Research Article

Preparation of BiFeO$_3$-Graphene Nanocomposites and Their Enhanced Photocatalytic Activities

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1. Introduction

Semiconductor-based photocatalysts have attracted considerable attention over the past decades due to their potential applications in solar energy conversion and environmental purification [1, 2]. Among them, TiO$_2$ has proven to be a powerful photocatalyst for the degradation of numerous organic compounds [3–5]. However, it can only respond to UV light owing to its wide bandgap (∼3.2 eV). To efficiently make use of solar energy that consists largely of visible light, it is essential to explore visible-light-driven photocatalysts.

BiFeO$_3$, exhibiting simultaneous ferroelectric and antiferromagnetic properties at room temperature, has been extensively studied as one of the most important multiferroic materials [6, 7]. Besides its multiferroic property, recent investigations have revealed that BiFeO$_3$ also exhibits visible-light responsive photocatalytic activity for the degradation of organic pollutants [8–13]. Generally, the overall photocatalytic activity of a photocatalyst depends on numerous factors. Among them, the effective separation of photogenerated electron-hole ($e^−$-$h^+$) pairs is very important in improving the photocatalytic activity. Graphene, being a two-dimensional (2D) sheet of $sp^2$-hybridized carbon atoms, possesses excellent properties including high electrical conductivity, electron mobility, thermal conductivity, mechanical strength, chemical stability, and so forth [14–16]. On account of its outstanding properties, graphene has been frequently used as an ideal support to integrate with a large number of functional nanomaterials to form unique nanocomposites with improved performances in the fields of photocatalysts [17–23], microsupercapacitors [24], field-emission emitters [25], and fuel cells [26]. Particularly, the combination of graphene with photocatalysts is demonstrated to be an efficient way to promote the separation of photogenerated $e^−$-$h^+$ pairs and then enhance their photocatalytic activities [17–23]. In these graphene-photocatalyst composites, photogenerated electrons can be readily captured by graphene which acts as electron acceptor; thus, more photogenerated holes are increasingly available for the photocatalytic reactions. Therefore, many efforts have been devoted to incorporating graphene into BiFeO$_3$-based composite materials.

Up to now, the BiFeO$_3$-graphene composites are often prepared by hydrothermal method and sol-gel route. In
the former method, the BiFeO$_3$ precursors were introduced into the dispersed aqueous of graphene or graphene oxide, followed by hydrothermal reaction, to yield BiFeO$_3$-graphene composites [23, 27]. For the latter route, the sol containing precursors and graphene oxide was dried, and then the resultant was thermally treated at N$_2$ atmosphere, leading to the formation of BiFeO$_3$-graphene hybrids [22]. However, it should be noted that the aforementioned processes are based on hydrothermal condition or high temperature thermal treatment procedure, which may damage the graphene lattice [28]. In this paper, we demonstrate that BiFeO$_3$ nanoparticles can be assembled onto graphene sheets by mixing BiFeO$_3$ nanoparticles and graphene into absolute ethanol solution followed by thermal drying. The photocatalytic activities of prepared samples were evaluated by the degradation of methylene orange (MO) under simulated sunlight irradiation. The production of ·OH radicals on the irradiated BiFeO$_3$-graphene photocatalyst was examined by the photoluminescence (PL) technique using terephthalic acid (TPA) as a probe molecule.

2. Experimental

The graphene used in this research was purchased from Nanjing XFNano Materials Tech Co. Ltd. BiFeO$_3$ nanoparticles were synthesized via a polyacrylamide gel route as described in the literature [29]. To assemble BiFeO$_3$ nanoparticles on graphene, number of BiFeO$_3$ nanoparticles and graphene were dispersed into absolute ethanol solution and ultrasonically treated for 10 min. The obtained mixture was dried at 60°C for 10 h in a thermostat drier, during which ethanol was vaporized, leaving behind BiFeO$_3$ nanoparticles well anchored on graphene nanosheets. By changing the graphene content, several BiFeO$_3$-graphene nanocomposite samples with graphene weight fractions of 1%, 3%, 5%, 7%, and 9% were prepared.

