Short Communication

Photocatalytic and electrochemical characteristics of BiFeO$_3$-TiO$_2$ nanoheterostructure for leather dyes degradation

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The present work was focused on hydrothermal synthesis of the titanium oxide (TiO$_2$) nanorods and bismuth ferrite (BiFeO$_3$)-TiO$_2$ nanoheterostructure on indium tin oxide (ITO) as photocatalysts for photodegradation of leather dyes under visible-light irradiation. The samples were characterized via the SEM, XRD, EIS and UV-Vis absorption spectra. SEM results revealed that high density and high aspect ratio of BiFeO$_3$-TiO$_2$ were successfully grown on ITO substrate. XRD analysis exhibits that both the TiO$_2$ and BiFeO$_3$ phases coexist, which shows that there aren’t any impurity phases at the interface between BiFeO$_3$ and TiO$_2$ with the synthesis condition. Optical characterization results revealed that BiFeO$_3$ nanoparticles leads to reduction the band-gap of TiO$_2$ nanorods which were calculated to be 2.93 and 2.58 eV for the TiO$_2$ and BiFeO$_3$/TiO$_2$ nanoheterostructure, respectively. EIS analysis shows that BiFeO$_3$/TiO$_2$ revealed lower recombination rate of electron-hole pairs which accelerate the photocatalytic reactions. The degradation efficiency for BiFeO$_3$/TiO$_2$ nanoheterostructure was 88% after 90 min under visible-light radiation which was significantly greater than its degradation efficiency (54%) in TiO$_2$ nanorods. These findings exhibited that the BiFeO$_3$/TiO$_2$ has the excellent visible-light harvesting performance for degradation of leather dyes.

Keywords: BiFeO$_3$/TiO$_2$ nanoheterostructure; Photocatalysts; Photodegradation of leather dyes; Optical and electrochemical properties

1. INTRODUCTION

Textile and leather dye effluents are one of the major concerns of contamination with azo dyes up to 50% [1, 2]. However, textile dyes have been widely tested for decolonization, studies on leather dyes are still growing [3]. While both leather and textile industries use various common dyes, the effluents produced by both vary in numerous aspects such as concentration, temperature, pH, etc[4, 5].
These pollutants are degraded by advanced oxidative procedures that create hydroxyl radicals as the major oxidant \cite{6, 7}. Hydroxyl radicals are highly efficient oxidizers. Thus, photoelectrocatalytic degradation has been broadly used as an alternative electrochemical method for environmental remediation \cite{8, 9}. Using semiconductor photo-catalysts and UV light can mineralize and degrade these dyes \cite{10}.

Titanium oxide (TiO\textsubscript{2})-based photo-catalysts have been used widely for degradation of the organic pollutants to remediate contaminated groundwater, hazardous wastes and controlling the toxic air contaminants \cite{11, 12}. Though, the optical band-gap of TiO\textsubscript{2} is wide-ranging that can only absorb UV-light, which is only 5\% at the source of sun \cite{13}. Therefore, other classes of oxides for example ferrites with narrowing optical band-gap in the visible-light region have been a great deal of interest in it as a potentially visible catalyst for industrial processes \cite{14-16}.

Multiferroic oxides have great potential for multi-functional capabilities in spintronic, random access memory, data storage, attenuators, filters, photovoltaic and sensor devices due to their basic physical properties \cite{17}. Among the multiferroic oxides, BiFeO\textsubscript{3} (bismuth ferrite) has received ever-increasing attraction due to its coupling of magnetism and ferroelectricity, promising for fabrication of magnetoelectric devices \cite{18, 19}.

This work focused on an efficient approach to attain multi-functionality in BiFeO\textsubscript{3} nanomaterial synthesized on wide band-gap TiO\textsubscript{2} nanorods substrate. To our best knowledge, the photo-catalysis activities based on the BiFeO\textsubscript{3}-TiO\textsubscript{2} nano-heterostructure have not been considered until now. Here, one-dimensional BiFeO\textsubscript{3}/TiO\textsubscript{2} nanostructure photocatalysts were synthesized by combining hydrothermal and spin coating techniques. The enhanced photocatalytic activity of BiFeO\textsubscript{3}/TiO\textsubscript{2} nano-heterostructure can be attributed to the light-harvesting property of BiFeO\textsubscript{3} and outstanding charge separation features of the shaped heterojunction between TiO\textsubscript{2} and BiFeO\textsubscript{3}.

