Spindly BiFeO$_3$ Nanoparticles for Photodegradation of Organic Pollutants Under a Compact Fluorescent Lamp

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Abstract. Spindly bismuth ferrite oxide (BiFeO$_3$, BFO) nanoparticles were fabricated by Bi(NO$_3$)$_3$, Fe(NO$_3$)$_3$, NaOH and urea solutions at 125°C. The BFO nanoparticles have a spindle-shaped of ~120 m in length and ~50 nm in width. Such nanoparticles could be used in the photocatalytic degradation of Malachite Green (MG) dye under irradiation by a 105 W compact fluorescent lamp. They were very stable and could be easily recovered by an applied magnetic field. There was an optimal photocatalyst amount of 1.0 g/L, at which the degradation efficiency of MG was improved to 72.6% under exposure of visible light for 240 min. The active hydroxyl (•OH) radicals formed during the photocatalytic process were tested using a photoluminescence–terephthalic acid (PL–TA) measurement, which were validate to be significantly affected by the photocatalyst amount. Other organic pollutants including phenol, bisphenol A and methylparaben could also be photodecomposed in the presence of similar conditions. These features demonstrated the BFO nanoparticles practical applications in environmental remediation.

1. Introduction
Since the photochemical utilization of solar energy concept was introduced, much scientific works have been performed to establish photocatalytic materials for splitting H$_2$O to generate H$_2$ energy, reducing CO$_2$ to fuel molecules and destruction of harmful organic pollutants. In order to harvest the visible light energy (~43%) of the total solar energy efficiently, one approach is to create photocatalytic materials that have appropriate band gaps to absorb the visible light. Of major interest in the photocatalytic materials, bismuth ferrite (BiFeO$_3$, noted as BFO) is recognized as one of the room temperature multiferroic materials with rhombohedral phase having the polar R$_3$c space group [1]. The recent researches in BFO materials as potential photocatalysts arise from their small band gaps (2.0–2.8 eV), chemical stability and low cost [2,3]. The small band gap of BFO materials enables them response in the visible light spectrum. For example, Gao et al. [4] revealed that BFO nanophotocatalysts displayed photoactivity for degradation of methyl orange under exposure of visible light. Humayun et al. [5] also tested that the aqueous phenol solution can be degraded by the TiO$_2$/BFO nanocomposites in the presence of visible light. Nevertheless, it should be mentioned that
BFO alone typically indicates a poor visible light photoactivity than those of other bismuth-based photocatalysts including Bi$_2$WO$_6$ and BiVO$_4$ [6,7]. In order to surmount these lapses and enhance the BFO photocatalytic performance, ion doping, coupling with semiconductor metal oxides and synthesis of perovskite oxides with larger surface area are highly desirable. It is well known that the microstructure of photocatalyst played a pivotal role on the catalytic performance [8,9]. Nanoscale photocatalyst is anticipated to improve photocatalytic performance because of a larger specific surface area and more surface active sites for the reaction. A myriad of wet chemical technique including co-precipitation, sol-gel, hydrothermal techniques and some wet-chemical solution processes have been extensively utilized to fabricate the BFO nanoparticles. Among these, the urea-assisted hydrothermal method [10,11] is relatively facile, cheap, surfactant-free and effective. Additionally, it can be conducted at short periods, normal pressure and at low temperature (<200°C). Despite this method has been utilized to synthesize the BFO nanoparticles, its ability to form different structures at adequately huge amounts for practical applications including photocatalysis still requires to be established.

In the present study, a novel spindly BFO nanoparticles has been prepared by an urea-assisted hydrothermal technique at low temperature (~125°C). Such a new structure has not been reported elsewhere. The prepared BFO was then characterized by various characterization techniques such as X-ray diffraction (XRD), field emission-scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and UV–vis diffuse reflectance spectroscopy (DRS) measurements. The •OH radicals concentration for different BFO amounts were evaluated upon the photocatalytic processes. More importantly, the prepared BFO displayed high photocatalytic activities in the degradation of organic pollutants such as malachite green (MG), phenol, bisphenol A (BPA) and methylparaben (MP) under irradiation by a low-power (105 W) compact fluorescent lamp.

