Enhanced Photocatalytic Degradation Activity of BiFeO$_3$ Microspheres by Decoration with g-C$_3$N$_4$ Nanoparticles

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In this work, the g-C$_3$N$_4$ nanoparticles decorated BiFeO$_3$ microspheres composites (g-C$_3$N$_4$/BiFeO$_3$) were successfully synthesized by hydrothermal treatment of g-C$_3$N$_4$ nanoparticles together with BiFeO$_3$ microspheres. The SEM and HRTEM observation indicate that the C$_3$N$_4$ nanoparticles with size of 30-50 nm are well decorated on the surface of BiFeO$_3$ microspheres. The photocatalytic activities of the samples are investigated by the degradation of methylene blue (MB) under the irradiation of simulated sunlight. The as-prepared g-C$_3$N$_4$/BiFeO$_3$ composites exhibit remarkable enhanced photocatalytic activity compared with bare BiFeO$_3$. More importantly, the photocatalytic performance of the composites is further confirmed by the degradation of colorless phenol. Furthermore, the favorable catalytic stability of composites is demonstrated through the recycling photocatalytic experiment. The enhanced photocatalytic activity of g-C$_3$N$_4$/BiFeO$_3$ composites is mainly attributed to the separation of the photogenerated electron-hole pairs, resulting from the migration of the photoinduced charge between g-C$_3$N$_4$ nanoparticles and BiFeO$_3$. A possible photocatalytic mechanism for dye degradation over g-C$_3$N$_4$/BiFeO$_3$ composite is proposed based on the active species trapping experiment, revealing that the photogenerated hole (h$^+$) and hydrogen peroxide (H$_2$O$_2$) are regarded as the major active species for the decomposition of dye, while hydroxyl radicals (•OH) plays a minor role in the photocatalytic reaction.

Keywords: BiFeO$_3$, g-C$_3$N$_4$ nanoparticles, composite, photocatalysis.

1. Introduction

Semiconductor based photocatalysis has attracted considerable attentions owing to its promising application in solar energy conversion and environmental purification$^{1-6}$. Perovskite oxide has been proven to be an important class of photocatalysts$^7$. As one of the perovskite photocatalysts, BiFeO$_3$ exhibits visible-light-driven photocatalytic activity for the degradation of dyes and water splitting due to its narrow bandgap and chemical stability$^{8-11}$. In addition to its photocatalytic property, BiFeO$_3$ has been also known to be a famous room-temperature multiferoic material$^{12}$. However, the photocatalytic performance of bare BiFeO$_3$ is not satisfactory owing to high recombination rate of photogenerated electron-hole pairs, and this shortage limits its practical applications in the field of photocatalysis. Therefore, many strategies have been employed to suppress the recombination of photoinduced charges$^{13-19}$. Among these methods, coupling BiFeO$_3$ with narrow-bandgap semiconductor of suitable band potential including BiVO$_4$, Ag/AgCl, Fe$_2$O$_3$, and Bi$_2$Fe$_4$O$_9$ is demonstrated to be an efficient way to promote photogenerated charges migration and separation, and then improve its photocatalytic activity$^{16-19}$.