2. MATERIALS AND METHOD

The TiO\textsubscript{2} nanostructures were grown on indium tin oxide (ITO) glass by a hydrothermal technique. The ITO substrate was cut in squares (10×10 mm\textsuperscript{2}) and cleaned with DI water and acetone. A mixed solution of DI water and hydrochloric acid, with a (1:1) volume ratio, including a suitable volume of Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4} was utilized for hydrothermal reactions. After that, the ITO was placed in an autoclave including the prepared solution and retained into an oven at 170 °C for 5h. Then, the TiO\textsubscript{2} nanorods were synthesized on the ITO substrate. Precursor solution of BiFeO\textsubscript{3}/TiO\textsubscript{2} was produced by a typical sol-gel method, in which Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O and Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O were utilized as a starting material. An equimolar volumes of Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O and Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O and was dissolved into 2-methoxyethanol for obtaining a clear and brown solution via a magnetic stirrer. After that, citric acid as an acidifier and a chelating agent was added in the solution. After one day, the precursor solution (0.3mol*l\textsuperscript{-1}) was used for doing experiments. Then, the prepared solution was spin-coated on TiO\textsubscript{2} nanorods four times to create uniform wet film. After per step, wet film was primarily dried at 170°C for 10 min for evaporation of all solvent. Then, the film quickly heated to 350°C for 15min to
eliminate the residual organic material. Then, the film was annealed at 500°C for 20 min to allow the BiFeO$_3$ for crystallization, and resulting BiFeO$_3$/TiO$_2$ nanoheterostructure were obtained.

The morphology of prepared specimens was considered through scanning electron microscopy (SEM). The X-ray diffractometer with Cu Ka radiation at wavelength of 1.5404Å operating at 30 kV and 20 mA was used to investigate the crystal structures of specimens. EIS tests were done in frequency range from 0.1 kHz to 1 MHz at 5 mV AC voltage using CHI 660D potentiostat (Chenhua Co. Shanghai, China) in a conventional three-electrode electrochemical cell which includes prepared films, Pt wire and Ag/AgCl electrode as working, counter and reference electrodes, respectively. The electrolyte solution was in 0.1 M KCl (99%). Photo-catalysis tests were performed by a photoreaction tool (125 Watt Mercury Lamp) as a light source. Leather dyes were supplied by Luthai Textile Co. Ltd., Shandong, China and was utilized as a model pollutant. The concentration of Leather dyes is 25 mg/L. The UV/Vis spectrophotometer (UV-2100, China) was used to measure the absorbance spectra of the Leather dye.

3. RESULTS AND DISCUSSION

![Figure 1. FESEM images of the (a) TiO$_2$ nanorods and (b) BiFeO$_3$/TiO$_2$ nano-heterostructure](image)

Figure 1 shows the FESEM images of the TiO$_2$ nanorods and BiFeO$_3$/TiO$_2$ nano-heterostructure. As shown in Fig. 1a, the nanorods were synthesized on the surface of ITO and were along the vertical direction to the ITO substrate. The TiO$_2$ nanostructures had rough square top and smooth side facets. Figure 1b indicates that after spin-coating BiFeO$_3$ onto the TiO$_2$ nanorods, the TiO$_2$ nanostructures may not be detected from the FESEM images, but the BiFeO$_3$ crystalline particles can be found.
Figure 2. XRD patterns of the TiO$_2$ nanorods and BiFeO$_3$/TiO$_2$ nano-heterostructure with Cu K$\alpha$ radiation at wavelength of 1.5404Å operating at 30 kV and 20 mA.

Figure 3. (a) UV-visible absorption spectra and (b) the band gap calculation through Tauc method for the TiO$_2$ nanorods and BiFeO$_3$/TiO$_2$ nano-heterostructure on ITO.
Figure 2 reveals the XRD patterns of the TiO$_2$ nanorods and BiFeO$_3$/TiO$_2$ nano-heterostructure on ITO. All diffraction peaks are indicated in Fig. 2 except ITO. For TiO$_2$ nanorods synthesized on ITO, the chief diffraction peaks appeared at about $36.7^\circ$ and $\sim55.3^\circ$, which associated with (101) and (211) crystal planes of TiO$_2$ structures (JCPDS Card No.21-1272) [20]. The diffraction peaks of perovskite phase BiFeO$_3$ are labeled with red color (JCPDS card No.86-1518), which indicates that well-crystallized BiFeO$_3$ may be attained by the synthesis condition. Furthermore, the XRD pattern of BiFeO$_3$/TiO$_2$ nanoheterostructure exhibit that both TiO$_2$ and BiFeO$_3$ phases coexist, which shows that there aren’t any impurity phases at interface between BiFeO$_3$ and TiO$_2$ with synthesis condition. 