The photocatalytic activity of the BiFeO$_3$-graphene nanocomposites was evaluated by the degradation of MO under simulated sunlight irradiation from a 200 W xenon lamp (incident light power: ~5 mW cm$^{-2}$) at room temperature. The initial dye concentration was 10 mg L$^{-1}$ with a catalyst loading of 2.5 g L$^{-1}$. Before illumination, the mixed solution was mildly stirred for 1 h in the dark in order to reach the adsorption-desorption equilibrium of MO on the catalyst. The concentration of MO after photocatalytic degradation was determined by measuring the absorbance of the solution at a fixed wavelength of 464 nm using a UV-visible spectrophotometer. Before the absorbance measurements, the reaction solution was centrifuged for 10 min at 4000 r min$^{-1}$ to remove the catalyst.

Terephthalic acid (TPA) was used as a probe molecule to examine ·OH radicals formed on the irradiated BiFeO$_3$-graphene photocatalyst. It is expected that TPA reacts with ·OH to generate a highly fluorescent compound, 2-hydroxyterephthalic acid (TAOH). By measuring the PL intensity of TAOH that is pronounced around 429 nm, the information about ·OH can be obtained. TPA was dissolved in $1.0 \times 10^{-3}$ mol L$^{-1}$ NaOH aqueous solution to make a $2.5 \times 10^{-4}$ mol L$^{-1}$ TPA solution, and then to the solution was added 2.5 g L$^{-1}$ photocatalyst. The mixed solution, after several minutes of ultrasound treatment in the dark, was illuminated under the 200 W xenon lamp. The reacted solution was centrifuged for 10 min at 4000 r min$^{-1}$ to separate the catalyst particles and was then used for the PL measurements at a fluorescence spectrophotometer with the excitation wavelength of 315 nm.

The morphology of the sample was observed using a field-emission transmission electron microscope (TEM). A fluorescence spectrophotometer was used to measure the photoluminescence (PL) emission spectra of the samples.

3. Results and Discussion

Figure I(a) presents the TEM image of pure graphene, indicating that graphene has typical two-dimensional sheet structure with crumpled feature. Figure I(b) shows the TEM image of BiFeO$_3$-graphene(5%) nanocomposite. It can be seen that BiFeO$_3$ nanoparticles are assembled onto the graphene sheet.
The BiFeO$_3$ nanoparticles mainly exhibit sphere-like shape and have an average particle size centered around 110 nm.

Figure 2 shows the photocatalytic degradation of MO over BiFeO$_3$-graphene nanocomposites as a function of irradiation time ($t$). The degradation percentage is defined as (C$_0$ - C$_t$)/C$_0$ × 100%, where C$_0$ and C$_t$ are the MO concentrations before and after irradiation, respectively. The blank experiment result is also shown in Figure 2, from which one can see that the MO is hardly degraded under simulated sunlight irradiation without photocatalysts, and its degradation percentage is less than 5% after 6 h of exposure. After 6 h irradiation in the presence of BiFeO$_3$ nanoparticles and graphene, about 37% and 16% of MO are observed to be degraded, respectively. When BiFeO$_3$ nanoparticles assembled on graphene, all samples of BiFeO$_3$-graphene nanocomposites exhibit higher photocatalytic activity than bare BiFeO$_3$ nanoparticles. Moreover, the photocatalytic activity of nanocomposites increases gradually with the increase in graphene content from 1% to 5%. Further increase in graphene content leads to the decrease of photocatalytic activity.

Figure 3 shows the PL spectra of the TPA solution after reacting 6 h over the irradiated BiFeO$_3$ nanoparticles and BiFeO$_3$-graphene (5%) nanocomposite.

