

Short Communication

Optical and Electrochemical Study on the Performance of Au@TiO₂ core-shell Heterostructured Nanoparticles as Photocatalyst for Photodegradation of Methylene Blue under Solar-light Irradiation

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The efficacy of Au@TiO₂ core-shell heterostructured nanoparticles for photodegradation of methylene blue (MB) under solar-light irradiation was investigated in this study. The hydrothermal approach was used to make Au@TiO₂ core-shell nanoparticles. According to structural studies utilizing SEM, TEM, and XRD analysis, the Au@TiO₂ core-shell nanostructures were successfully produced. The optical band gap values of TiO₂ and Au@TiO₂ core-shell nanoparticles were 3.15 and 2.66 eV, respectively, indicating that the optical band gap value of Au@TiO₂ toward TiO₂ was decreased due to Au incorporation and the presence of a defect-induced narrowed band gap in Au@TiO₂ such as Ti³⁺ formation and/or oxygen vacancies. Electrochemical investigations revealed that charge transfer resistance and recombination kinetics in Au@TiO₂ were reduced. Under solar-light irradiation, TiO₂ and Au@TiO₂ core-shell nanoparticles removed 90% of 100ml of 50mg/l MB solution in 85 and 60 minutes, respectively, whereas the entire removal took 120 and 95 minutes, respectively. According to a comparison of the photocatalytic activities of Au@TiO₂ core-shell nanoparticles with other reported photocatalysts for MB degradation, the fast degradation rate of Au nanoparticles was related to the SPR absorption characteristics of the Au nanoparticles, which can act as a sensitizer to increase visible light absorption. Furthermore, the results demonstrated that the proposed photocatalyst was effective in degrading MB in an actual sample of paint and pigment industrial effluent.

Keywords: Au@TiO₂; Core-shell; Hydrothermal; Methylene blue; Photodegradation

1. INTRODUCTION

Paint, pigment, and textile manufacturing are the most polluting sectors on the planet [1, 2]. VOCs and other chemicals in most paints and stains produce harmful vapors that can stay indoors for

lengthy periods of time [3, 4]. Some chemical molecules cause ozone depletion, while others are recognized to be harmful to human health. Paints include solid pigments that can cause water to become murky [5, 6]. In addition to making the water murky and ugly, they can cause debris to clog fish gills and impair their capacity to breathe [7-9]. The absorption and reflection of sunlight entering the water is a major environmental concern with dyes. Increased turbidity can obstruct sunlight from reaching plants, reducing photosynthesis [10-12]. The dying process releases a variety of compounds into polluted water and chemicals, resulting in the death of aquatic life, soil degradation, and pollution of drinking water [13-15].

In addition, the textile dyes also significantly compromise the aesthetic quality of water bodies [16-18]. About 15% of synthetic textile dyes are lost in waste water streams during the manufacturing process, which causes unimaginable harm to the environment, increases biochemical and chemical oxygen demand, enters the food chain, provides recalcitrance and bioaccumulation, and can promote toxicity, mutagenicity and carcinogenicity [19-21]. Methylene blue (MB; [7-(dimethylamino) phenothiazin-3-ylidene]-dimethylazanium chloride) is a water-soluble azo dye that is used as both a dye and a medication [22-24]. MB forms quaternary ammonium cations in aqueous solutions, has a high chroma, and results in serious environmental pollution [25-27]. MB as a textile dye can also cause allergies such as contact dermatitis and respiratory diseases, allergic reactions in the eyes, skin irritation, and irritation to the mucous membrane and the upper respiratory tract. Studies have been shown that MB has the potential to be carcinogenic in high doses [28-30].

As a result, various effective water treatment technologies such as biological methods, advanced oxidation and adsorption processes, Fenton and electro-Fenton processes, electrocoagulation, membrane technology, ozone based processes, and photocatalytic reactors have gotten a lot of attention in recent decades for removing pollutant dyes from industrial wastewater [31-33]. Among these treatment technologies, photocatalytic reactors are a low-cost method for removing a wide variety of dyes from wastewaters by photo-activated chemical reactions that occur when free radical mechanisms and powerful oxidizing and reducing agents (h^+ and e^-) are generated by the UV or visible light on the surface of semiconductors such as ZnS, TiO_2 , ZnO as photocatalysts [34-36].