2. Experimental

Bi(NO$_3$)$_3$·5H$_2$O (0.005 mol), Fe(NO$_3$)$_3$·9H$_2$O (0.005 mol), urea (0.1 mol) and nitric acid (2 mL) was first prepared in 20 mL distilled water and stirring continuously for 20 min. The mixture was slowly added into 10 M NaOH solution under magnetic stirring. Subsequently, the mixed suspensions were placed into a 100 mL stainless-steel Teflon-lined autoclave for the hydrothermal treatment. After being tightly closed, the autoclave was heated up to 125°C for 60 min and then cooled to room temperature naturally. The as-formed products were filtered, washed with distilled water and ethanol and dried at 70°C for 3 h.

The samples were then analyzed using X-ray diffraction (XRD) pattern recorded using a Philips PW1820 diffractometer with Cu Kα radiation at a scanning rate of 2° min$^{-1}$ in the range of 20°–80°. The morphology of the samples was scanned using a Quanta FEG 450 field emission-scanning electron microscope (FESEM) with an energy dispersive X-ray spectroscopy (EDX) analysis. UV–vis diffuse reflectance spectroscopy (DRS) spectrum was recorded on a Perkin Elmer Lambda 35 UV-vis spectrophotometer with BaSO$_4$ as a reference. The infrared spectrum was tested using a Thermo scientific Nicolet IS10 Fourier Transform Infrared (FTIR) spectrometer at scanning range from 500 to 4000 cm$^{-1}$. Photoluminescence (PL) spectroscopy was conducted at room temperature using a Perkin Elmer Lambda S55 spectrophotometer using a Xe lamp with an excitation wavelength of 315 nm.

In a typical experiment, the photocatalytic experiments were performed under a low-power (105 W) compact fluorescent lamp. The average light intensity striking the surface of the reaction solution was about 6,500 lux, as determined by a digital luxmeter. This lamp was positioned about 12 cm above the reaction solution. The catalyst (100 mg) was added in 100 mL malachite green (MG) solution (10 mg/L) in a beaker. The mixture was subjected to magnetic stirring for 1 h in the dark prior to the exposure of light irradiation. At specific time intervals, 5 mL of the sample was removed from the system, centrifuged and the MG concentration at different time intervals was evaluated by an UV-visible spectrophotometer (HACH DR6000). For mineralization test, 2 mL of filtered supernatant was added into COD vial and placed inside the Hach DRB 200 COD reactor at 150°C for 2 h. The COD vial was then measured using an UV-Vis spectrophotometer to determine mineralization efficiency of MG dyes. The photodegradation efficiencies of other organic pollutants including phenol, BPA and MP in the presence of prepared samples were monitored based on our previous report [12].
3. Results and Discussion

Figure 1a displays the XRD pattern of the as-prepared BFO samples. All of the diffraction peaks were indexed to rhombohedral perovskite structure of BFO (JCPDS Card file No. 20–0169) [4,5]. The strong and sharp XRD peaks in the figure indicated that the as-prepared BFO crystals were highly crystalline. Further evidence of formation of BFO samples came from the EDX analysis. The presence of Bi, Fe and O peaks can be easily found in Figure 1b. The UV–vis DRS spectrum of the BFO product (Figure 1c) depicted a steep absorption edge which lay between 500 and 580 nm. The observed region was a characteristic region for the absorption band of the rhombohedral structure of BFO [10,11]. The band gap energy of the BFO sample can be acquired from the plot of $(F(R)hν)^{0.5}$ versus photon energy $(E)$. The band gap energy was measured to be 2.5 eV (Figure 1d), which was concordance with the reported BFO catalyst [10,11].

![Figure 1](image1.png)

**Figure 1.** (a) XRD spectrum, (b) EDX spectrum, (c) UV-vis DRS spectrum and (d) plot of $(F(R)hν)^{0.5}$ vs $E (hν)$ of spindly BFO nanoparticles.

