Visible Light Photocatalytic Degradation of Sunset Yellow Dye and Industrial Textile Wastewater Using Pd-BiFeO₃ Composite

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Abstract. Herein, pristine BiFeO₃ and Pd-incorporated BiFeO₃ (Pd-BiFeO₃) composite were synthesized using hydrothermal synthesis method. The physiochemical and optical properties of the synthesized materials were investigated using numerous techniques. The Pd-BiFeO₃ composite significantly enhanced the photocatalytic degradation of sunset yellow (SSY) dye in comparison with the pristine BiFeO₃ under visible light irradiation. The enhanced photoactivity was credited to the improved photogenerated charge carrier separation, which was in accordance with the photoelectrochemical measurements. Moreover, the Pd-BiFeO₃ composite can be recycled for seven consecutive runs without sufficient loss of photocatalytic activity. Radical trapping studies suggested that the hydroxyl radical (·OH), hydrogen peroxide (H₂O₂) and hole (h⁺) were the key reactive oxidizing species. A possible photocatalytic enhancement mechanism of Pd-BiFeO₃ composite was stated. Finally, for the first time, the Pd-BiFeO₃ composite was also applied towards the effective degradation of industrial textile wastewater.

1. Introduction
The textile industry mainly consumes dyes, water and different chemicals during numerous stages of textile processing. The large quantity of generated effluents is unsuitable for further use. According to an estimation, annually, around 5000 tons of textile dyes are released to the environment [1]. Such acts are aesthetically detrimental, carcinogenic and mutagenic upon their release without prior treatment. Normally, the textile wastewater characteristics significantly vary in colour, chemical oxygen demand (COD), turbidity, suspended solids and pH [2]. Currently, the governments are introducing more strict effluent discharge laws, as water requirement for public and industrial uses have increased. Hence, the textile industries are obligated to improve their current treatment techniques to meet the effluents discharge limits. The visible light driven heterogeneous photocatalysis is an auspicious green technology to tackle global environmental concerns [3], [4]. Synthesizing highly effective photocatalytic materials and enhancing their visible light photocatalytic activities are thus instantly needed.

Recently, Bi-based semiconductor materials have obtained significant attentions due to their high chemical and thermal stability along with satisfying photocatalytic properties [5], [6]. Among them, perovskite bismuth ferrite (BiFeO₃) with a smaller bandgap energy ~2.4-2.7 eV, environment friendly nature, ferroelectric and ferromagnetic properties is a well renowned visible light active photocatalyst [7]–[9]. However, the rapid recombination of charge carriers has severely undermined its
commercialization [10]. To overcome these shortcomings, noble metals (Ag, Pd, Pt and Au) incorporations have been effectively used to increase the photocatalytic activity and good stability [10], [11]. The noble metals can enhance the absorbability in a visible-light region and also have the strong capability to capture and transfer the photogenerated electron (e−) from the photocatalyst, hence improved the charge carrier separation efficiency [12], [13]. For instance, Niu et al. [8] synthesized Pt-doped BiFeO3 composite using a hydrothermal-synthesis process, and they establish that 1wt% Pt-BiFeO3 showed 5.1 times higher photocatalytic activity towards methyl orange dye than those of the pristine BiFeO3 under visible light irradiation. Zhang et al. [14] also synthesized M@BiFeO3 (M=Ag and Au) with the improved photocatalytic activities against the removal of Rhodamine B than those of the pristine BiFeO3. Until now, there are few reports available on the Ag, Pt, Pd and Au-doped BiFeO3 photocatalysts and their activities towards different organic pollutants. Nonetheless, there is not a single report on the photodegradation of industrial textile wastewater using BiFeO3-based composite. Based on the above discussion, it is anticipated that the metallic Pd nanoparticles deposition on BiFeO3 can successfully enhance the charge carrier separation efficiency, which will lead to the improvement in photocatalytic activity. In the present study, Pd-BiFeO3 composite were synthesized using hydrothermal route. The optical and physicochemical characteristics of the synthesized materials were analysed via numerous techniques. The photocatalytic activities of pristine BiFeO3 and Pd-BiFeO3 composite were assessed against sunset yellow (SSY) dye degradation under visible light irradiation. A thorough probable photodegradation mechanism was proposed with the assistance of electrochemical measurement and radical trapping experiments. Finally, for the first time, the Pd-BiFeO3 composite was utilized for the degradation of industrial textile wastewater.