Recently, A metal-free organic semiconductor photocatalysts, graphite-like carbon nitride (g-C$_3$N$_4$) with small bandgap of 2.7 eV, has been found to be a promising candidate for photocatalytic applications because of its narrow bandgap, non-toxicity, low cost and excellent chemical stability$^{20,21}$. Particularly, it can be easily obtained by the heat treatment of nitrogen-rich precursors at relatively low temperature$^{20,21}$. More importantly, g-C$_3$N$_4$ has been frequently employed as an ideal narrow-bandgap cocatalyst to combine with appropriate photocatalysts to form heterostructured composites with enhanced photocatalytic performance$^{22,23}$. It is worth noting that energy-band potentials of g-C$_3$N$_4$ and BiFeO$_3$ are well-matched$^{24,25}$. This suggests that the composites constructed by the two photocatalysts are expected to exhibit favorable photocatalytic performance. Wang et al. firstly reported that the bulk g-C$_3$N$_4$/BiFeO$_3$ composite can achieve the efficient separation of photoinduced charges$^{24}$. It is generally accepted that the photocatalytic performance of g-C$_3$N$_4$/metal oxides composites strongly related to the morphology and size of g-C$_3$N$_4$$^{23}$. Especially for the nanoscale g-C$_3$N$_4$ (such as nanosheets and nanoparticles), these materials possess large specific surface area, and thus provide more available surface active sites for the photocatalytic reaction and larger contact area for photogenerated charges transformation$^{23,26}$. Until now, g-C$_3$N$_4$ nanosheets have been successfully combined...
with BiFeO₃ to form g-C₃N₄ nanosheets/BiFeO₃ composites, and the composites exhibit enhanced photocatalytic activity towards the dye degradation²⁵. To the best of our knowledge, however, the enhanced photocatalytic activity of BiFeO₃ by decorated with g-C₃N₄ nanoparticles is rarely reported.

In this work, the g-C₃N₄ nanoparticles decorated BiFeO₃ microspheres (g-C₃N₄/BiFeO₃) composites with enhanced photocatalytic activity were prepared. The methylene blue (MB) and colorless phenol were selected as model pollutant to evaluate the photocatalytic properties of the composites under simulated sunlight irradiation. The promotion mechanism of g-C₃N₄ nanoparticles on the photocatalytic performance of BiFeO₃ microspheres was investigated in detail.

2. Experimental Section

2.1 Chemicals

All raw materials were purchased from Sinopharm Chemical Reagent Co., Ltd, which were analytical reagents and used without any purification.

2.2 Synthesis of g-C₃N₄ nanoparticles

The bulk g-C₃N₄ was prepared by directly heating melamine in a semiclosed system²⁷. Briefly, about 5 g of melamine was put into a corundum boat with a cover and calcinated at 520 ºC for 4 h. After the reaction, the product was ground and collected for further use.

The g-C₃N₄ nanoparticles were synthesized via the treatment of bulk g-C₃N₄ in H₂SO₄. 1 g of bulk g-C₃N₄ was added into 50 mL of H₂SO₄ (98 wt %) and magnetically stirred for 10 h. Subsequently, the mixture was ultrasonicated for 10 h. During the ultrasonic process, the color of the suspension was changed from yellow to slight yellow. After that, the as-prepared suspension was placed for 12 h to obtain the flocculent precipitate, and the absorbance was removed. The obtained precipitate was washed several times with distilled water to near-neutral pH, and then dried at 60ºC for 12 h to obtain final g-C₃N₄ nanoparticles.

2.3 Synthesis of g-C₃N₄ nanoparticles/BiFeO₃ composites

The BiFeO₃ microspheres were fabricated according to the hydrothermal route described in the literature²⁸. Then the g-C₃N₄/BiFeO₃ composites were prepared as follows: a certain amount of g-C₃N₄ nanoparticles were added into 40 ml of distilled water and then ultrasound for 2 h. Subsequently, BiFeO₃ microspheres were dispersed into the above suspension under magnetically stirring. After the suspension was uniform, this mixture was transferred into a 50 ml Te flon-lined stainless steel autoclave and heated at 130ºC for 2 h. Finally, the obtained precipitate were collected by centrifugation and dried at 70ºC for 10 h to get the composites. To study the effect of the g-C₃N₄ nanoparticles content on the photocatalytic activity of the composites, a series of sample were prepared with different g-C₃N₄ mass ratios of 4 %, 8 %, 16 % and 24 % (mₚ-C₃N₄/(mₚ-C₃N₄+mₚ-BiFeO₃)) and the corresponding samples were named as 4CN/BFO, 8CN/BFO, 16CN/BFO and 24CN/BFO, respectively.