FESEM analysis of as-prepared BFO samples was carried out under different magnifications. Figure 2a shows the spindle-like BFO particles were synthesized in a large scale. This image indicated also that the obtained BFO spindle-like nanoparticles presented good dispersion and uniformity. The magnified image in Figure 2b indicated that average length of these spindles were about 120 nm and average width of about 50 nm.
Figure 2. FESEM images of spindly BFO nanoparticles at different magnifications (a) 20,000x and (b) 100,000x.

Figure 3 presents FTIR spectrum of spindly BFO nanoparticles. Two strong absorption peaks observed around 450 cm\(^{-1}\) and 556 cm\(^{-1}\) in the FTIR spectrum could be assigned to O–Fe–O bending vibrations and the Fe–O stretching of FeO\(_6\) groups in FeO\(_6\) octahedral unit in perovskite compounds \([13,14]\). The absorption peak that appeared at 1626 cm\(^{-1}\) could be attributed to the asymmetric stretching of carboxylate ligands. Moreover, the broad band around 3448 cm\(^{-1}\) could be arisen from the antisymmetric and asymmetric stretching of absorption H\(_2\)O and OH\(^-\) groups. This FTIR result confirmed that spindly BFO nanoparticles possessed perovskite structures, which was in agreement with the result of XRD (Figure 1a).

Figure 3. FTIR spectrum of spindly BFO nanoparticles.

The photoactivity of as-prepared BFO samples was examined by degrading MG under visible light irradiation. Figure 4a displays the absorption spectrum of MG solution in the presence of BFO nanospindles at different durations. The absorption peak at 625 nm conforming the MG molecule and decreased steadily as the irradiation time prolonged. Figure 4b shows that the MG solution was degraded about 72.6% by BFO nanospindles under 240 min. Further experiments were conducted to examine the photoactivity of photocatalysts. When the solution with the nanospindles was kept in the dark or when the solution was irradiated without the BFO nanospindles, only small amounts of MG were adsorbed or degraded. The degree of MG degradation of the two experiments attained 2.1% and 18.8%, respectively under identical conditions. It inferred that the as-prepared BFO samples were active photocatalysts.
Figure 4. Photoactivity of spindly BFO nanoparticles in the MG degradation. (a) UV-vis absorption spectra of MG solution at different time intervals, (b) MG degradation dependence on irradiation time at different conditions, (c) Changes of COD during the photodegradation of MG and (d) Isolation of the spindly BFO nanoparticles using an external magnetic field.

The COD test (Figure 4c) was conducted to examine the performance of spindly BFO nanoparticles on the MG mineralization under irradiation of a 105 W compact fluorescent lamp. The initial COD value was 24.0 mg/L and then this value gradually weakened upon the irradiation in 240 min. This verified the mineralization extent of MG resulting from an efficient degradation of benzene-ring products. The COD efficiency of MG attained at 62.5% at the point that the solution was degraded, which showed several organic intermediates were still remained in solution. Furthermore, the recovering process of photocatalysts from the reaction medium is another important factor for their practical applications. Figure 4d shows that spindly BFO nanoparticles found to be relatively easier to filter from the mixtures owing to magnetically attractive property.

The influence of the photocatalyst amount on the degradation of MG was investigated at different BFO nanospindles under visible-light irradiation (as recorded in Figure 5a). When the amount of photocatalyst at 1.0 g/L, the degradation efficiency was 72.6%, which was higher than that at 0.25, 0.5 and 2.0 g/L. Higher amount of photocatalyst indicated more availability of total active sites or surface area of the photocatalyst. A decline in degradation efficiency was typically found at photocatalyst overloading because of optical opaque and agglomeration of the excess photocatalysts in the solution. This indicated that an optimal photocatalyst amount was 1.0 g/L.