Because of its abundant availability, non-toxicity properties, excellent chemical and mechanical stability, thermal stability, fast absorption ability, low cost, good reversibility, non-volatility, and high photoactivity, TiO_2 has been shown to be an effective photocatalyst for the treatment of organic pollutants in studies [37-39]. However, due to its wide band (3.2 eV), TiO_2 is photoactive only in the ultraviolet (UV) region, and its inefficient solar adsorption capacity and high rate of recombination of photo-generated carriers allow it to face some significant technological challenges that obstruct its commercialization. As a result, interest in its potential application in visible light photocatalysis and the utilization of solar energy as an unlimited source of renewable energy continues to grow [40-42]. Therefore, this study has been conducted on an electrochemical study on the performance of $Au@TiO_2$ core-shell heterostructured nanoparticles for photodegradation of MB under solar-light irradiation.

2. EXPERIMENTAL

2.1. Synthesis of the Au@TiO₂ core-shell

The Au@TiO₂ core-shell nanostructure was synthesized using the hydrothermal method as described in the literature [43]. 5 ml of 10 mM sodium citrate (99%, Sigma-Aldrich) aqueous solution was added to 2 ml of 10 mM HAuCl₄ (99.9%, Sigma-Aldrich) aqueous solution and agitated for 5 minutes. Then, using a magnetic stirrer, 5 mL of 10 mM ascorbic acid (99%, Merck, Germany) solution was combined with the resulting mixture for 4 minutes. The mixture was then combined with 5 ml of 50 mM TiF₄ (99.0%, Sigma-Aldrich) solution. After that, the mixture was diluted to 100 mL and transported to a stainless steel autoclave lined with Teflon. The mixture was then heated at 190°C for 10 hours in a 120 Teflon-lined stainless steel autoclave (Microreactor, Yanzheng Instrument Ltd., Shanghai, China). After complete reaction, the resultant product was washed with deionized water and dried at room temperature.

2.2. Material characterizations

An X-ray diffractometer (XRD; DMAX 2500; Rigaku, Tokyo, Japan) operating at 40 kV and current of 30 mA and equipped with a Cu X-ray target was used to examine the crystal structure of TiO₂ and Au@TiO₂ core-shell nanoparticles. Scanning electron microscopy (SEM; SSX-550, Shimadzu, Japan) and transmission electron microscopy were used to examine the shape and structure of produced nanoparticles (TEM; JEOL, Tokyo, Japan). The electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (ZAHNER-IM6ex, ZAHNER Co., Germany) that included a TiO₂ and Au@TiO₂ core-shell nanostructured modified GCE as a working electrode, a platinum wire as a counter electrode, and a saturated Ag/AgCl electrode as a reference electrode. The EIS data were collected at a frequency range of 106 Hz to 10⁻¹ Hz in a 0.5 M Na₂SO₄ (99%, Sigma-Aldrich) solution with an open circuit voltage of 5 mV and fitted to equivalent circuits using Zview and Zsimpwin. For modification of the GCE surface with TiO₂ and Au@TiO₂ core-shell nanostructures, 0.9 ml of dimethylformamide (DMF, 99.9%, Shandong Pulisi Chemical Co., Ltd., China) was ultrasonically added to 50 mg/ml of synthesized nanostructure suspension. Then 0.1 ml of the products were dropped on the surface of GCE and dried in the air.

2.3. Analyses of photocatalytic activity

Under solar light irradiation, photodegradation of 100 ml of 50 mg/l MB solution was used to investigate the photocatalytic activity of TiO₂ and Au@TiO₂ core-shell nanostructures. The amount of photocatalysts in the MB solution was 10 mg. The solar light source was a 150 W Xenon lamp with a UV-light cutout filter ($\lambda \geq 420\text{nm}$), which was situated at the top of the device. The mixture of MB solution and photocatalysts was magnetically agitated in a dark environment for one hour before to the start of light irradiation to create an adsorption/desorption equilibrium between dye molecules and the photocatalyst. The distance between the light source's surface and the solution's surface was kept

constant at 10 cm. After irradiation with light, irradiated samples were filtered through a 0.45 μm cellulose, and the concentration of the irradiated MB solutions was determined using UV-vis absorbance at $\lambda_{\text{max}} = 663 \text{ nm}$ [44, 45]. The photocatalytic removal efficiency was calculated as the equation (1) [46, 47]:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 = \frac{I_0 - I_t}{I_0} \times 100 \quad (1)$$

