

## Sonochemical synthesis, characterization and evaluation of photocatalytic activities of Ag/BiFeO<sub>3</sub> photocatalysts

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Being a visible-light responsive semiconductor, BiFeO<sub>3</sub> (BFO) is considered as a potential material for photocatalysis. To enhance the photocatalytic efficiency, in this work, BiFeO<sub>3</sub> was dispersed with various amount of Ag. Morphologies and phases of the as-synthesized samples were evaluated by using scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. UV-Vis diffuse reflectance spectroscopy (DRS) was used to analyse the absorption properties. The photocatalytic activities of the products were evaluated via the photocatalytic degradation of aqueous rhodamine-B (RhB) solution under simulated solar-light irradiation. The results indicated the important role of Ag nanoparticles on improving catalytic efficiency of BiFeO<sub>3</sub>. The enhancement in the photocatalytic activity is explained on the basis of surface plasmon resonance effect of the dispersed Ag nanoparticles over the surface of BiFeO<sub>3</sub>.

**Key words:** BiFeO<sub>3</sub>, Ag nanoparticle, Photocatalyst, Rhodamine B, Surface plasmon resonance.

### Introduction

Titanium dioxide and zinc oxide are the most commonly investigated semiconductor photocatalysts for organic pollutants degradation and water splitting [1–4]. These materials have characteristics corresponding to good photocatalysts, such as low cost of fabrication, high stability in room temperature and non-toxicity. However, due to their relatively larger band gap values (3.2 eV for TiO<sub>2</sub>, and 3.4 eV for ZnO), the application is limited only in UV light that comprises about 4–5% of the total solar light radiation [1–4]. Recently, BiFeO<sub>3</sub> is considered as a potential visible light photocatalyst for both pollutants degradation and water splitting, due to its high chemical stability and narrow band gap (2.0 eV–2.8 eV) [5–7]. In addition, with perovskite structure, BiFeO<sub>3</sub> is known as one of several compounds that demonstrate the coexistence of ferroelectric and antiferromagnetic orders above room temperature ( $t_N \sim 370^\circ\text{C}$ ,  $t_C \sim 830^\circ\text{C}$ ) [5, 6, 8]. The ferroelectric properties of BiFeO<sub>3</sub> with spontaneous polarization has a significant influence on the separation of charge carriers, such properties help to inhibit the recombination of holes and electrons, resulting to increasing the lifetime of photo-induced charge carriers [9]. However, the practical application of BiFeO<sub>3</sub> is limited by the leakage current problems because of secondary phases as well as other impurities.

In order to promote photocatalytic activities, semiconductor materials were decorated noble metals (Ag

[10, 11], Au [11, 12], Pt [13], etc). These noble metal nanoparticles efficiently capture the photo-generated electrons and leave behind the holes on the photocatalyst surface. Thus, they could inhibit the recombination of photo-generated electron-hole pairs and enhance the photocatalytic activity [10]. In addition, the localized surface plasmon resonance (LSPR) effect also has an important influence on improving photocatalytic activity. This effect serves to scatter the incident radiation in the visible region and to increase the photon trapping capability. Among the modified noble metals, Ag nanoparticles have been extensively investigated because this metal is less expensive, nontoxic and has unique photocatalytic properties [14].

In this work BiFeO<sub>3</sub> was synthesized by ultrasound, a method arises from acoustic cavitation which is related to the formation, growth and implosive collapse of bubbles in liquid medium, therefore, influences on chemistry reactions and reduces particle size. Meanwhile, Ag/BFO was prepared by photodeposition method based on the degradation of AgNO<sub>3</sub> in UV irradiation. Such green methods do not need high temperature or any surfactant, thereby reduce the investment and costs.

### Experiment Details

Bismuth Nitrate (Bi(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O) 99.99% from Aldrich, Ferric Nitrate (Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O) 99+% from Acros, Silver Nitrate (AgNO<sub>3</sub>) 99.8% from DaeJung, and Ammonia 70% solution from Duksan were used without further purification. RhB from Alfa Aesar was used as received. Ethanol and other chemicals were analytical grade and used without further purification.

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De-ionized water was used for all synthesis and treatment process.

### Synthesis of BFO

A solution of 5 mmol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was sonicated in water for 10 min using 1 ml  $\text{HNO}_3$  70% to form transparent solution. Then, 5 mmol  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 25 ml of distilled water in a separate beaker. Two aqueous solutions were mixed together and poured into a 100 ml beaker, the final concentration of each metallic ions were made to 0.1 M. The solution in the beaker was then subjected for ultrasonic treatment at 400 W ultrasound operating at 20 kHz with a titanium 13 mm-probe dipped in the solution (ultrasonic processor 750 W, model VC750). During the sonication, 30 wt%  $\text{NH}_4\text{OH}$  solution was added drop by drop to adjust pH 9 for the complete precipitation. Sonication time was chosen as 1 h for the present study. The subsequently formed brown orange precipitate was then separated out by centrifuging several times with de-ionized water and finally with ethanol. The products were dried in an oven at 80 °C and then calcined for 1 h at 600 °C with 5 °C/min heating rate.