For comparison, sample 16CN/BFO was synthesized under the same condition mentioned above except that the g-C₃N₄ nanoparticles were replaced by bulk g-C₃N₄, and this sample is termed as 16bulkCN/BFO. On the other hand, the sample denoted M16CN/BFO was fabricated by direct mixing of BiFeO₃ microspheres and g-C₃N₄ nanoparticles (mₚ-C₃N₄/(mₚ-C₃N₄+mₚ-BiFeO₃) =16 %).

2.4 Characterization

The phase purity of the samples was detected by X-ray diffractometer (Bruker D8 Advance XRD). The field mission scanning electron microscope (JEOL JSM-7610F FE-SEM) and transmission electron microscope (JEOL JEM-2010 TEM) was employed to observe the morphology and structure of the-products. Fourier transform infrared spectroscopy (FTIR) analysis was performed on a Bruker IFS 66v/S spectrometer. A UV-visible spectrophotometer with an integrating sphere attachment (PERSEE TU 1901) was used to measure the diffuse reflectance spectra of the samples.

2.5 Photocatalytic activity test

The photocatalytic activities of samples were evaluated by the degradation of MB and phenol under the simulated sunlight irradiation of a 300 W xenon lamp. In a typical experiment, the sample (0.1 g) was added into the solution of MB or phenol (200 mL, 5 mg/L). Before the photocatalytic reaction, the mixture was magnetically stirred in dark for 0.5 h to reach the adsorption-desorption equilibrium of organic molecule on the surface of catalysts. Under the simulated sunlight irradiation, a small amount of reaction solution was taken at a given time intervals and centrifuged at 6000 rpm/min for 10 min to separate the photocatalysts. During the photocatalytic reaction, the xenon lamp was cooled with water-cooling system to keep the solution at room temperature (~ 20ºC). The concentrations of MB and phenol were measured by detecting the absorbance of the supernatant at a given wavelength (λₑ(AO7) = 665 nm and λₑ(phenol) = 270 nm) on an UV-visible spectrophotometer. In order to evaluate the photocatalytic reusability of the samples, the recycling catalytic experiments toward the degradation of MB were carried out under the same conditions. After the first catalytic experiment, the photocatalyst in the reaction solution was recovered by centrifugation (6000 rpm/min, 10 min), washing with distilled water and drying in an oven (70ºC, 10 h). The collected photocatalyst was dispersed into the fresh MB solution for the next cycle of the catalytic experiment. In the 1st run, the photocatalysts was 100% used. The recovery percentage of photocatalysts for 2nd, 3rd, 4th and 5th run was ~ 97 %, ~ 93 %, ~ 87 % and ~ 82 %, respectively.
To detect the active species formed in this photocatalytic reaction, ammonium oxalate (AO, 2mM) and ethanol (10% by volume) were introduced aiming to trap photogenerated hole (h\textsuperscript+) and hydroxyl radicals (•OH), respectively\textsuperscript{29,30}. Furthermore, the N\textsubscript{2} purging experiment (0.1 L/min) was also performed to expel the effect superoxide radicals (O\textsubscript{2}•) and/or hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) on the photocatalytic degradation. The active species trapping experiments procedure were similar to the above photocatalytic experiment process.

