic tests have been performed in the presence of oxygen as an electron acceptor, in the absence of oxygen (continuously purging with nitrogen gas), and in the presence of methanol to trap the $\cdot\text{OH}$ radicals. Figure 4.19 shows the time course of these EPR-photocatalytic tests at 1000 μM TEMPOL over 8 hours. It is apparent from figure that the presence or the absence of the electron acceptor (molecular oxygen) does not significantly change the initial rate of TEMPOL deactivation,

especially during the first hour of the process. Only about 20% and 25% of TEMPOL are deactivated in the presence and absence of oxygen, respectively.

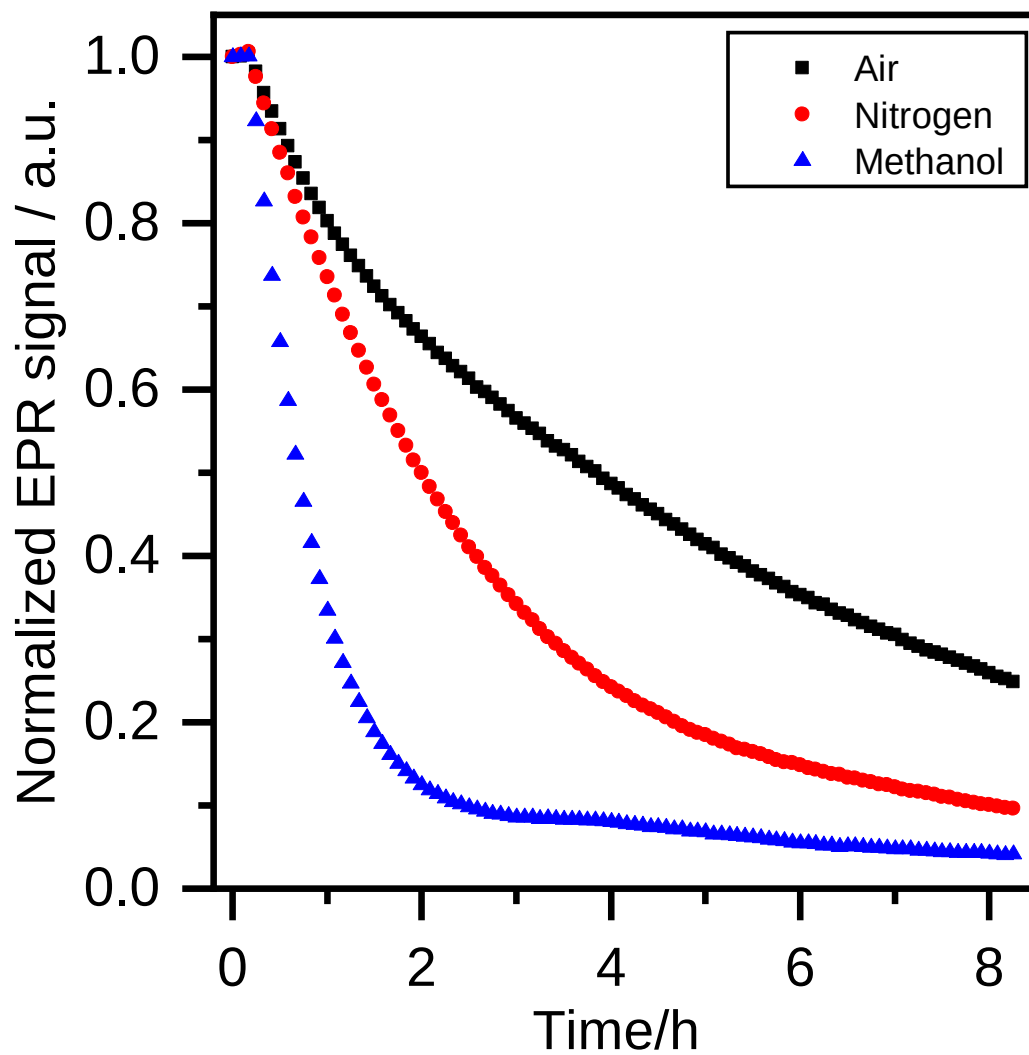


Figure 4. 19. Rates of the photocatalytic deactivation of TEMPOL over TiO_2 P25 under UV(A) light illumination in the presence and absence of an electron acceptor (i.e. O_2) and the presence of methanol as an electron donor.

4.5.1 Product analysis in the presence of oxygen (O₂)

The TEMPOL photocatalytic deactivation products detected in the presence of oxygen are in good agreement with the recently published work by D. L. Marshall et al. [157]. The deactivation decay of the photocatalytic reaction of TEMPOL in the presence of TiO₂ P25 under UV(A) light illumination in the presence of air is shown Figure 4.20. The results indicated that only 20% TEMPOL is deactivated in the presence of oxygen and the remaining 80% could be TEMPOL or other nitroxide radical species.