### Synthesis of Ag/BFO

First of all, 100 mg of as-prepared BFO was placed in a glass reactor with 10 ml of ethanol and ultrasonicated for 10 min. Then, 10 ml of ethanol solution with different contents of  $\text{AgNO}_3$ , corresponding to 1, 2, 3 wt% of Ag, after vigorously stirring in 10 min, was added to the reactor. The mixture was ultrasonicated for 5 min to ensure the complete disaggregation of agglomerated particles. Afterwards, the slurry was maintained for 1 h under magnetic stirring at 200 rpm and under UV light irradiated with two 20 W UVC lamps. Then, the suspension was placed on a hotplate at 80 °C to evaporate the ethanol. The solid was completely dried overnight in an oven at 80 °C.

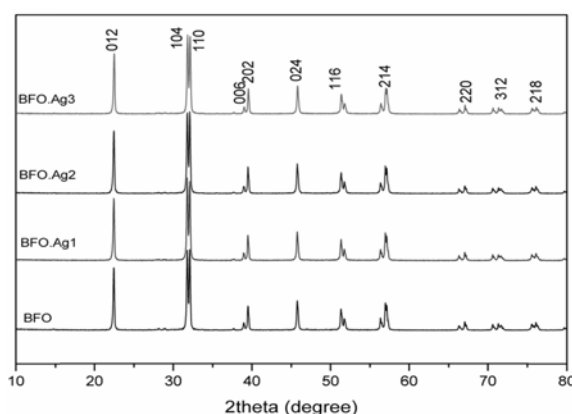
The crystalline structure of the obtained catalysts was identified by X-ray diffraction (XRD, Rigaku X-Ray Diffractometer) employing  $\text{Cu K}\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation in the 2-theta range from 10 ° to 90 °. Morphology and particle size of the samples were examined with scanning electron microscope (SEM, JEOL-2020). The light absorption ability was recorded by UV-Vis diffuse reflectance spectrophotometer (DRS, UV-Vis spectrophotometer NIR JASCO 570). Photocatalytic activities of  $\text{BiFeO}_3$  and Ag/BFOs were carried out by RhB degradation in a photoreactor using solar simulator (portable solar simulator PEC-L01, Pecell). Absorption spectrum of the dye was measured by using a UV-Vis spectrophotometer (SCINCO UV-Vis Spectrophotometer Mega 2100).

The photocatalytic activities of the as-synthesized BFO and Ag/BFO samples were evaluated by studying the photocatalytic degradation of RhB in aqueous solution. In a typical experiment, 50 mg of the catalyst sample was added to 70 ml of 20 ppm RhB solution in

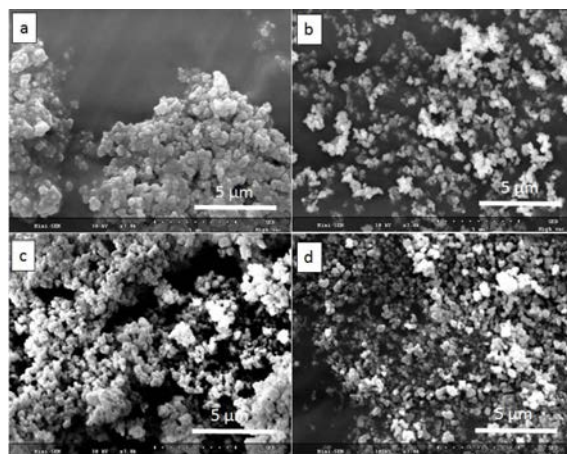
a Pyrex glass vessel. The pH value of the mixture was adjusted at 2 by using HCl. At this pH value, RhB shifts to acidic form which interacts with the surface of BFO more easily [15]. The solution was continuously stirred in dark for 30 min to ensure the samples adsorption/desorption equilibrium. Then the solution was irradiated under simulated solar light without UV cut-off filters. After certain intervals of time, 5 ml of the suspension was sampled and separated from the solution by external magnetic field. The change in concentration of RhB was measured by the intensity of absorbance peak at 553 nm.