3. Results and Discussion

3.1 Morphology and structure characterization

Fig. 1 shows the XRD patterns of bulk g-C\textsubscript{3}N\textsubscript{4}, g-C\textsubscript{3}N\textsubscript{4} nanoparticles, bare BiFeO\textsubscript{3}, and g-C\textsubscript{3}N\textsubscript{4}/BiFeO\textsubscript{3} samples. For bulk g-C\textsubscript{3}N\textsubscript{4}, the peaks at 13.0° and 27.4° can be indexed to (100) and (002) crystal planes of the graphite-like carbon nitride, respectively. After the H\textsubscript{2}SO\textsubscript{4} treatment, it is seen that the (100) peak of g-C\textsubscript{3}N\textsubscript{4} nanoparticles almost disappears which is mainly attributed to the decreased planar size of the g-C\textsubscript{3}N\textsubscript{4} layers. Similar phenomenon is also found in the g-C\textsubscript{3}N\textsubscript{4} nanosheets prepared though the H\textsubscript{2}SO\textsubscript{4} exfoliation of bulk g-C\textsubscript{3}N\textsubscript{4}\textsuperscript{26}. In the XRD pattern of BiFeO\textsubscript{3}, all the diffraction peaks are consistent with the standard diffraction data of rhombohedral structured BiFeO\textsubscript{3} (PDF card 74-2016), indicating the preparation of high-quality BiFeO\textsubscript{3}. After BiFeO\textsubscript{3} composing with g-C\textsubscript{3}N\textsubscript{4}, only the characteristic diffraction peaks of BiFeO\textsubscript{3} are observed in the XRD pattern of g-C\textsubscript{3}N\textsubscript{4}/BiFeO\textsubscript{3} samples, and no traces of g-C\textsubscript{3}N\textsubscript{4} are visible. This is possibly due to the low weight loading of g-C\textsubscript{3}N\textsubscript{4} and weak diffraction intensity of g-C\textsubscript{3}N\textsubscript{4} nanoparticles. Moreover, the impurity peaks cannot be detected in the XRD pattern of composite, suggesting that no any byproducts are generated during the fabrication of the composites.

The chemical functional groups and composition of bulk g-C\textsubscript{3}N\textsubscript{4}, g-C\textsubscript{3}N\textsubscript{4} nanoparticles, bare BiFeO\textsubscript{3}, and g-C\textsubscript{3}N\textsubscript{4}/BiFeO\textsubscript{3} composites were further investigated by FTIR spectrum, as shown in Fig. 2. Most of absorption peaks in the bulk g-C\textsubscript{3}N\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4} nanoparticles are the same, indicating that the two g-C\textsubscript{3}N\textsubscript{4} samples have similar chemical structure. The sharp absorption peak at about 808 cm\textsuperscript{-1} belongs to the bending vibration of C-N heterocycles. Several adsorption peaks at 1200-1700 cm\textsuperscript{-1} are assigned to the stretching vibration of C-N. The typical adsorption peak for the C=\text{N} stretching vibration is detected at ~1644 cm\textsuperscript{-1}. As to the spectrum of bare BiFeO\textsubscript{3}, the obvious absorption peaks located at around 440 and 560 cm\textsuperscript{-1} are attributed to the Fe-O stretching and bending vibrations, respectively\textsuperscript{31}. For the g-C\textsubscript{3}N\textsubscript{4}/BiFeO\textsubscript{3} composites, all the characteristic adsorption peaks of g-C\textsubscript{3}N\textsubscript{4} nanoparticles and BiFeO\textsubscript{3} can be observed. This suggests that the as-prepared composites are composed of g-C\textsubscript{3}N\textsubscript{4} nanoparticles and BiFeO\textsubscript{3}. Further observation finds that compared with the absorption peak of C-N stretching vibration (1644 cm\textsuperscript{-1}) for g-C\textsubscript{3}N\textsubscript{4} nanoparticles, a slight shift to higher wavenumber in g-C\textsubscript{3}N\textsubscript{4}/BiFeO\textsubscript{3} composites is detected , indicating the interaction between the two materials.