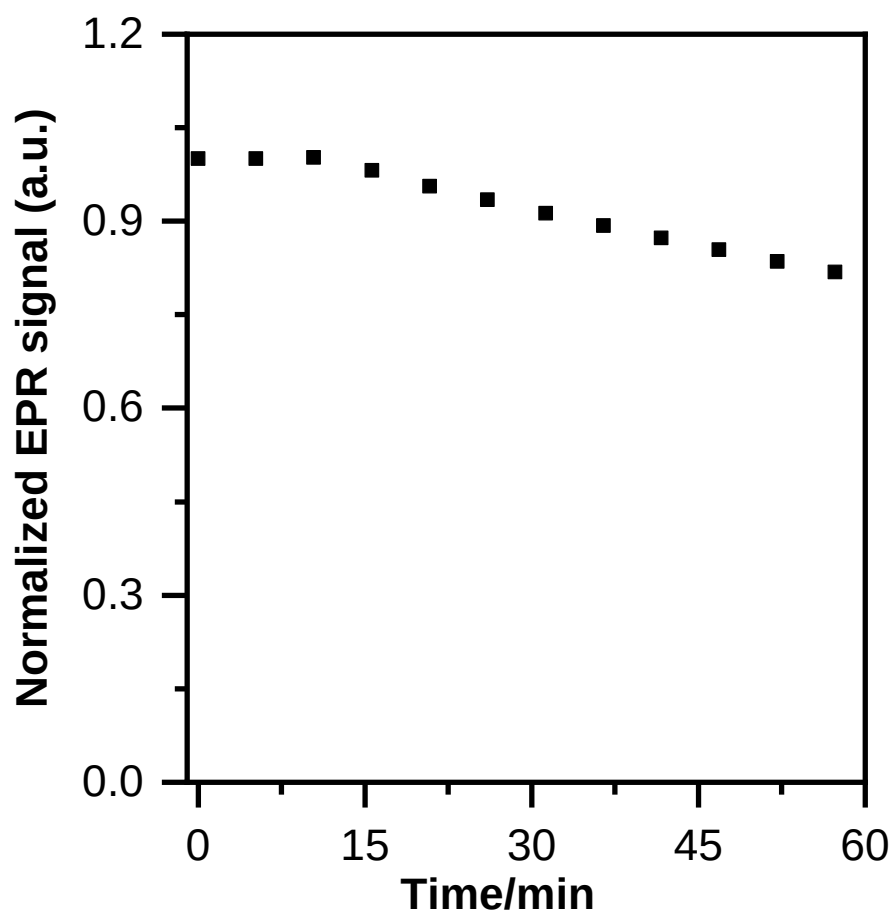


Figure 4. 20. Rates of the photocatalytic deactivation of TEMPOL over TiO₂ P25 under UV(A) light illumination in the presence of an electron acceptor (i.e. O₂).

The molecular models of the most possible radical species namely, TEMPOL and TEMPONE, have been used to optimize their molecular geometry and to estimate their hyperfine constants. Figure 4.21 shows the optimized TEMPOL and TEMPONE Molecular geometries with their atomic number labels that are used in the DFT-UB3LYP's EPR-molecular orbital calculations with a 6-31G+ basis set. The estimated isotropic Fermi constants, i.e., hyperfine constants, coupling per the active isotope of atom of TEMPOL and TEMPONE are listed in Tables 4.4 and 4.5, respectively.

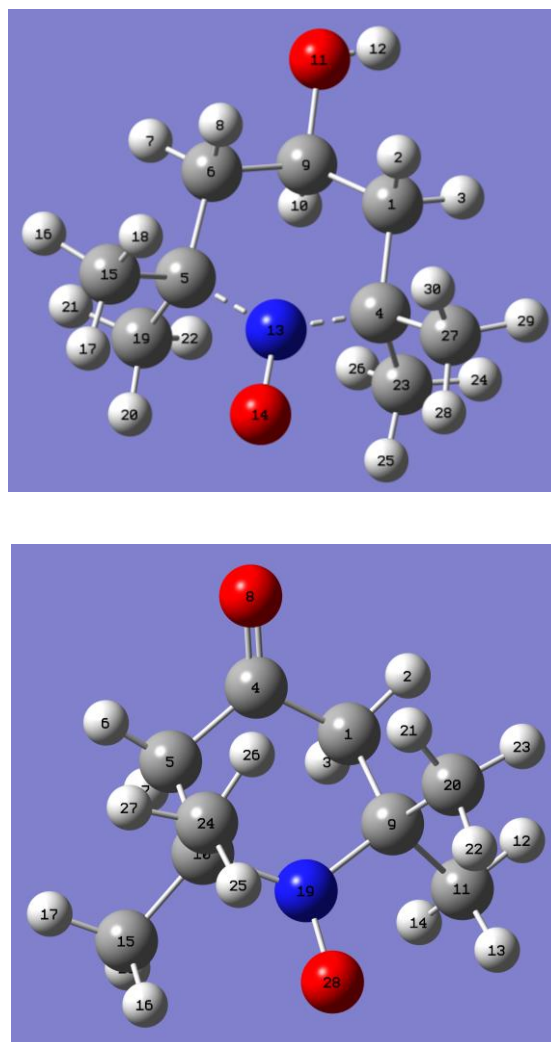


Figure 4. 21. The optimized molecular geometry of (a) TEMPOL and (b) TEMPONE with their atomic number labs used in the DFT calculations of the EPR hyperfine constants per atom.

Table 4. 4. The estimated isotopic Fermi coupling (i.e. Hyperfine coupling) constants of TEMPOL using different units.

Atoms		Isotropic Fermi Constant Couplings			
Number	Isotope	a.u.	MegaHertz	Gauss	cm ⁻¹ / (10 ⁻⁴)
1	C(13)	0.0012	1.34782	0.48094	0.44958
2	H(1)	-0.00013	-0.60019	-0.21416	-0.2002
3	H(1)	-0.00034	-1.50615	-0.53743	-0.5024
4	C(13)	-0.01096	-12.3263	-4.39833	-4.11161
5	C(13)	-0.01075	-12.08496	-4.31221	-4.03111
6	C(13)	0.00125	1.401	0.49991	0.46732
7	H(1)	-0.00036	-1.62116	-0.57847	-0.54076
8	H(1)	-0.00014	-0.61724	-0.22025	-0.20589
9	C(13)	-0.00045	-0.50607	-0.18058	-0.16881
10	H(1)	0.00003	0.12117	0.04324	0.04042
11	O(17)	0.00035	-0.21377	-0.07628	-0.0713
12	H(1)	0.00000	0.02147	0.00766	0.00716
13	N(14)	0.13342	43.10828	15.38211	14.37938
14	O(17)	0.11622	-70.45217	-25.13909	-23.50031
15	C(13)	0.00743	8.35743	2.98214	2.78774
16	H(1)	-0.00045	-2.01327	-0.71839	-0.67156
17	H(1)	-0.00022	-0.97772	-0.34887	-0.32613
18	H(1)	-0.00026	-1.16027	-0.41401	-0.38703
19	C(13)	0.01613	18.13379	6.47059	6.04878
20	H(1)	-0.00063	-2.83277	-1.0108	-0.94491
21	H(1)	0.00075	3.35464	1.19702	1.11899
22	H(1)	-0.00045	-2.00098	-0.714	-0.66745
23	C(13)	0.01626	18.27525	6.52106	6.09597
24	H(1)	0.00074	3.32295	1.18571	1.10842
25	H(1)	-0.00063	-2.83721	-1.01239	-0.94639
26	H(1)	-0.00045	-2.00116	-0.71406	-0.66751
27	C(13)	0.00751	8.44739	3.01424	2.81774
28	H(1)	-0.00022	-0.97871	-0.34923	-0.32646
29	H(1)	-0.00045	-2.01666	-0.71959	-0.67268
30	H(1)	-0.00026	-1.16952	-0.41731	-0.39011

Table 4. 5. The estimated isotopic Fermi coupling (i.e. Hyperfine coupling) constants of TEMPONE using different units.