## Results and Discussion

Fig. 1 shows the XRD patterns of as-prepared samples. XRD patterns of Ag/BFOs are compared with that of BFO powder without Ag particles. It is evident that  $\text{BiFeO}_3$  has rhombohedral structure belonging to the R3c group (JCPDS 86-1518). In XRD patterns of all samples, there is not any peak for other impurities or secondary phases observed. However, the clear peaks for Ag were not detected in Ag/BFOs samples. It



**Fig. 1.** XRD patterns of  $\text{BiFeO}_3$  and Ag/BFO with different contents of Ag.



**Fig. 2.** SEM images of; a)  $\text{BiFeO}_3$ , b) BFO.Ag1, c) BFO.Ag2, and d) BFO.Ag3 samples.

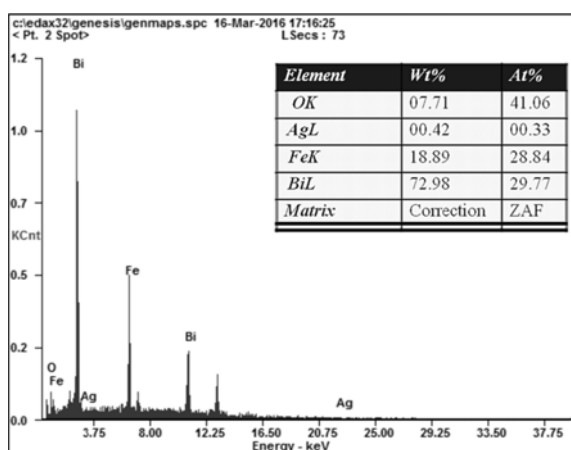


Fig. 3. EDX analysis of Ag/BFO with 2 wt% of Ag.

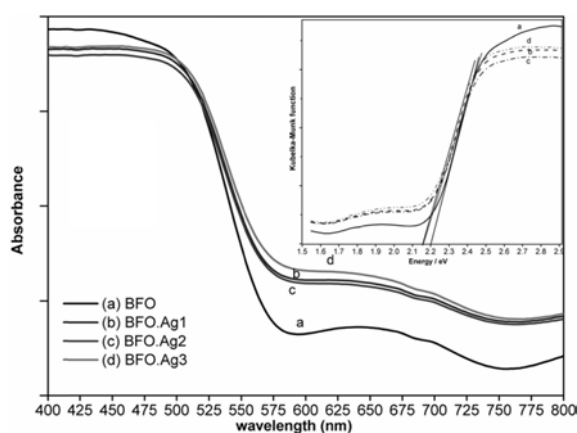


Fig. 4. UV-Vis diffuse absorption spectra of BiFeO<sub>3</sub> and Ag/BFOs with different contents of Ag. Inset is the Kubelka-Munk function vs. band gap energy plot.

might be due to the small quantity of dispersed Ag particles that might be below the detection limit by XRD.

The morphology of BiFeO<sub>3</sub> sample was investigated by SEM image Fig. 2(a), which shows the clear uniform spherical particles of about 300 nm in size. This morphology is also observed in SEM images of Ag/BFO samples Fig. 2(b-d). Compared to the reference BFO sample, Ag/BFO particles were found to be disaggregated because of Ag decorating process. On these images, Ag particles are not seen due to the limit of SEM machine, thus, EDX analysis was performed to elucidate the presence of Ag (Fig. 3). The results show the appearance of Ag peak, indicating that silver nanoparticles were successfully dispersed onto the photocatalyst powder.

UV-Vis diffuse reflectance spectra of as-prepared BiFeO<sub>3</sub> and Ag/BFOs samples are shown in Fig. 4. It is evident that the BiFeO<sub>3</sub> and Ag/BiFeO<sub>3</sub> catalysts have shown the visible light absorption in the range of 400–530 nm. All Ag loaded BFO samples have shown another strong absorption band at 600–725 nm, attributed to the LSPR effect caused by the Ag nanoparticles [16]. The band gap energy of the samples was evaluated by

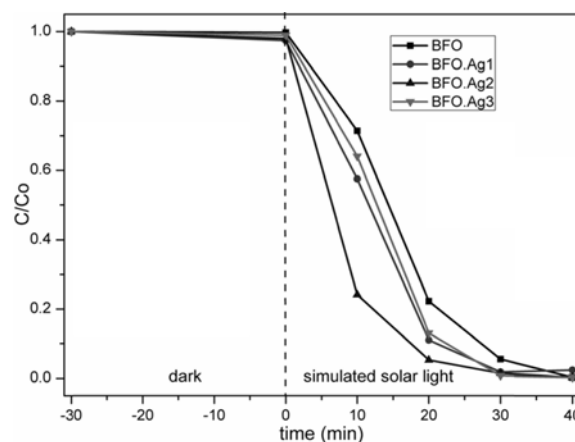


Fig. 5. The degradation of RhB (20 ppm) at pH = 2 by BiFeO<sub>3</sub> and Ag/BFO samples.

applying the Tauc equation [17]. As shown in inset of Fig. 4, the band gap energy of BFO was about 2.2 eV, indicating BiFeO<sub>3</sub> powders can exhibit an excellent photocatalytic properties for the degradation of organic pollutants in the visible light range. Meanwhile the band gap of Ag dispersed BFO samples were around 2.15 eV, slightly smaller than that of BFO. The reduction of band gap energy indicated that photon-excited electrons jumped from the valence band to an energy band which is lower than the conduction band of the semiconductor. In another word, the presence of Ag nanoparticles on BFO surface causes the localized energy levels in the band gap of the semiconductor and results the decrease in the band gap energy of the catalyst.