Where C_0 and C_t are the starting concentration and degraded MB solution concentrations at time t , respectively, and I_0 and I_t are the corresponding MB solution absorbance intensities. The real sample of wastewater was centrifuged at 1500 rpm for 5 minutes to study the applicability of Au@TiO_2 core-shell nanoparticles for MB degradation in a prepared real sample of paints and pigments industrial wastewater (Zhejiang Deqing Multisinox Pigment Technology Co., Ltd., China), and the supernatant was used to prepare the 50mg/l MB solution. The control sample was a 50 mg/l MB solution made with deionized water.

3. RESULTS AND DISCUSSION

3.1. Structural studies

Figure 1 shows SEM and TEM pictures of TiO_2 nanoparticles and Au@TiO_2 core-shell nanostructures. Figure 1a shows SEM and TEM images of TiO_2 nanoparticles, which show spherical nanoparticles with an average diameter of 50nm. Figure 1b shows SEM images of Au@TiO_2 nanostructures, which show uniform and spherical shaped Au@TiO_2 nanoparticles with an average diameter of 70 nm, and Figure 1c shows TEM images of Au@TiO_2 nanostructures with a core-shell structure composed of 20 nm Au nanoparticles at the core and a 50 nm TiO_2 shell layer. Furthermore, well distributed Au@TiO_2 core-shell nanostructures show minimal damage or deformation after the dispersing process, indicating their high stability.

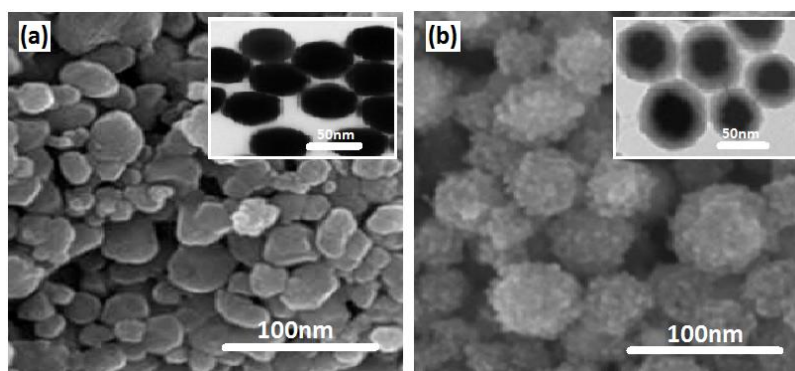


Figure 1. SEM and TEM images of (a) TiO_2 nanoparticles, and (b) Au@TiO_2 core-shell nanostructures

XRD patterns of powders of TiO_2 and Au@TiO_2 core-shell nanoparticles are shown in Figure 2. As observed, XRD patterns of TiO_2 nanoparticles in Figure 2a displays diffraction peak at $2\theta = 25.08^\circ, 37.99^\circ, 47.59^\circ, 53.54^\circ, 54.98^\circ, 62.50^\circ, 68.56^\circ, 70.28^\circ$ and 74.76° , corresponding to formation

to anatase crystal phase of TiO_2 with (101), (004), (200), (105), (211), (204), (116), (220) and (215) reflections, respectively (JCPDS card no. 01-075-2552) [48, 49]. XRD patterns of Au@TiO_2 nanostructures in Figure 2b exhibits additional diffraction peaks at $2\theta = 44.32^\circ$, 64.48° and 77.39° , corresponding to the creation to a face-centered cubic crystal phase of metallic Au with (200), (220) and (311) planes, respectively (JCPDS card no. 01-071-4614) [50, 51]. Therefore, the results of SEM, TEM and XRD analyses reveal that the Au@TiO_2 core-shell nanostructures were successfully synthesized using the hydrothermal method.