Atoms		Isotropic Fermi Constant Couplings			
Number	Isotope	a.u.	MegaHertz	Gauss	cm ⁻¹ / (10 ⁻⁴)
1	C(13)	0.00201	2.25585	0.80494	0.75247
2	H(1)	-0.0003	-1.3346	-0.47622	-0.44518
3	H(1)	-0.00016	-0.71947	-0.25672	-0.23999
4	C(13)	-0.00054	-0.60509	-0.21591	-0.20184
5	C(13)	0.00201	2.25585	0.80494	0.75247
6	H(1)	-0.0003	-1.3346	-0.47622	-0.44518
7	H(1)	-0.00016	-0.71947	-0.25672	-0.23999
8	O(17)	0.00042	-0.25175	-0.08983	-0.08398
9	C(13)	-0.01097	-12.33592	-4.40176	-4.11482
10	C(13)	-0.01097	-12.33592	-4.40176	-4.11482
11	C(13)	0.00635	7.13631	2.54641	2.38042
12	H(1)	-0.00048	-2.16713	-0.77329	-0.72288
13	H(1)	-0.00018	-0.80725	-0.28805	-0.26927
14	H(1)	-0.0002	-0.90239	-0.32199	-0.301
15	C(13)	0.00635	7.13631	2.54641	2.38042
16	H(1)	-0.00018	-0.80725	-0.28805	-0.26927
17	H(1)	-0.00048	-2.16713	-0.77329	-0.72288
18	H(1)	-0.0002	-0.90239	-0.32199	-0.301
19	N(14)	0.13239	42.77719	15.26397	14.26894
20	C(13)	0.01616	18.1629	6.48098	6.05849
21	H(1)	-0.00044	-1.95046	-0.69597	-0.6506
22	H(1)	-0.00062	-2.78945	-0.99535	-0.93046
23	H(1)	0.00099	4.43519	1.58259	1.47942
24	C(13)	0.01616	18.1629	6.48098	6.05849
25	H(1)	-0.00062	-2.78945	-0.99535	-0.93046
26	H(1)	-0.00044	-1.95046	-0.69597	-0.6506
27	H(1)	0.00099	4.43519	1.58259	1.47942
28	O(17)	0.11724	-71.06889	-25.35914	-23.70603

The EPR spectrum peaks in Figure 4.22 indicated that TEMPOL and its oxidized form TEMPONE are the only nitroxide species existing by the photocatalysis process. The comparison between the observed and estimated hyperfine values of TEMPOL and

TEMPONE (see Table 4.6) confirm the accuracy of the used computational models and TEMPOL and TEMPONE are the only existing nitoxide radicals by the end of the reaction mixture in addition to a 20% conversion to a non-radical product(s).

Table 4. 6. The hyperfine coupling constants of experimental and theoretical estimated values of TEMPOL and TEMPONE by the end of a photochemical deactivation reaction mixture of Tempol in the presence of O₂.

	Hyperfine values (gauss)	Hyperfine values (gauss)	Radical %
	Experimental	Theoretical	Distribution
TEMPOL	15.0	15.38	48
TEMPONE	14.9	15.26	52

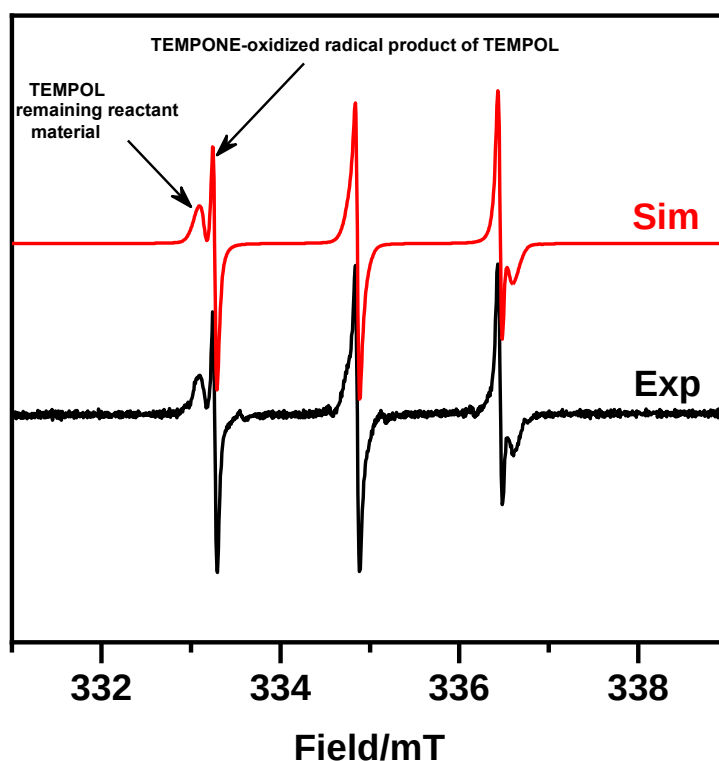


Figure 4. 22. EPR signal recorded after one hour of the photocatalytic deactivation of 100 mM TEMPOL purged with dry air. The simulated spectrum using 48% TEMPOL and 52% TEMPONE radical parameters is also given. TiO₂ P25 loading was 1.0 mg mL⁻¹ and light intensity was 7.0 mW cm⁻².

The exact percentage of these two radicals obtained by using WinSim-EPR software with hyperfine coupling constants of nitrogen, the most abundant isotope and has the highest constant of the optimized structures and the only contributor to the observed triplet ERP-

peaks. The comparison between the simulated spectrum and the experimental ones indicated that 39 % TEMPOL and 41 % TEMPONE is present in the remaining reaction mixture.