2. Experimental
All the reagents were purchased from Sigma Aldrich and applied directly without any additional processing. Ultrapure water was used throughout the experiments. The BiFeO3 with coral-like morphology was synthesis via hydrothermal technique as reported in our previous report [7]. In the Pd-BiFeO3 synthesis, 0.035 g of palladium chloride was dissolved in methanol solution (30 mL). Then, 1 g of synthesized coral-like BiFeO3 was inserted in the above mixture and ultra-sonicate for further 15 min. Afterwards, the mixture was transferred to a Teflon-lined autoclave reactor at 100 °C for 240 min. Upon completion of the reaction, the mixture was collected, washed with water for several times and dried in an oven at 70°C.

The synthesized materials were analysed using X-ray diffraction (XRD, Philips PW 1820), transmission electron microscopy (TEM, Philips CM-12), field emission scanning electron microscope (FESEM, Quanta FEG 450), energy dispersive X-ray (EDX), Fourier transform infrared (FTIR, PerkinElmer Lambda 35), UV-vis diffused reflectance spectrometer (UV-vis DRS, Perkin Elmer Lambda 35) and photoluminescence (PL, Perkin Elmer S55). A three-electrode scanning potentiostat (Gamry Interface 1000) was applied to study the photoelectrochemical properties of synthesized samples. The working electrode was separately prepared by dip-coating the samples on fluorinated tin oxide (FTO) glass. Briefly, 10 mg of the sample was inserted into a Nafion-ethanol solution. After 40 min of sonication, the paste was coated onto an FTO glass and allowed to be dried naturally. During the photoelectrochemical analysis, a 0.5M sodium sulfate (Na2SO4) solution was applied as the electrolyte. The reference and counter electrode were an Ag/AgCl and platinum wire, respectively.

For photocatalytic reaction, 150 mg materials were inserted into a 250 mL beaker containing 100 mL of 10 mg/L SSY dye solution. Initially, the mixture was magnetically stirred in dark for 30 min to attain equilibrium. Then, a 105 W visible light with 7.03 × 104 lux intensity was applied throughout the experiment. After a fixed time interval, 4 mL samples were withdrawn and centrifuged at 4000 rpm to remove the catalysts. The final SSY dye solution was monitored via UV-vis spectrophotometer (Hach DR-6000) at 480 nm wavelength. To detect the reactive species that affect the photodegradation of SSY dye, trapping experiments were performed using various trapping agents, such as IPA (+OH trapping agent), BQ (+O2− trapping agent), KI (h+ trapping agent) and catalase (H2O2 trapping agent), using the similar procedure to that of the photocatalytic experiment.

The photodegradation of industrial textile wastewater was also performed through similar procedure as stated above. The textile wastewater was obtained from a textile industry located at Penang, Malaysia.
The chemical oxygen demand (COD) was calculated via high range COD vials. The 2 mL of the sample was inserted into the high range COD vial and then digested at for 2 h at 150 °C. To examine biological oxygen demand (BOD5), sample (10 mL) was added into the 300 mL of ultrapure water and then incubated for 5 days at 20 °C. The dissolved oxygen (DO) for BOD5 were calculated. The ammoniacal nitrogen (NH3−N) was calculated via Nessler reagent at 425 nm. The turbidity was determined via turbidimeter (Lovibond Turbicheck). The TSS was calculated via an UV-vis spectrophotometer in accordance with the 8006 photometric methods [15]. The colour of the wastewater sample was investigated according to a colorimetric platinum cobalt technique. Finally, solution pH was determined via a pH meter.