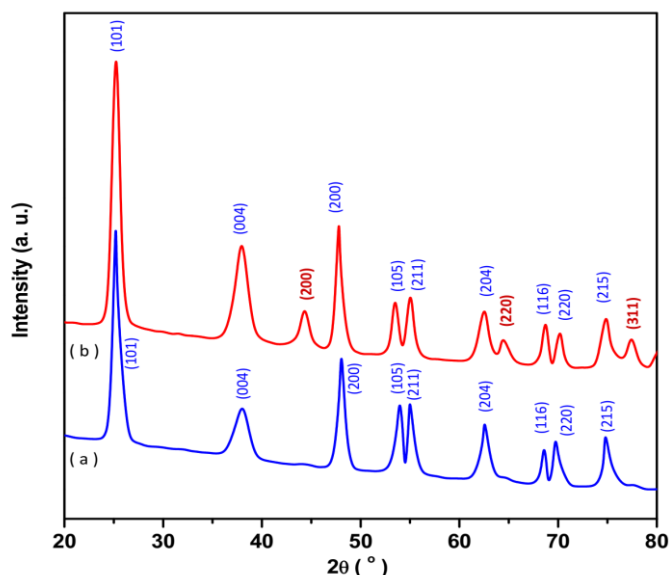


Figure 2. Result of XRD analyses of powders of (a) TiO_2 and (b) Au@TiO_2 core-shell nanoparticles.

3.2. Optical analysis

Figures 3a and 3b show UV-vis spectra and Tauc diagram of $(\alpha h\nu)^2$ vs $(h\nu)$ of TiO_2 nanoparticles and the Au@TiO_2 core-shell nanostructures. As observed from UV-vis spectra, there is a red shift of the light absorption edge of Au@TiO_2 core-shell nanoparticles toward the TiO_2 nanoparticles, which is attributed to the incorporation of Au and the narrower band gap energy and the introduction of metal atom energy levels into the band gap of TiO_2 [52]. The interaction between the Au and TiO_2 particles and presence of energy levels below the conduction band and above the valence band can improve catalytic activity because of the electron scavenger activity of the Au atom [52, 53]. On the other hand, for Au@TiO_2 core-shell nanoparticles, the surface plasmon resonance (SPR) and visible light responses of Au nanoparticles in the core can significantly enhance the absorption of visible light [54, 55]. Therefore, the excitation of metallized TiO_2 occurs with lower energy radiation [56]. The SPR generated by the collective oscillations of highly energetic electrons on the surface of Au nanoparticles extends visible-light absorption and allows us to utilize more visible light to photoinduce charges for the degradation of pollutants and enhance visible light harvesting [57]. The optical band gap of TiO_2 and Au@TiO_2 core-shell nanoparticles is determined using the Tauc plot as the following equation [46, 58, 59]:

$$(\alpha h\nu)^2 = A(h\nu - E) \quad (2)$$

Where α is the absorption coefficient, $h\nu$ represents the photon energy, A is the proportionality constant, and E is the optical band gap. The Tauc plots in Figure 3b reveal that the obtained optical band gap values of TiO_2 and Au@TiO_2 core-shell nanoparticles are 3.15 and 2.66 eV, respectively. The results demonstrate that the optical band gap value of Au@TiO_2 is decreased because of the presence of a defect-induced narrowed band gap in Au@TiO_2 such as Ti^{3+} formation and/or oxygen vacancies, which as consequence improve the photocatalytic activities under visible light irradiation [60, 61]. Moreover, with the synergetic effect of the narrow band gap of the Au@TiO_2 core-shell and the SPR phenomena of Au nanoparticles in the core, a large number of photo-induced electrons and holes are generated and separated, which contribute to the photodegradation reactions and enhance photocatalytic performance [62-64]. When Au nanoparticles are incorporated into the TiO_2 matrix, the formed metal-semiconductor Schottky barrier can facilitate the transfer of photo-induced charges from the conduction band of Au nanoparticles to the conduction band of TiO_2 , through the interface [65, 66]. It is demonstrated that Au@TiO_2 core-shell nanoparticles could have a synergistic effect and promote the photocatalytic activity of nanostructured semiconductors.