For NMR spectroscopic experiments, several photocatalytic tests were conducted. At the end of the test, the suspended TiO_2 was separated by filtration using a syringe filter (Millipore, PTFE 0.2 μm), and the filtrates were subjected to complete slow vaporization at 50 °C. The residues of the reaction mixture were added to each other's and were then dissolved in deuterated-chloroform and transferred into a regular 5-mm NMR tube. ^1H -NMR and ^{13}C -NMR spectroscopy tests were performed to characterize the non-radical product(s) using a Bruker NMR 400 MHz Avance III spectrometer (Bruker Corporation, Billerica, MA, USA). The analysis of the NMR results of the residues of the reaction mixture confirmed that only single non-radical product, namely, 4-oxo-2,2,6,6-tetramethylpiperidine, is produced as shown in Figure 4.23 and Figure 4.24, what are attributed to ^1H -NMR and ^{13}C -NMR, respectively.

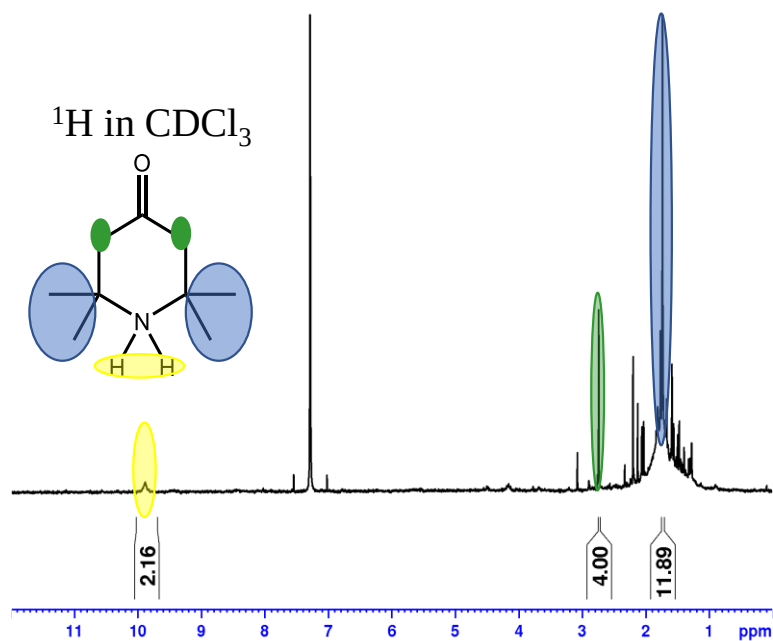


Figure 4. 23. ¹H-NMR, spectra of the non-radical products extracted in deuterated chloroform after the photocatalytic deactivation of 1000 μ M TEMPOL after 8 h irradiation. TiO₂ P25 loading was 1.0 mg mL⁻¹ and light intensity was 7.0 mW cm⁻².

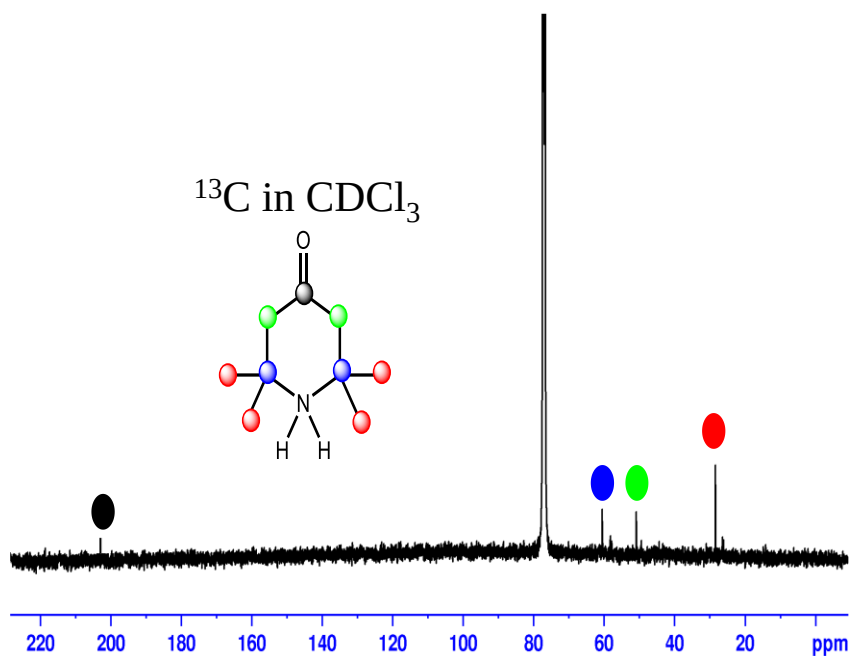


Figure 4. 24. ¹³C-NMR spectra of the non-radical products extracted in deuterated chloroform after the photocatalytic deactivation of 1000 μ M TEMPOL after 8 h irradiation. TiO₂ P25 loading was 1.0 mg mL⁻¹ and light intensity was 7.0 mW cm⁻².

Based on the NMR and EPR analysis results and the computed models of the Marshall group [157], the possible mechanism of photocatalytic deactivation of TEMPOL is proposed. In this mechanism, the photogenerated $\text{OH}^\bullet$ radicals firstly convert part of the TEMPOL to TEMPONE through α -proton abstraction at the 4-piperidine position. Then they will continue the deactivation process at the nitroxide group of TEMPONE to produce the non-radical product 4-oxo-tetramethylpiperidine (Figure 4.25).