In order to evaluate the photocatalytic activity of BiFeO<sub>3</sub> and Ag/BFO powders, the degradation of aqueous RhB solution was carried out under simulated solar light irradiation. Fig. 5 shows the time-dependent degradation efficiency of RhB by the BFO and Ag/BFO samples. As presented, in all the cases, there was a negligible initial adsorption of RhB (~2%) by catalysts under dark condition. In the visible light irradiation, there was a sharply decrease of RhB concentration with the irradiation time, demonstrating the excellent photocatalytic activities of BiFeO<sub>3</sub> and Ag/BFO photocatalysts. After 20 min of irradiation, RhB dye in solution was degraded by 78%, 89%, 95% and 87% with BFO samples loaded with 0, 1, 2 and 3 wt% of Ag, respectively. After 30 min of irradiation, the color of RhB changed to almost colorless for Ag/BFOs while there was still fade color remained for BFO sample at this interval, indicating that the presence of Ag in BFO enhances the photocatalytic activity. Similar observation in enhancement of photocatalytic activities of different host materials, dispersed with Ag nanoparticles, has been reported in the past by different authors [10,16,18]. Kinetics of photodegradation was calculated by Langmuir-Hinshelwood model [15]. Based on this model, the half-life time and rate

**Table 1.** The total organic carbon (TOC) in the RhB solutions after 1 h irradiation in simulated solar light.

| Sample | RhB solution | BFO | BFO • Ag1 | BFO • Ag2 | BFO • Ag3 |
|--------|--------------|-----|-----------|-----------|-----------|
| % TOC  | 100          | 86  | 77        | 74        | 80        |

**Table 2.** The kinetics parameters of photocatalytic degradation reaction of RhB by BFO and Ag/BFOs with different contents of Ag.

| Sample                             | BFO   | BFO.Ag1 | BFO.Ag2 | BFO.Ag3 |
|------------------------------------|-------|---------|---------|---------|
| Half-life time (min)               | 7.07s | 5.06    | 4.20    | 4.85    |
| Rate constant (min <sup>-1</sup> ) | 0.098 | 0.137   | 0.165   | 0.143   |

constants of reaction were determined by assuming pseudo-first-order reaction kinetics. These kinetics parameters were shown in Table 2. The degradation rates of RhB were 0.098 min<sup>-1</sup>, 0.137 min<sup>-1</sup>, 0.165 min<sup>-1</sup>, 0.143 min<sup>-1</sup> with catalysts were BFO samples dispersed with 0, 1, 2 and 3 wt% of Ag, respectively. It is evident that 2 wt% Ag dispersed BFO sample has the highest reaction rate, that is nearly two times higher than that of reference BFO sample. Particularly, the photocatalytic degradation rate increases following the increase Ag contents, but slightly decreases at 3 wt% of Ag sample. This fall in degradation rate might be attributed to the formation Ag cluster which plays a role as charge recombination center, thus inhibits photocatalytic activity [16].

To assess the mineralization ability of as-prepared photocatalysts, an analysis of total organic carbon (TOC) was performed with the RhB aliquot taken out after 1 h of simulated solar light irradiation. The percentage of TOC in the catalyst free solution is summarized in Table 1. According to the presented TOC values, as the Ag content increases in BFO, the mineralization percentage of RhB dye also increased from 14% in BFO case to 26% in BFO.Ag2. It is noteworthy that TOC value of BFO.Ag2 was higher than that of other Ag loaded samples, which is well supported by the kinetics (C/C<sub>0</sub>) results. Hence, it can be concluded that photocatalytic activity is enhanced with the increase Ag content in the samples. However, if the percentage of Ag is too high, photocatalytic activity might be inhibited due to the formation of metal cluster on the surface of semiconductors [16].

## Conclusions

Pure BiFeO<sub>3</sub> powders were synthesized successfully by ultrasonic method without the use of any surfactants in a short time at room temperature. Ag particles were loaded successfully on BFO powders by photodeposition method.

Spectroscopic and microscopic analyses revealed the formation of pure and uniform BFO particles in all the synthesized samples. The band gap energies of Ag/BiFeO<sub>3</sub> samples were slightly smaller than the pure BFO sample. The photocatalytic degradation of aqueous RhB solution and the total organic carbon measurement revealed the strong influence of Ag in improving photocatalytic activities.

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