3. Result and discussion

3.1 Material characterizations

The crystal structure and phase of the synthesized samples were investigated via XRD and results are displayed in Figure 1(a). The diffraction peaks marked with * can be indexed to the single perovskite phase with the rhombohedral structure of BiFeO3 (JCPDS No. 20–0169) [9]. In case of Pd-BiFeO3 composite, two additional peaks situated around 40.1° and 46.9° were recorded, which can be attributed to the (1 1 1) and (2 0 0) crystal planes of face-centered cubic phase of Pd (marked with #, JCPDS No 88-2335) [16]. The narrow and sharp diffraction peaks clearly proved the synthesis of highly crystalline materials. Moreover, no other peak was recorded, suggesting the high purity of the synthesized materials. Functional groups present on the surface of synthesized samples were studied using FTIR analysis. As exhibited in Figure 1(b), the BiFeO3 and Pd-BiFeO3 composite had the absorption peaks around 450 cm−1 and 554 cm−1 originated from the Fe-O stretching and Fe-O bending vibrations of the FeO6 perovskite, respectively [17], [18]. The peaks around 1612 cm−1 and 3408 cm−1 were credited to the bending vibration of absorbed H2O molecules and O−H stretching mode of −OH group on the surface of the catalysts, respectively [19]. The existence of −OH group ensured their effective photodegradation activities since the −OH group served as a main trapping agent for the photogenerated charge carriers, which led to the generation of reactive •OH radical, a highly favourable reactive specie for organic pollutants degradation.

![Figure 1. (a) XRD patterns and (b) FTIR spectra of pristine BiFeO3 and Pd-BiFeO3 composite.](image)
nm. The elemental analysis in Figure 2(d) can easily show the existence of Bi, Fe, O and Pd peaks in Pd-BiFeO$_3$ composite.

![Figure 2. FESEM of (a) pristine BiFeO$_3$, (b) Pd-BiFeO$_3$ composite, (c) TEM images of Pd-BiFeO$_3$ composite and (d) EDX spectrum of Pd-BiFeO$_3$ composite.](image)

3.2 Optical and electronic traits

Figure 3 (a) displays the UV–Vis DRS of pristine BiFeO$_3$ and Pd-BiFeO$_3$ composite. Relative to pristine BiFeO$_3$, Pd-BiFeO$_3$ composite possessed considerably superior light absorption properties in the visible light region, signifying that the metallic Pd could act as a light-absorbing sensitizer and charge carrier separation center. Hence, higher photocatalytic performance is expected [20]. The bandgap energies were calculated using Tauc plot $E_g = 1240/\lambda$ (nm), where $E_g$ is the bandgap energy (eV) and $\lambda$ is the wavelength (nm). The $E_g$ values of the pristine BiFeO$_3$ and Pd-BiFeO$_3$ composite were calculated to 2.5 and 2.23 eV, respectively (Figure 3 (b)), which was close to the reported literature [8,11]. Figure 3(c) depicts the transient photocurrent response of pristine BiFeO$_3$ and Pd-BiFeO$_3$ composite. The results displayed a highly sensitive photocurrent response under light irradiation using both materials. The Pd-BiFeO$_3$ composite exhibited a higher current intensity than that of the pristine BiFeO$_3$, proving the metallic Pd can effectively enhance the photogenerated charge carrier separation. The EIS was also utilized to examine the dynamics of interfacial charge transfer in the photocatalysts. Figure 3(d) shows the Nyquist plots of pristine BiFeO$_3$ and Pd-BiFeO$_3$ composite. It can be seen that the arc radius of Pd-BiFeO$_3$ composite was much lower compared with the pristine BiFeO$_3$. These outcomes established that the Pd-BiFeO$_3$ showed much lower charge transfer resistance, which will highly expedite its photocatalytic efficiency. Moreover, the pristine BiFeO$_3$ and Pd-BiFeO$_3$ composite were also applied to study the LSV analysis. As shown in Figure 3(e), the current density of pristine BiFeO$_3$ was lower compared with the Pd-BiFeO$_3$ composite. The greater current density and lower overpotential suggested that the Pd-BiFeO$_3$ composite highly improved the transfer and separation ability of photogenerated charge carriers. PL spectroscopy is also frequently applied to study the separation of photogenerated charge carriers in photo-responsive materials. The emission peaks in Pd-BiFeO$_3$ composite were quite identical to that of the pristine BiFeO$_3$ (Figure
However, their intensities were much lower, which proposed that the incorporation of metallic Pd can highly improve the charge carrier separation. The PL findings were also in good agreement with the photoelectrochemical results, indicating that the incorporation of metallic Pd was an effective route to enhance the photo-redox reaction.