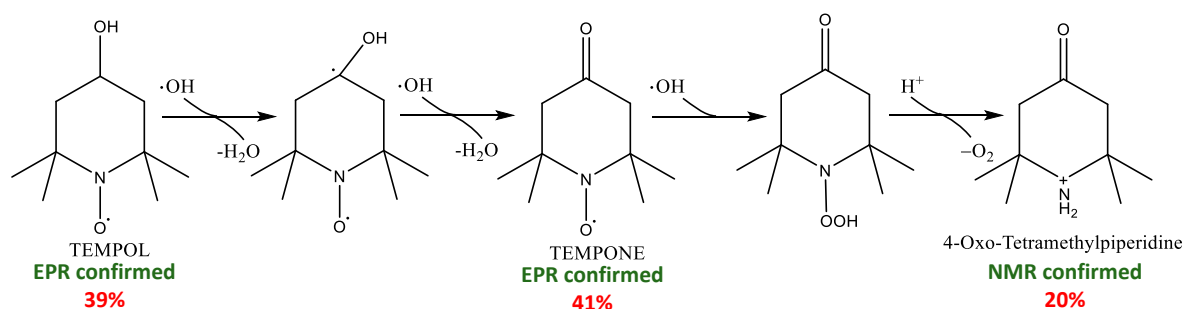


Figure 4. 25. Proposed hydroxyl radical deactivation of tempol in the presence of air and nitrogen to form TEMPONE and none radical 4-oxo-tetramethylpiperidine in addition to the starting materials.

4.5.2 Product analysis in the presence of oxygen (O_2) and methanol

In the presence of methanol in aerated solution, the initial rate of TEMPOL deactivation increased by four times compared to that observed in the absence of methanol. The observed enhancement of TEMPOL deactivation could be correlated with the known ability of methanol to react with the photogenerated holes within less than 10 ns and/or $\text{OH}^\bullet$ radicals to form α -hydroxyl radicals ($\text{CH}_2\text{OH}^\bullet$) [59, 158-160]. The reaction was carried out up to 8h to analyze the complete deactivation of TEMPOL to final products. Figure 4.26 showing the deactivation of TEMPOL up to 8h.

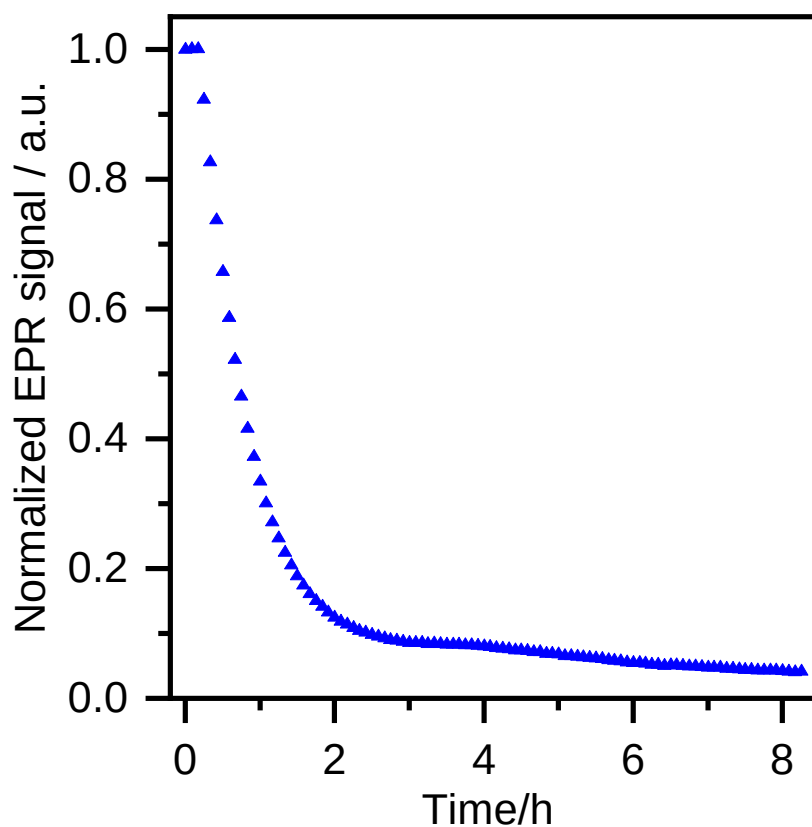


Figure 4. 26. Rates of the photocatalytic deactivation of TEMPOL over TiO₂ P25 under UV(A) light illumination in the presence of oxygen and methanol.

The deactivation results of TEMPOL indicated that almost 95% TEMPOL is converted into non-radical product(s) and a remaining of 5% nitroxide radical(s) as paramagnetic species are obtained. The use of the estimated hyperfine coupling constants (Table 4.7) of TEMPOL and TEMPONE in the SimWin-EPR simulation software (see Figure 4.27) indicated that by the end of the reaction the 5% radicals are only related to TEMPOL and its oxidized form, namely TEMPONE. The exact percentage of these two radicals obtained by using WinSim-EPR software indicated that only 4.7 % are in the form of TEMPOL and 0.25 % are converted to TEMPONE in the remaining reaction mixture.

Table 4. 7. The hyperfine coupling constants of experimental and theoretical estimated values of TEMPOL and TEMPONE by the end of a photochemical deactivation reaction of TEMPOL in the presence of O₂ and methanol.

	Hyperfine values (gauss)	Hyperfine values (gauss)	Radical %
	Experimental	Theoretical	Distribution
TEMPOL	15.0	15.38	95
TEMPONE	14.9	15.26	5