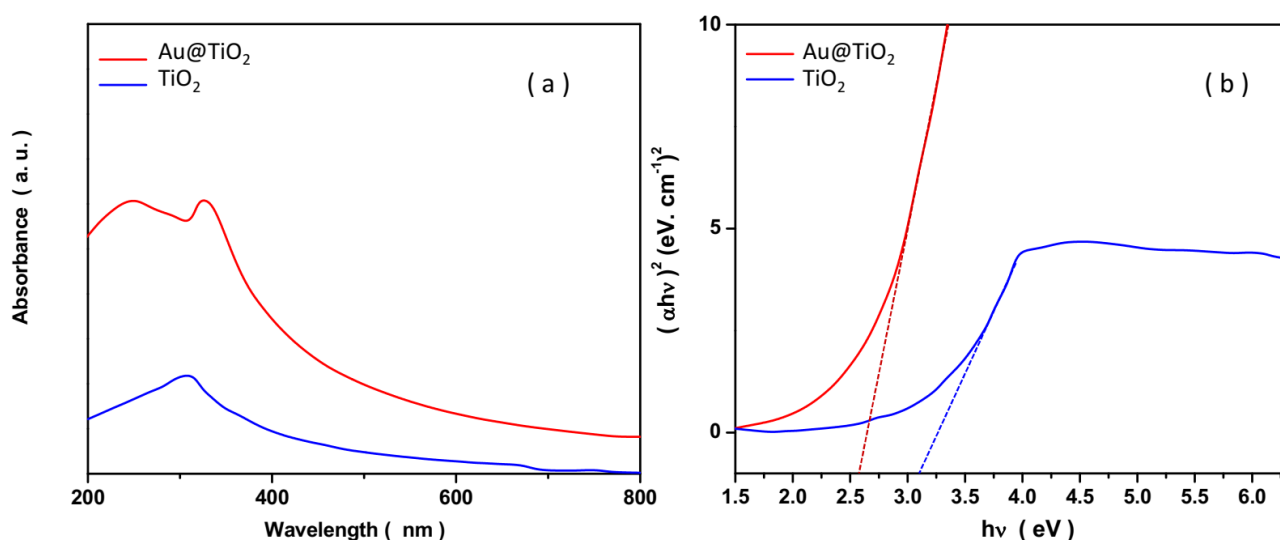


Figure 3. (a) UV-vis spectra and (b) Tauc plot of TiO_2 and Au@TiO_2 core-shell nanoparticles.

3.3. Electrochemical analysis

In order to evaluate the charge transfer resistance at the photocatalyst/electrolyte interface among the TiO_2 and Au@TiO_2 core-shell nanoparticles, the obtained EIS and bode plots under applied open circuit potential at a frequency range from 10^6 Hz to 10^{-1} Hz are presented in Figure 4. Furthermore, in Figure 4a, R_s and C_2 represent the solution resistance and chemical capacitance of the electrode, respectively, and Q represents the electrochemical double-layer capacitance. R_{ct1} and R_{ct2} which correspond to charge transport resistance at high frequency and mid frequency semicircles, respectively. Table 1 presents the resulted values for fitting the data of the circuit elements, indicating the value of R_{ct1} value is obviously decreased in the Au@TiO_2 core-shell nanoparticle sample, which

is attributed to decrease the charge transfer resistance and efficient charge transportation [67-69]. In addition, the R_{ct2} value at the $Au@TiO_2$ core-shell nanoparticle sample interface gets reduced, which is associated with the reduced recombination kinetics [70-72].