Figure 4 schematically shows the photocatalytic mechanism of BiFeO$_3$-graphene nanocomposite toward the degradation of MO. Under the simulated sunlight irradiation, the valence band (VB) electrons of BiFeO$_3$ are promoted to the conduction band (CB), inducing the production of e$^-$$^*$-h$^*$ pairs. The photogenerated electrons and holes then participate in a series of redox reactions to form a number of active species. However, the redox reaction processes are strongly related to the CB and VB edge potentials of BiFeO$_3$. The VB potential of the BiFeO$_3$ can be calculated using the following relation [30]:

$$E_{VB} = X - E^e + 0.5E_g$$  \hspace{1cm} (1)

where $X$ is the absolute electronegativity of the semiconductor, $E^e$ is the energy of free electrons on the hydrogen scale (−4.5 eV), and $E_g$ is the bandgap energy of the semiconductor (for the as-prepared BiFeO$_3$, $E_g$ is 2.06 eV [31]). The value of $X$ for BiFeO$_3$ is obtained, by the arithmetic mean of the electron affinity and the first ionization of the constituent atoms reported in the literatures [32, 33], to be 5.93 eV. Thus, the CB and VB potentials of BiFeO$_3$ are calculated to be 0.4 and 2.46 V versus normal hydrogen electrode (NHE), respectively. It can be seen that the VB potential of sample is more positive than the redox potential of OH$^-$/$^*$OH (1.89 V/NHE), indicating that the photogenerated holes have strong oxidative ability and they can oxide OH$^-$ into OH. However, the CB potential of sample is not negative enough to reduce O$_2$ to O$_2^*$ ($^*$OH (−0.13 V/NHE) via e$^-$$^*$. As a result, it is reasonable to infer that OH radicals derived by the reaction of the photogenerated h$^*$ with OH$^-$ are the main active species responsible for the degradation of MO over simulated sunlight irradiated BiFeO$_3$. Therefore, the effective separation of e$^-$$^*$$^*$-h$^*$ pairs and increased availability of h$^*$ are the key points to improve the photocatalytic activity of the BiFeO$_3$. When BiFeO$_3$ nanoparticles assembled on graphene, that is, an excellent electron acceptor and conductor, the photogenerated electrons readily transfer from the BiFeO$_3$ conduction...
band to graphene, which could suppress the recombination of photoexcited $e^−$-$h^+$ pairs, thus leading to the increase in the number of holes which participate in the photocatalytic reaction. The results shown in Figure 3 confirm the enhanced yield of $\cdot$OH radicals on the irradiated BiFeO$_3$-graphene nanocomposite. As a result, with the introduction of an amount of graphene, the resulted BiFeO$_3$-graphene nanocomposites exhibit an improved photocatalytic activity compared to bare BiFeO$_3$ nanoparticles. However, when the graphene content is further increased above its optimum value, the photocatalytic efficiency begins to exhibit a decreasing trend. This is ascribed to the following reasons: (i) the excessive graphene may shield the light and decrease the number of photon absorption on BiFeO$_3$ particles; (ii) the amount of available surface active sites tends to be reduced due to an increasing coverage of graphene onto the surface of BiFeO$_3$ particles.

4. Conclusions

BiFeO$_3$ nanoparticles were prepared via a polyacrylamide gel method. BiFeO$_3$-graphene nanocomposites were fabricated by mixing BiFeO$_3$ nanoparticles and graphene into ethanol followed by thermal drying at 60°C. It is found that the BiFeO$_3$ nanoparticles are well anchored onto graphene sheet. The photocatalytic experiments indicate that the BiFeO$_3$-graphene nanocomposites exhibit higher photocatalytic activity for the degradation of MO under simulated sunlight irradiation than bare BiFeO$_3$ nanoparticles, which is attributed to the fact that the photogenerated electrons are captured by graphene, leading to an increased availability of $h^+$ for the photocatalytic reaction.

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References