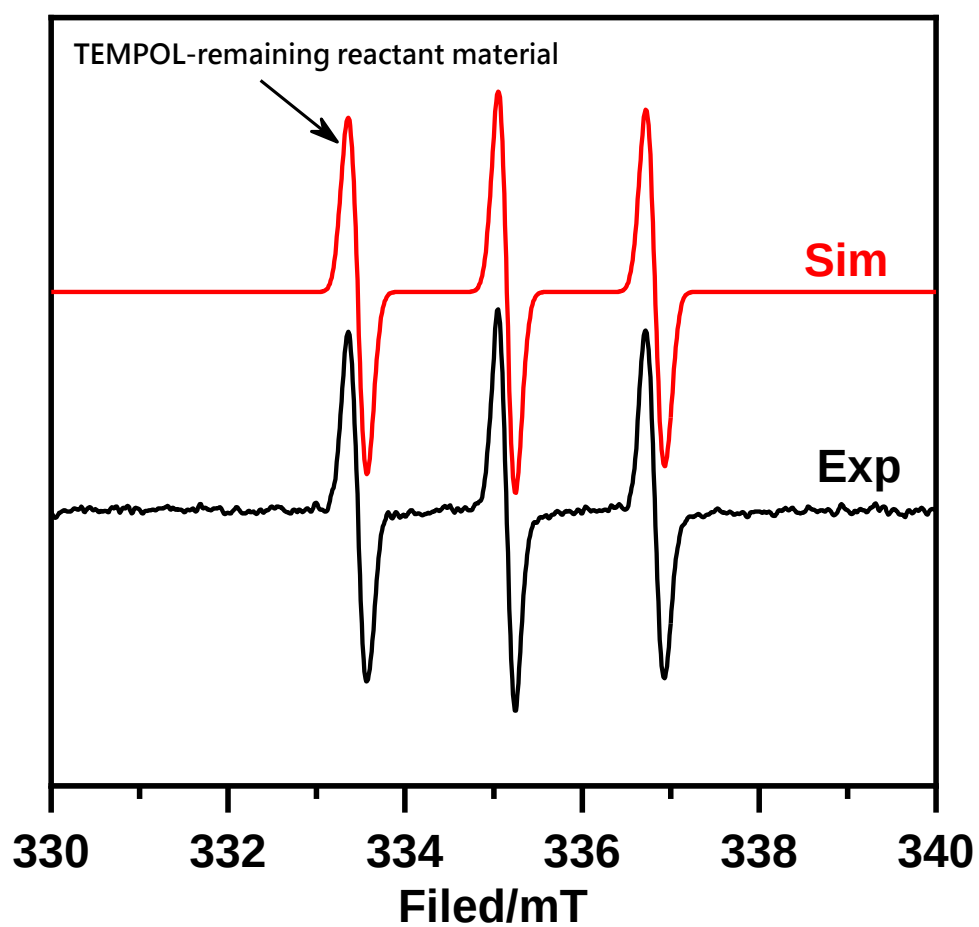


Figure 4. 27. EPR signal was recorded after one hour of the photocatalytic deactivation of 100 μM TEMPOL in presence of 100 mM methanol and purged with dry air. The simulated spectra using 95% TEMPOL and 5% TEMPONE radical parameters are also given in parts. TiO₂ P25 loading was 1.0 mg mL⁻¹ and light intensity was 7.0 mW cm⁻².

Similar to the air-saturated reaction mixture, the residues of the reaction mixture containing methanol has been tested by NMR using the dissolved residues in deuterated-chloroform that are transferred into a regular 5-mm NMR tube and then tested by ^1H -NMR spectroscopy to characterize the non-radical product(s). The obtained results are shown in Figure 4.28. The analysis of this NMR indicated that mostly a single deactivated products of TEMPOL is produced, namely, 4-hydroxyl-tetramethypiperidine (Figure 4.28).

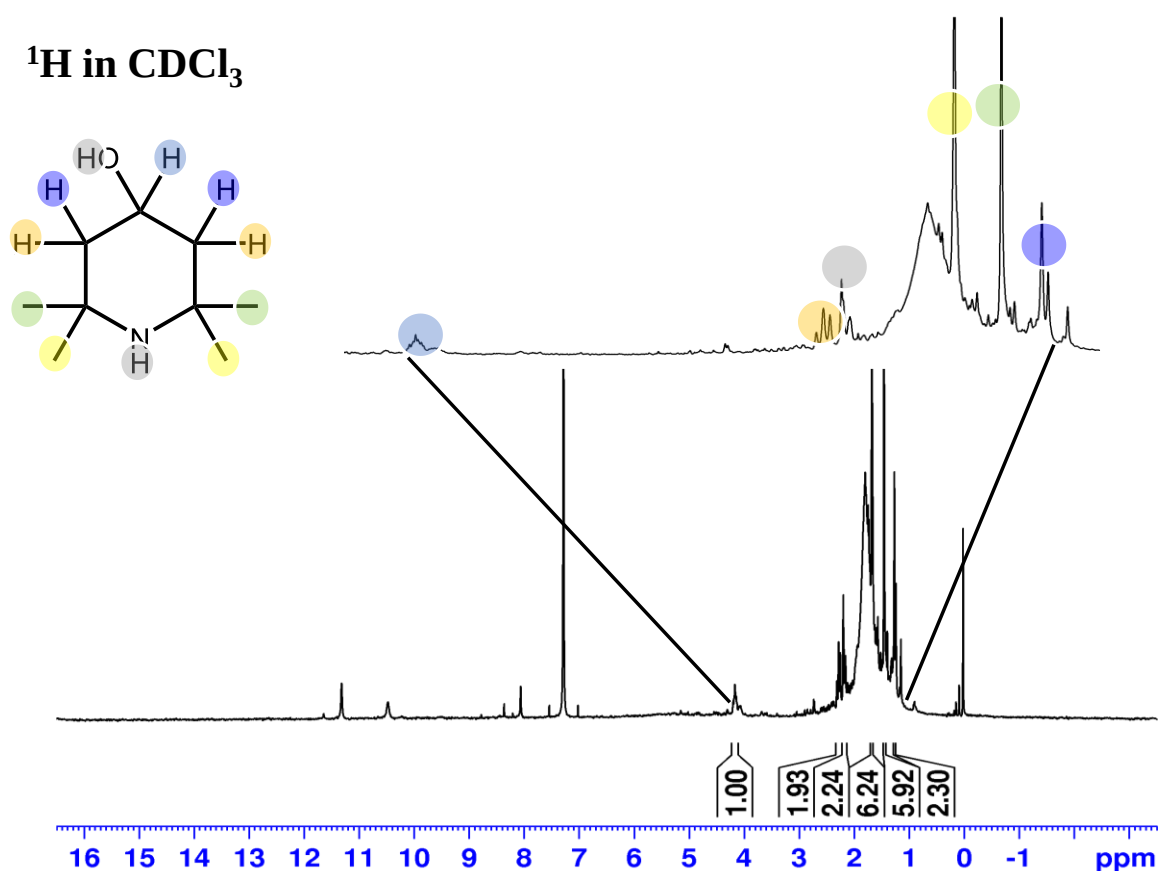


Figure 4. 28. ^1H -NMR spectra of the non-radical products extracted in deuterated chloroform after the photocatalytic deactivation of 1000 μM TEMPOL after 8 h irradiation. TiO_2 P25 loading was 1.0 mg mL^{-1} and light intensity was 7.0 mW cm^{-2} .