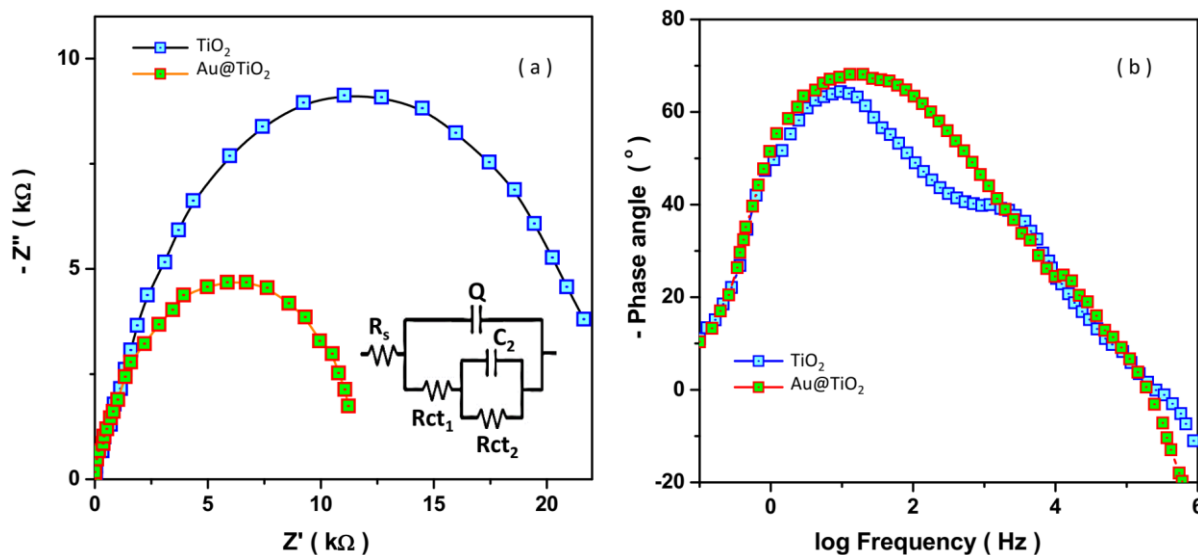


Figure 4. (a) The obtained EIS and the resulted equivalent circuit, and (b) Bode plots under applied open circuit potential at frequency range from 10^6 Hz to 10^{-1} Hz.

Table 1. The resulted values for fitting data of the circuit elements.

Sample	R_s (Ω)	C_2 (μF)	R_{ct1} (Ω)	R_{ct2} (Ω)
TiO_2	42.31	10.091	48.30	22501
$Au@TiO_2$	13.95	17.58	35.92	12011

3.4. Photocatalytic analyses

The photocatalytic performance of TiO_2 and $Au@TiO_2$ core-shell nanoparticles was investigated for degradation of 100 ml of 50 mg/l MB solution under solar-light irradiation. Figure 5 shows that before light irradiation, the removal efficiency of MB solution in the dark was obtained $\leq 0.9\%$ after 60 minutes, and after solar-light irradiation the removal efficiency was drastically increased, which corresponded to the light effect on physicochemical treatment of MB. Moreover, the blank sample as the sample, without a photocatalyst, displays a degradation $\leq 2\%$ after 125 minutes light irradiation. Comparisons are made in terms of removal efficiency of TiO_2 and $Au@TiO_2$ core-shell nanoparticles which show 90% removal of MB in 85 and 60 minutes, respectively, whereas total removal is obtained in 120 and 95 minutes, respectively. The fast rate of degradation of MB solution in the $Au@TiO_2$ core-shell nanoparticle sample under solar-light irradiation can be related to the SPR absorption characteristics of the Au nanoparticles which can act as sensitizer to increase the visible

light absorption, and the formation of Ti^{3+} and/or oxygen vacancy as light absorption centers in the Au@TiO_2 core-shell structure, which extends the absorption edge to the visible light region and promotes the charge separation efficiency [60, 73, 74]. Furthermore, the combination of plasmonic noble metal nanostructures with the defect-induced narrow band gap of the Au@TiO_2 core-shell nanoparticle sample resulted in a narrow band gap. It is suggested that heterogeneous photocatalytic degradation reactions occur through the generation of photo-excited electrons in the conduction band and positive holes in the valence band of photocatalyst samples by light irradiation that these photo-generated carriers, which are responsible for the creation of H^+ and $\text{OH}^\cdot$ radicals, which act as highly reactive species to degrade the dye molecules [75-77]. The introduction of plasmonic noble metals reinforces the photocatalytic performance of TiO_2 because the metallic nanoparticles hinder the recombination of photo-excited electrons and holes [78-80]. These results are in agreement with the results of EIS and optical analyses.