The UV-visible absorption spectra of the samples are shown in Figure 3. The absorption spectra indicate that the BiFeO$_3$ nanostructures can absorb significant amounts of visible light, signifying their potential application as visible-light photo-catalysts. It can be attributed to the small intrinsic band-gap of BiFeO$_3$. The optical direct band-gap ($E_g$) may be calculated by the following equation [21]:

$$ (\alpha h \nu)^2 = A (h \nu - E_g) \quad (1) $$

where $h \nu$ shows the photon energy, $\alpha$ and $A$ are the absorption coefficient and a material dependent constant, respectively [22]. The measured band-gap of the TiO$_2$ and BiFeO$_3$/TiO$_2$ nanoheterostructure were calculated to be 2.93 and 2.58 eV, respectively. The band-gap energy decreased with spin coating of the BiFeO$_3$ on TiO$_2$ nanorods because of the quantum-size effect.

Moreover, electrons and holes can be created in the semiconductor band structure under UV-Vis light irradiation. The photo-generated charge-carrier may enhance the photocatalytic activities [23]. As a result, spin coating of BiFeO$_3$ can prevent the recombination of holes and electrons, improving the catalytic activities and make robust light-harvesting abilities.

![Nyquist plots of TiO2 nanorods and BiFeO3/TiO2 nano-heterostructure visible-light irradiation with frequency range of 0.1kHz to 1MHz at 5 mV applied voltage into 0.1M KCl (99%)](image)

**Figure 4.** Nyquist plots of TiO2 nanorods and BiFeO3/TiO2 nano-heterostructure visible-light irradiation with frequency range of 0.1kHz to 1MHz at 5 mV applied voltage into 0.1M KCl (99%)

To further explore the charge-transfer behaviors EIS assessment is a powerful method to analyze the charge-transfer mechanisms at the solution/photocatalyst interface [24]. In the Nyquist plots, the EIS semicircle diameter indicates charge-transfer resistance ($R_{ct}$) of sample surface. For photocatalytic reaction, a reduction in the $R_{ct}$ value always means a faster charge-transfer and slower
recombination of holes and photoelectrons occurred, which is helpful for relevant photocatalytic activity. As shown in Figure 4, the semicircle radius reduces in the BiFeO$_3$/TiO$_2$ nanoheterostructure sample. An $R_{ct}$ of 4840 $\Omega$ was obtained for TiO$_2$ nanorods, which was much bigger than the other specimen, proposing that the TiO$_2$ nanorods under visible-light irradiation require overcoming a great energy-barrier to occur in a photocatalytic reaction. In BiFeO$_3$/TiO$_2$ sample, The $R_{ct}$ was sharply decreased to 2620 $\Omega$, indicating that the close contact of TiO$_2$ with BiFeO$_3$ was rather efficient in elimination of the hole-electron recombination and acceleration of the photocatalytic reaction. As a result, more long-lived photo-generated electrons contribute with the photo-degradation organic pollutants [25].

In order to study the photocatalytic degradation behavior of the prepared BiFeO$_3$/TiO$_2$ nanoheterostructure in visible-light radiation, the direct irradiation (Blank), TiO$_2$ nanorods and BiFeO$_3$/TiO$_2$ nanoheterostructure were used to test. As shown in Figure 5a that the leather dye content of the blank has practically no variation under visible-light, which indicates that leather dyes are difficult to degradation by visible-light alone. In TiO$_2$ nanorods and BiFeO$_3$/TiO$_2$ nano-heterostructure, leather dye degradation was clearer, which confirmed that leather dye was removed via catalyst under visible radiation.

![Figure 5](image.png)

**Figure 5.** (a) Photodegradation leather dye performance and (b) degradation rate for 25 mg/L Leather dyes in visible-light radiation.