The photodegradation processes of photocatalyst amount displayed a pseudo-first-order kinetic model against to the irradiation time. The linear relationship is expressed in equation (1) [12]:

\[ \ln \left( \frac{C_o}{C} \right) = kt \]  

where \( C_o \) is the initial concentration of a pollutant, \( C \) is the concentration of pollutant at time \( t \), and \( k \) is the reaction constant of first-order reaction. The results are illustrated in Figure 5b. The results clearly
demonstrated the optimal photocatalyst amounts 1.0 g/L with the maximal degradation rate constant of 0.0059 min$^{-1}$ as compared to those of other photocatalyst amounts.

Figure 5. (a) Photocatalytic degradation of 10 mg/L MG at different photocatalyst amounts and (b) kinetic contants for degradation of MG under a compact fluorescent lamp.

Photocatalyst-based catalytic mechanism included a portion of photogenerated charge carriers reacted with adsorbed O$_2$ and H$_2$O to form active species such as •OH radicals that further partook in the degradation of organic pollutant [1]. The generated •OH radicals over BFO nanospindles in the photocatalytic reaction can be evaluated by PL technique with terephthalic acid (TA) as a probe molecule. The generated •OH radicals in the photocatalytic reaction could readily react with TA and produce the highly fluorescent compound, 2-hydroxyterephthalic acid (2HTA) (equation (2)) [1].

\[
•\text{OH} + \text{TA} \rightarrow \text{HO}−\text{TA} \quad (2HTA)
\]

Figure 6 displays the PL spectra changes observed during the irradiation of the as-prepared BFO samples in the aqueous basic solution of TA. Generally, PL intensity at about 425 nm was accordance to the amount of generated •OH radicals. It can be clearly seen that the amount of generated •OH radicals on 1.0 g/L BFO nanospindles were larger than that of other samples. With increasing the BFO nanospindles amount, the excess •OH radicals would react each other (equation (3)) [15] rather involve the degradation process of organic pollutants. This result was also consistent with the results of photocatalytic test in Figure 5a.

\[
•\text{OH} + •\text{OH} \rightarrow \text{H}_2\text{O}_2
\]

Figure 6. PL spectra of BFO nanospindles at different photocatalyst amounts in basic TA solution for 120 min of irradiation.
In addition to MG degradation, the spindly BFO nanoparticles could be utilized in photodegradation of other organic pollutants as shown in Figure 7. Phenol and bisphenol A (BPA) were effectively decomposed under the same experimental conditions as those in the degradation of MG. The results indicated that the spindly BFO not only can degrade the dye colorants but also can degrade the non-absorbing visible organic compounds. When BFO nanoparticles were added into the phenol and BPA solutions, the degradation efficiencies were found to be 59.1% and 55.4%, respectively. For methylparaben (MP), the BFO nanospindles increased the degradation efficiency from 3.1% (for photolysis alone) to 42.6% in 240 min. Obviously, BFO nanoparticles indicated different photoactivities in degradation of various organic pollutants and however, it could improve the degradations of all pollutants aforementioned owing to their photocatalytic ability.

![Figure 7. Photodegradation of (a) MG, (b) phenol, (c) BPA and (d) MP under irradiation by a 105 W compact fluorescent lamp (photocatalyt amount: 1.0 g/L; volume of pollutant: 100 mL; concentration of pollutant: 10 mg/L; treatment time: 240 min).](image)

4. Conclusion
Spindly BFO nanoparticles were successfully synthesized via an urea-assisted hydrothermal route. The proposed method was facile and suitable to yield a large production of BFO nanospindles. The structural, morphological and optical properties of the as-prepared BFO nanospindles were confirmed by XRD, UV–vis DRS, FESEM, EDX, TEM and FTIR analyses. The BFO nanospindles have showed good photocatalytic performance for the MG degradation under visible light irradiation. The amount of BFO nanospindles of about 1.0 g/L has resulted in the superior degradation rate of MG solution at which the generated •OH radicals showed their maximum as shown in the PL–TA test. These nanospindles could be utilized in photodegradation of organic pollutants such as MG, phenol, BPA and MP. The light source and spindly BFO nanospindles have no harmful effects and readily available. These provide the photocatalytic system practicality in degrading various organic pollutants.

5. References
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