Based on the above photocatalytic results, product analysis, and the proposed computational models by Marshall et al.[157], the mechanism of TEMPOL deactivation in the presence of methanol is presented in Figure 4.29. It consists of two parallel pathways, a minor one to form TEMPONE initiated by direct-attach of $\cdot\text{OH}$ radicals at the α -hydrogen in the 4-piperidine position. While the major path starts with the α -hydroxyl radicals ($\cdot\text{CH}_2\text{OH}$) attack at the nitroxide side of TEMPOL to produce the none radical product (4-hydroxy-tetramethylpiperidine) and the oxidation form of methanol.

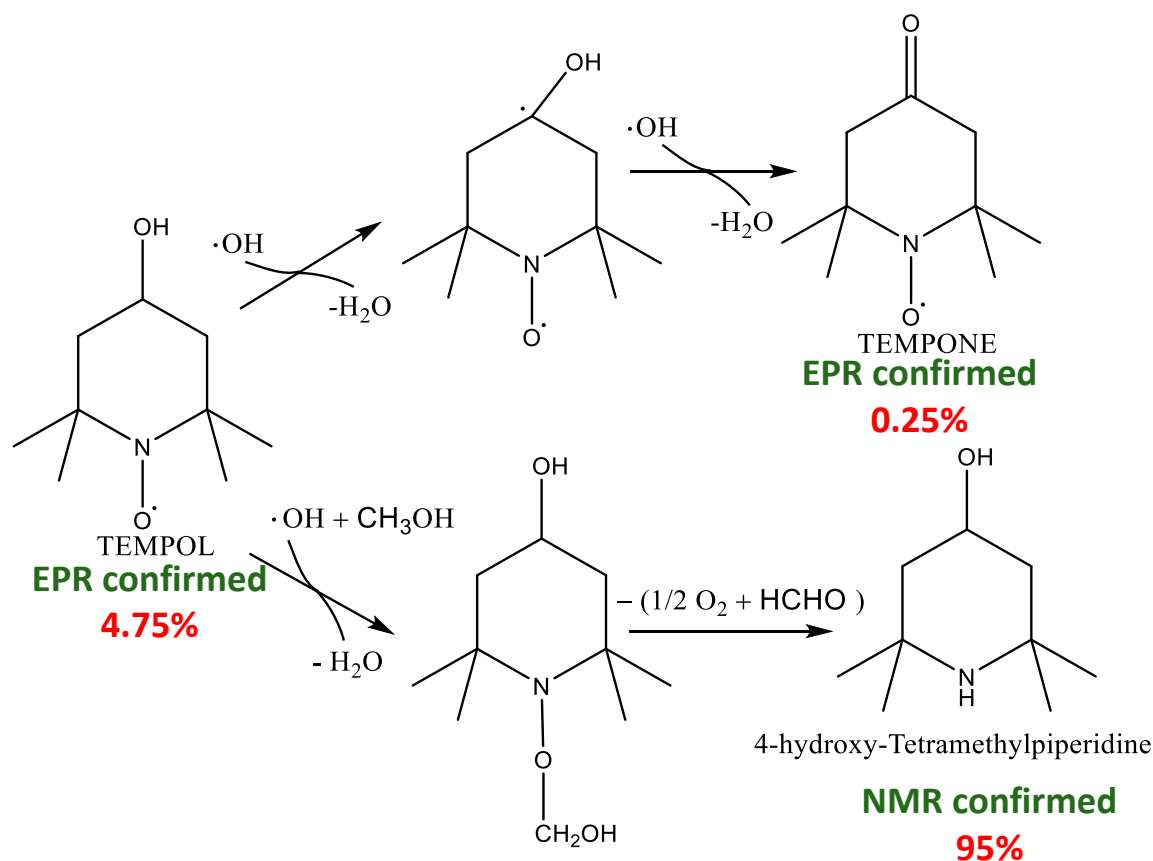


Figure 4. 29. Proposed hydroxyl radical deactivation of tempol in the presence of methanol to form the none radical 4-hydroxy-tetramethylpiperidine as a primary product and a tiny amount of both TEMPONE (minor product) and TEMPOL starting materials.

4.6 Photocatalytic activity test for other catalysts

To test the potential application of TEMPOL to monitor the photocatalytic activity of different photocatalysts, different crystalline forms of TiO_2 have been prepared and characterized according to Reference [93]. Figure 4.30 shows the time course of TEMPOL deactivation over rutile, anatase, and brookite TiO_2 photocatalysts in comparison with that of TiO_2 P25. The photocatalytic activities of the same photocatalysts have been assessed by following the rate of photocatalytic methanol oxidation by measuring spectrophotometrically the main oxidation product, i.e. formaldehyde [149] (Figure 4.31). By comparing the two methods, TiO_2 P25 has the highest activity and TiO_2 rutile has the lowest activity. It can also be seen that TiO_2 anatase has better activity than brookite and rutile. It is worth mentioning that the difference in the photocatalytic activities of the investigated photocatalysts towards the methanol oxidation is more obvious than that of the TEMPOL deactivation. This can be attributed to two reasons: (1) the initial methanol concentration is 2500-fold higher than that of TEMPOL and (2) methanol can react with $\cdot\text{OH}$ radicals and directly with the photogenerated holes [161] but TEMPOL reacts more likely with $\cdot\text{OH}$ radicals only. Nevertheless, it seems from our results that following the TEMPOL deactivation reaction by using EPR can be used to fast evaluate the photocatalytic activity of photocatalyst suspensions without the need for filtration or the wait for a long time to establish adsorption equilibrium. TiO_2 P25 can be used as a standard photocatalyst and the initial rate of the investigated photocatalysts can be reported relative to that of TiO_2 P25 for the ease of comparing the results produced at different labs.