Table 2 shows the comparison between photocatalytic activities of Au@TiO_2 core-shell nanoparticles by other reported photocatalysts for degradation of MB. It can be observed that Au@TiO_2 core-shell nanoparticles displays the effective performance for degradation of MB under solar-light irradiation because of formation of heterojunctions and intermediate energy levels inside TiO_2 band gap and decrease in Fermi level of TiO_2 which can depress the charge transfer transition from the valence band to the conduction band [56, 81].

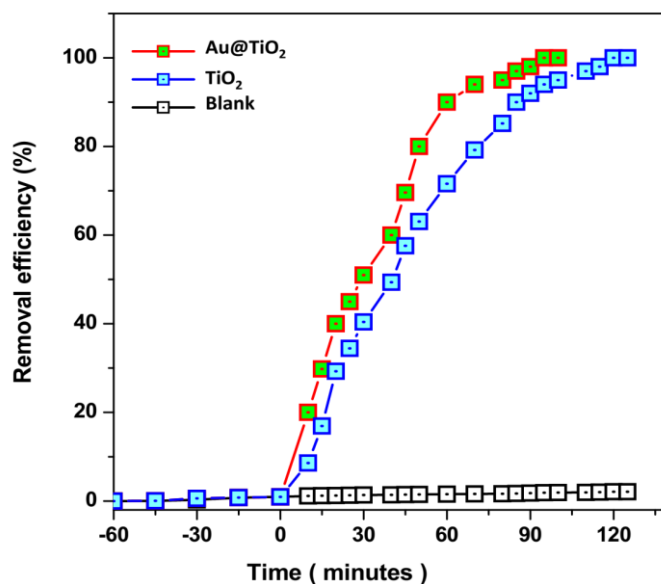


Figure 5. The photocatalytic performance of blank sample and TiO_2 and Au@TiO_2 core-shell nanoparticles for degradation of 100 ml of 50 mg/l MB solution under solar-light irradiation

Figure 6 shows the effect of different initial MB concentrations on the removal efficiency of Au@TiO_2 core-shell nanoparticles under solar-light irradiation. It is discovered that as the initial concentration of MB increases, the removal efficiency decreases noticeably. The complete degradation of 10, 20, 50 and 100 mg/l of MB is obtained after 60, 70, 100 and 130 minutes of solar-light irradiation, respectively. The lowest degradation efficiency is obtained at 100 mg/l initial concentration

of MB, which could be associated with the occupation of photoactive sites on the Au@TiO₂ core-shell nanoparticles surface in the presence of excessive MB molecules in the solution. Thus, a decrease in photoactive sites could decrease the formation of hydroxyl radicals. Moreover, light scattering is increased due to the presence of excessive dye molecules in the solution.

Table 2. Comparison between photocatalytic activities of Au@TiO₂ core-shell nanoparticles with other reported photocatalysts for degradation of MB.

Photocatalyst	MB content (mg/l)	Light source	Degradation time (minute)	Degradation efficiency (%)	Ref.
Au@TiO ₂ core-shell nanoparticles	50	Solar	60	90	This work
			95	100	
TiO ₂	0.06	UV	120	100	[82]
BiSbO ₄	10	UV	80	95	[83]
SrGeO ₃	10	UV- visible	240	83.22	[84]
MnV ₂ O ₆	10	visible	60	72.96	[85]
Graphene oxide /TiO ₂	10	UV	150	95.8	[86]
TiO ₂ P25/graphene	10	UV	120	90	[87]
N,P-Carbon quantum dots /TiO ₂	---	UV- visible	120	93.6	[88]