3.3 Photocatalytic degradation of SSY dye

The photocatalytic activities of synthesized samples were investigated towards the SSY dye degradation. SSY has been widely used in textile, pharmaceutical, cosmetic and food industries. Several countries reported numerous SSY contamination cases in food products [21]. Indeed, the SSY complex molecular structure was hard to be degraded using microorganisms, hence dangerous to the natural water resources. In vivo studies suggested that SSY dye could cause chromosomal aberration in the germinative and liver cells, and enhanced abnormalities in mice spermatozoids [21,22]. Figure 4(a) depicts the SSY dye degradation as a function of light irradiation duration. Only around 5.3 and 13.7% SSY dye was removed under photolysis and dark conditions, respectively. It suggested that the SSY dye was extremely stable and it needs both photocatalyst and light for the effective degradation. Under visible light irradiation, Pd-BiFeO₃ composite displayed the highest degradation performance of 100% much higher than that of the pristine BiFeO₃ (77.5%) as well as commercial TiO₂ (56.1%). The rate constant (k) of applied photocatalysts were determined using first-order reaction kinetics ln(C₀/C) = kt, where C₀ and C are the initial and final dye concentration at time interval t, as displayed in Figure 4(b). The results suggested that the k value for the Pd-BiFeO₃ composites was around (0.01688/min), which was 2.57 and 5.22 times greater than those of the pristine BiFeO₃ (0.006577/min) and commercial TiO₂ (0.003228/min), respectively. The enhanced photocatalytic activity of Pd-BiFeO₃ can be credited to the unique coral-like morphology, improved optical and electronic properties. The extent of mineralization over pristine BiFeO₃ and Pd-BiFeO₃ composite was investigated using COD analysis. Figure 4(c) depicts a comparison among the COD removal after 4 h of light irradiation. The Pd-BiFeO₃ composite clearly exhibited much improved mineralization than the pristine BiFeO₃, which proved the role of enhanced separation of charge carriers in the Pd-BiFeO₃ composites. Figure 4(d) depicts the recyclability of the photocatalysts. A clear decline witnessed in both pristine BiFeO₃ and Pd-BiFeO₃ due to the photodecomposition and loss of the material during
each round washing and rinsing process. However, the Pd-BiFeO₃ can still sustain photoactivity above 91% even after 7th cycle, on the other hand, the pristine BiFeO₃ shows only 54.2%. The recycling test proved that the photocatalytic stability of BiFeO₃ can sufficiently be enhanced through the incorporation of metallic Pd.

**Figure 4.** (a) Photocatalytic degradation of SSY dye over commercial TiO₂, pristine BiFeO₃ and Pd-BiFeO₃ composite, (b) corresponding first-order kinetics plots and rate constant k over numerous samples, (c) COD removal of SSY dye over pristine BiFeO₃ and Pd-BiFeO₃ composite and (d) SSY degradation over seven consecutive runs using pristine BiFeO₃ and Pd-BiFeO₃ composite.

### 3.4 Photocatalytic mechanism of Pd-BiFeO₃ composite

With the help of obtained results, a possible enhanced SSY dye photodegradation mechanism using Pd-BiFeO₃ was proposed, as illustrated in Figure 5(a). Under light irradiation, the photoexcited electron from the BiFeO₃ surface migrated to the CB and leaving an equal quantity of holes in the VB. In the case of pristine BiFeO₃, only a limited number of electrons could reach the photocatalyst surface due to the fast recombination of photogenerated charge carriers, which resulted in a lower photocatalytic activity [4]. On the other hand, the incorporation of metallic Pd can introduce the energy band banding at the interface, which facilitates the free flow of electrons from BiFeO₃ to Pd nanoparticles to accelerate the charge carrier separation [12]. These migrated electrons then easily react with the surface absorbed oxygen (O₂) molecules and hydrogen ions (H⁺) to form hydrogen peroxide (H₂O₂) molecules. Meanwhile, the holes situated in the valance band were scavenged by the hydroxyl group and produced •OH radicals. The H₂O₂, h⁺ and •OH radicals then attacked the organic dyes molecules and degrade them into small and simple species like CO₂ and H₂O.