Clearly, the degradation efficiency of BiFeO$_3$/TiO$_2$ was considerably higher than degradation efficiency of TiO$_2$ nanorods. After 90 min of visible irradiation, the removal efficiency of leather dye
reached 88%. The synthesized BiFeO$_3$/TiO$_2$ was an outstanding photocatalyst and had a good application in organic removal and degradation. As shown in Figure 5b, the -lnC$_t$/C$_0$ consistent with each photocatalyst was fundamentally linearly associated with reaction time t, therefore revealing that leather dye degradation followed pseudo-first order kinetics. Reaction rate constant (k) for blank, TiO$_2$ nanorods and BiFeO$_3$/TiO$_2$ nano-heterostructure are 0.00046, 0.0068 and 0.021 min$^{-1}$, respectively. BiFeO$_3$/TiO$_2$ had the robust visible-light photocatalytic activity. Compared with TiO$_2$, the photocatalytic degradation behavior was significantly enhanced by the BiFeO$_3$. BiFeO$_3$ nanoparticles improved the visible-light absorption of BiFeO$_3$/TiO$_2$, and improved its visible-light utilization. The prepared BiFeO$_3$/TiO$_2$ nanostructure had regular and uniform morphologies, and more active sites for dye adsorption were exposed on the surface of crystal, which was favorable for the utilization of visible-light and the adsorption of leather dye [26]. The presence of BiFeO$_3$ nanoparticles leads to the creation of photoexcited electron-hole pairs in TiO$_2$ nanorods under visible-light irradiation [27]. It can promote the separation of holes and electrons and delay their recombination. It significantly enhances the photocatalytic performance. Furthermore, BiFeO$_3$/TiO$_2$ could better prepare more catalytic current than bare TiO$_2$ under visible-light. Hence, it seriously increased the free carrier content, activated radicals and facilitated the creation of stronger oxidizing holes (h$^+$) and then accelerated leather dye removal and degradation.

Comparison of the photodegradation efficiency of leather dye on BiFeO$_3$/TiO$_2$ nano-heterostructure with other nanostructured photocatalysts is presented in Table 1. As seen, by considering the time of photodegradation, BiFeO$_3$/TiO$_2$ nano-heterostructure show the degradation efficiency of 88% for 90 min, which are higher than the reported degradation efficiency values in [28-31].

| Photocatalysts          | Leather dye concentration (mg l$^{-1}$) | Time (minutes) | Degradation efficiency (%) | Ref. |
|---------------- ------- |---------------------------------------|----------------|---------------------------|------|
| La doped Nb$_2$O$_5$    | 100                                   | 100            | 80                        | [28] |
| CeO$_2$–SnO$_2$ Nanocomposite | 50                                   | 240            | 50                        | [29] |
| Laccase                | 20                                    | 360            | 75                        | [30] |
| CS-ZnS-NPs             | 30                                    | 165            | 92                        | [31] |
| BiFeO$_3$/TiO$_2$       | 25                                    | 90             | 88                        | This work |

4. CONCLUSIONS

Textile and leather dye effluents are one of the major concerns of contamination with azo dyes. This work was focused on hydrothermal synthesis of the TiO$_2$ nanorods and BiFeO$_3$-TiO$_2$ nano-
heterostructure on ITO glass substrate as photocatalysts for photodegradation of leather dyes under visible-light irradiation. The samples were characterized via the SEM, XRD, EIS and UV-Vis absorption spectra. SEM results revealed that high density and high aspect ratio of BiFeO$_3$-TiO$_2$ were successfully grown on ITO substrate. XRD analysis exhibits that both TiO$_2$ and BiFeO$_3$ phases coexist, which shows that there aren’t any impurity phases at the interface between BiFeO$_3$ and TiO$_2$ with the synthesis condition. Optical characterization results revealed that BiFeO$_3$ nanoparticles improved the visible-light absorption of BiFeO$_3$/TiO$_2$, and improved its visible-light utilization. EIS analysis shows that BiFeO$_3$/TiO$_2$ revealed lower recombination rate of electron-hole pairs which accelerate the photocatalytic reactions. The degradation efficiency for BiFeO$_3$/TiO$_2$ nano-heterostructure was 88% after 90 min under visible-light radiation which was significantly greater than its degradation efficiency (54%) in TiO$_2$ nanorods. These results exhibited that the BiFeO$_3$/TiO$_2$ increased the free carrier content, activated radicals and facilitated the creation of stronger oxidizing holes ($h^+$) and then accelerated leather dye removal and degradation.

References

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