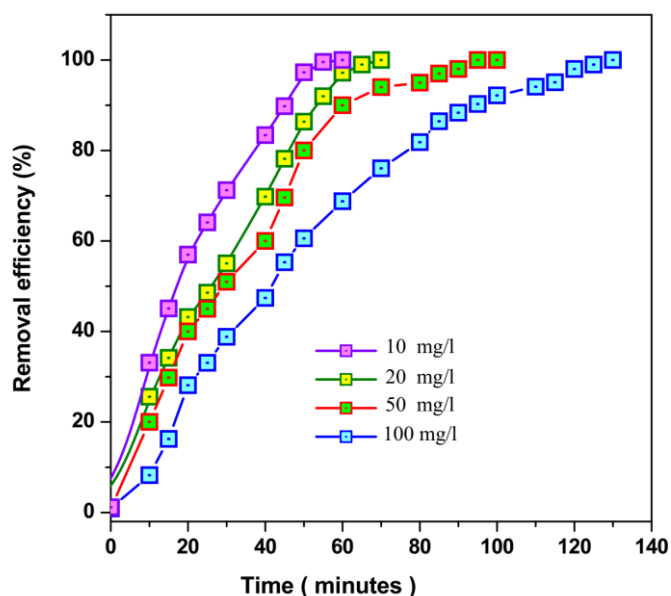


Figure 6. Effect of different initial MB concentrations (10, 20, 50 and 100 mg/l) on the removal efficiency of Au@TiO₂ core-shell nanoparticles under solar-light irradiation

Figure 7 shows the results of the study on the applicability of the Au@TiO₂ core-shell nanoparticle for degradation of MB in the prepared real sample of paints and pigments industrial

wastewater. As observed, the comparison between the degradation of 100 ml of 50 mg/l MB solution prepared in real samples of industrial wastewater (sample 'a') and prepared in deionized water (sample 'b') using Au@TiO₂ core-shell nanostructures under solar-light irradiation reveals that the complete degradation of MB solutions is obtained after 107 and 95 minutes for samples 'a' and 'b', respectively, indicating the more time required for complete degradation of MB in sample 'a' because of the presence of MB molecules and other organic compounds in the wastewater, and successful application of the proposed photocatalyst for degradation of MB in the prepared real samples of paints and pigments industrial wastewater [89].

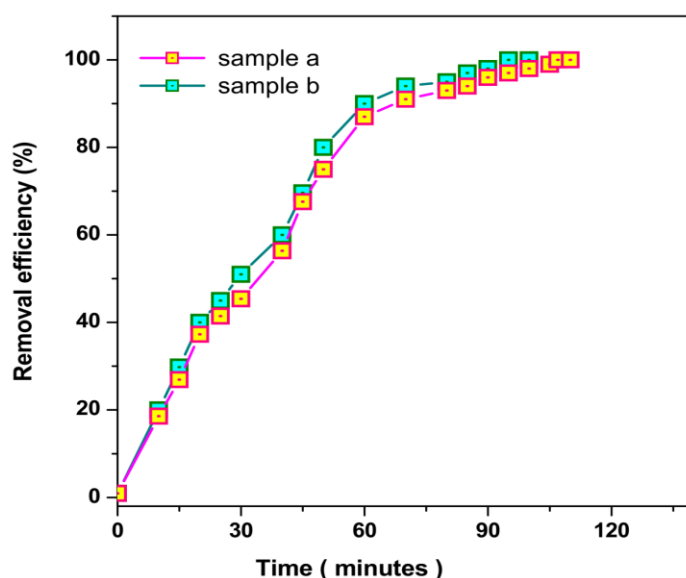


Figure 7. The degradation of 100 ml of 50 mg/l MB in (a) prepared real sample of paints and pigments industrial wastewater and (b) prepared in deionized water using Au@TiO₂ core-shell nanostructures under solar-light irradiation.

4. CONCLUSION

In summary, this study presents electrochemical study on the performance of Au@TiO₂ core-shell heterostructured nanoparticles for photodegradation of MB under solar-light irradiation. Structural studies revealed that the Au@TiO₂ core-shell nanostructures were successfully synthesized using a hydrothermal method. Optical analysis showed that the optical band gap values of TiO₂ and Au@TiO₂ core-shell nanoparticles were obtained at 3.15 and 2.66 eV, respectively. Results of electrochemical analyses indicated reduced charge transfer resistance and recombination kinetics in Au@TiO₂. Results of photocatalytic analyses demonstrated that the removal efficiency of TiO₂ and Au@TiO₂ core-shell nanoparticles showed that total removal was obtained in 120 and 95 minutes, respectively. Comparison between photocatalytic activities of Au@TiO₂ core-shell nanoparticles by other reported photocatalysts for degradation of MB is indicted by the fast degradation rate of Au@TiO₂ core-shell nanoparticles. Results indicated the successful application of the proposed

photocatalyst for degradation of MB in the prepared real sample of paint and pigment industrial wastewater.

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