The above-stated photodegradation mechanism was further confirmed by the radical trapping study. Figure 5(b) displays the effects of numerous radical trapping agents on SSY dye degradation using Pd-BiFeO₃ composite. It can be seen that the presence of BQ, a trapping agent for •O₂⁻ radical had a minor impact on SSY dye degradation, while the presence of IPA, KI and catalase, trapping agents for •OH, h⁺ and H₂O₂, respectively led to a dramatic decrease in the SSY degradation. It suggested that the •OH, h⁺ and H₂O₂ served as a key reactive species in photodegradation reaction.
3.5 Photodegradation of industrial textile wastewater

Figure 6 shows the Pd-BiFeO₃ photocatalytic degradation performance against industrial textile wastewater. After 240 min of light irradiation, the COD and BOD₅ concentrations of textile wastewater were declined around 85.84%, 82.59%, respectively. An initial lower BOD₅/COD ratio of 0.14 revealed the non-biodegradable properties of textile wastewater, hence, considering some new advanced oxidation treatment process was vital. After photocatalytic reaction, a surge in BOD₅/COD ratio was recorded and reached to 0.18. Hence, the treated textile wastewater presented a clear enhancement in the biodegradability as confirmed from the increased final BOD₅/COD ratio.

Table 1 depicts the other quality parameters of industrial wastewater before and after photocatalysis over Pd-BiFeO₃ composite. It was observed that the NH₃−N, TSS, color, and turbidity degradation efficiencies were 79.79%, 84.23%, 86.63% and 85.23%, respectively. It can be attributed to the occurrence of dyes mixture and various impurities such as Cl⁻ ions as well as dissolved organic matters in real textile wastewater. Different inorganic ions and functional groups of dyes can affect the photocatalytic mechanism, which resulted in a complex degradation reaction [23]. At the end of photocatalytic reaction, the solution pH was declined from pH 12.99 to pH 7.07. Styliadi et al. [24] explained the decrease in the solution pH after photodegradation reaction was because of the production of different aliphatic acids like formic, lactic, maleic, acetic etc. The decline in the solution pH in the current study might also be associated with the generation of smaller aliphatic acids. Therefore, the synthesized Pd-BiFeO₃ composite was undoubtedly useful in the treatment of real textile wastewater.
5. Conclusion

In summary, we synthesized Pd-BiFeO₃ composite using hydrothermal synthesis method. The fabricated materials were analyzed using XRD, FTIR, FESEM, TEM, EDX, UV-vis DRS, PL and photoelectrochemical measurements. As compared with the pristine BiFeO₃, the Pd-BiFeO₃ composite exhibited much enhanced photodegradation and mineralization of SSY dye with outstanding recycling potential. The enhanced photocatalytic activity was credited to the efficient separation and transfer of the photogenerated charge carrier. The radical trapping test proved that the •OH, H₂O₂ and h⁺ were the main reactive oxidizing agents. In case of real textile wastewater, the degradation efficiencies of COD (85.84%), BOD₃ (82.59%), turbidity (85.23%), color (86.63%), TSS (84.23%) and NH₃–N (79.79%) were attained after 240 min of treatment. These findings suggest that the Pd-BiFeO₃ composite can act as a green photocatalysts in aqueous environmental remediation.

Table 1. Quality parameters of textile wastewater before and after photocatalysis over Pd-BiFeO₃ composite.

| Parameters     | As-received wastewater | After 240 min | Removal efficiency (%) |
|----------------|-------------------------|---------------|------------------------|
| COD (mg/L)     | 2267                    | 321           | 85.84                  |
| (BOD)₃ (mg/L)  | 317                     | 55            | 82.59                  |
| Turbidity (NTU)| 92.44                   | 13.65         | 85.23                  |
| Color (Pt-Co)  | 726                     | 97            | 86.63                  |
| TSS (mg/L)     | 1072                    | 169           | 84.23                  |
| NH₃–N (mg/L)   | 3.91                    | 0.79          | 79.79                  |
| pH             | 12.95                   | 7.07          | –                      |

4. Reference

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