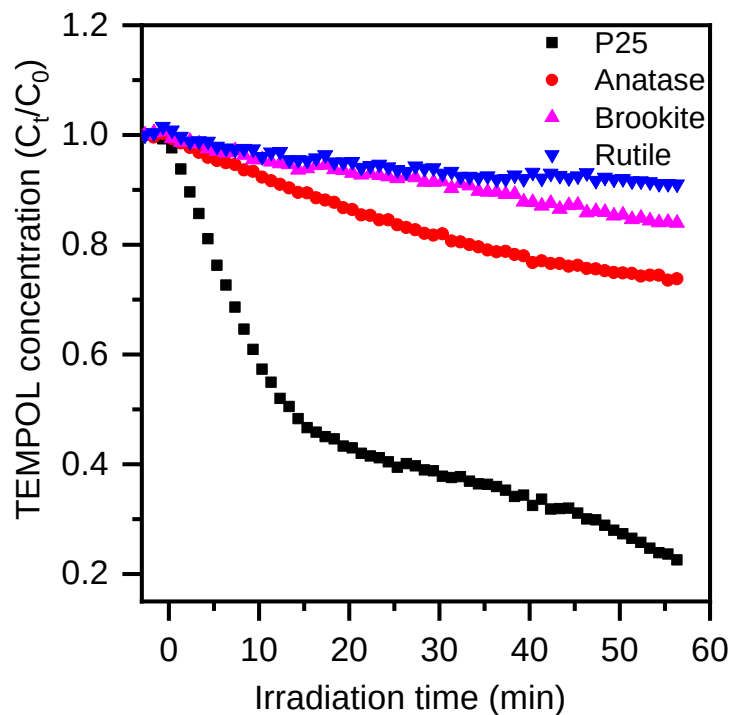


Figure 4. 30. Time course of photocatalytic TEMPOL deactivation over TiO₂ P25, anatase, brookite, and rutile photocatalysts under UV(A) light illumination. TEMPOL concentration was 100 μ M, methanol concentration was 250 mM, and Light intensity was 7 mW cm⁻².

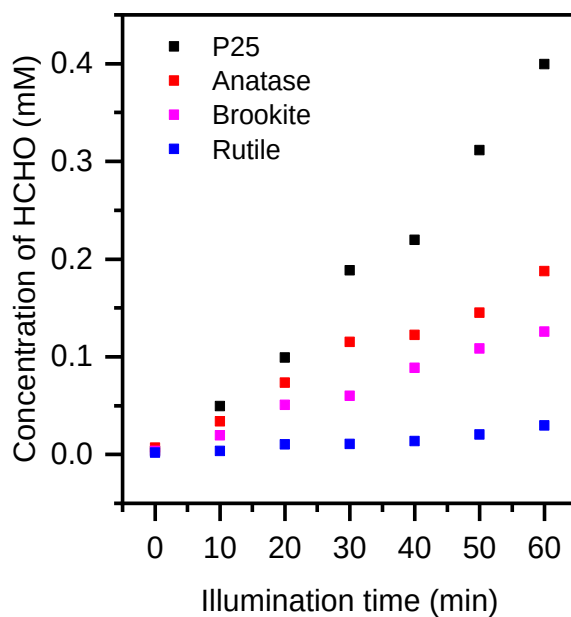


Figure 4. 31. Time course of methanol oxidation over TiO₂ P25, anatase, brookite, and rutile photocatalysts under UV(A) light illumination. TEMPOL concentration was 100 μ M, methanol concentration was 250 mM, and Light intensity was 7 mW cm⁻².

CHAPTER 5

CONCLUSIONS

Photocatalysis has been attracting great attention due to its potential uses in the fields of energy and environmental sciences. Many photocatalytic materials have been developed in the past few years. The photocatalytic activity of particulate photocatalyst suspension is commonly evaluated by monitoring the rate of methylene blue bleaching and phenols degradation. De-colorization of organic dyes such as methylene blue (MB) has been proposed as a standard test method. Unfortunately, this method suffers from many drawbacks like dye-self degradation and the need for sample filtration before measurements. Thus, the development of a direct and fast method for monitoring the photocatalytic activity of particulate photocatalyst suspension is urgently needed. TEMPOL radicals have been tested as a model compound to monitor the photocatalytic activity of TiO_2 suspension using EPR directly. In the absence of TiO_2 , it showed outstanding stability in an aqueous solution in the dark and under UV(A) illumination. TEMPOL does not absorb UV(A) and visible light, and thus the photosensitization problem associated with the dyes (e.g., MB) and phenolic compounds can be readily overcome. The dark adsorption results indicated that the adsorption of TEMPOL on TiO_2 is negligible. Unlike MB, the TEMPOL can be directly used without spending a long-time establishing adsorption equilibrium before the photocatalytic test. The influence of TEMPOL concentration, TiO_2 loadings, and light intensity on the rate of photocatalytic deactivation of TEMPOL have been investigated and analyzed. It was found that the initial rate of the

photocatalytic deactivation reaction is sensitive to the concentration of TEMPOL, light intensity, and TiO₂ loading. It was concluded that the rate is limited by the diffusion of TEMPOL to the surface of TiO₂ and by the availability of OH• radicals. The analysis of the photocatalytic deactivation products formed in the presence and absence of oxygen indicated that TEMPOL is mainly oxidized by the OH• radicals via the abstraction of the α-hydrogen at the 4-piperidine position, and two main products are formed (i.e., TEMPONE (4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl, radical and 4-oxo-2,2,6,6-tetramethylpiperidine). In the presence of methanol electron donors, it reacts with the photogenerated OH• radicals leading to the formation of •CH₂OH radicals. The latter radicals deactivate TEMPOL by the attack at the nitroxide side of TEMPOL leading to the formation of a mainly non-radical compound, namely, 4-hydroxyl-tetramethylpiperidine. Gaussian molecular modeling and the estimated spectroscopic parameters of the observed intermediate radicals and non-radical products show good agreement and support the proposed TEMPOL photo-deactivation reaction mechanisms. Finally, the studied photocatalytic system has great potential for application as a standard method for assessing the photocatalytic activity of particulate photocatalyst suspensions without the need for filtration or the wait for a long time to establish adsorption equilibrium.

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