Fig. 3 shows the SEM and HRTEM images of bulk g-C\textsubscript{3}N\textsubscript{4}, g-C\textsubscript{3}N\textsubscript{4} nanoparticles, bare BiFeO\textsubscript{3}, and 16CN/BFO samples. It can be seen that bulk g-C\textsubscript{3}N\textsubscript{4} exhibits an aggregated layered structure about several micrometers in size (Fig. 3(a)). After H\textsubscript{2}SO\textsubscript{4} treatment, the bulk g-C\textsubscript{3}N\textsubscript{4} becomes irregular nanoparticles with 30-50 nm in particle size (Fig. 3(b)). As shown in Fig. 3(c) and (d), the bare BiFeO\textsubscript{3} exhibits regular sphere-like shape with diameter about 30-40 micrometers. The magnified SEM image (Fig. 3(e)) taken from a part of BiFeO\textsubscript{3} microsphere (Fig. 3(d)) shows that the single microsphere is composed of numerous particles with a size of several hundred nanometers and possesses a smooth and clean surface. The SEM image of 16CN/BFO sample obviously displays that the BiFeO\textsubscript{3} microsphere undergo no morphology change in the composite (Fig. 3(f)). The detail view of the sample shows that the g-C\textsubscript{3}N\textsubscript{4} nanoparticles are uniformly attached on the surface of BiFeO\textsubscript{3} microspheres (Fig. 3(g)). From the HRTEM image of 16CN/BFO sample (Fig. 3(h)), it is seen that the interplanar spacing of ~0.287
Figure 3. SEM images of bulk g-C₃N₄ (a), g-C₃N₄ nanoparticles (b), bare BiFeO₃ (c, d and e) and 16CN/BFO sample (f and g); (h) HRTEM image of 16CN/BFO sample.
nm corresponds to the BiFeO$_3$ (110) planes and the g-C$_3$N$_4$ with low crystallinity is on the edge of BiFeO$_3$, indicating that the intimate contact between the two materials is formed.

### 3.2 Optical absorption properties

To study the optical absorption properties of samples, the UV-visible diffuse reflectance spectra of samples are recorded (Fig. 4 (a)). Moreover, the corresponding first derivative spectra of the reflectance (R) with respect to wavelength ($\lambda$) are also obtained (Fig. 4 (b)), in which the peak wavelength are characterized to be the absorption edge of sample. The bandgap energy ($E_g$) of sample is evaluated by the formula: $E_g = \frac{1240}{\lambda_g}$, where $\lambda_g$ is the absorption edge of sample. For the bare g-C$_3$N$_4$ samples, one can see from the Fig. 4 (b) that the light absorption edge of sample presents a blue shift from $\sim 455$ nm for the bulk to $\sim 430$ nm for the nanoparticles. According to these absorption edges, the bandgap energies of bulk g-C$_3$N$_4$ and g-C$_3$N$_4$ nanoparticles are calculated to be $\sim 2.72$ and $\sim 2.88$ eV, respectively. Compared with bulk g-C$_3$N$_4$, the enlarged bandgap of g-C$_3$N$_4$ nanoparticles is mainly attributed to the quantum confinement effect. As seen from the Fig. 4 (b), the absorption edge of BiFeO$_3$ is located at $\sim 563$ nm, and the corresponding bandgap energy is estimated to be $\sim 2.2$ eV. It is worth noting that the g-C$_3$N$_4$/BiFeO$_3$ composites exhibit almost the same absorption edge as BiFeO$_3$ and g-C$_3$N$_4$ nanoparticles, suggesting that BiFeO$_3$ and g-C$_3$N$_4$ nanoparticles undergo no obvious bandgap change in the composites. On the other hand, according to the bandgap energies of BiFeO$_3$ and g-C$_3$N$_4$ nanoparticles, the valence band (VB) and conduction band (CB) potentials of the two materials can be estimated using the following relation (Eq (1) and (2)):

$$E_{CB} = X - E^* - 0.5E_g$$  

$$E_{VB} = X - E^* + 0.5E_g$$  

In the above equation, the X and $E^*$ are the absolute electronegativity of materials (defined as the arithmetic mean of the electron affinity and the first ionization of the constituent atoms) and energy of free electrons on the hydrogen scale (~ 4.5 eV), respectively. The X value of BiFeO$_3$ is calculated to be 5.93 eV based on the data reported in literatures, and the X value for g-C$_3$N$_4$ nanoparticles is reported to be 4.72 eV. The VB potentials of BiFeO$_3$ and g-C$_3$N$_4$ nanoparticles are calculated to be 2.53 and 1.66 V vs. NHE, and the CB potentials of BiFeO$_3$ and g-C$_3$N$_4$ nanoparticles are estimated to be 0.33 and -1.22 V vs. NHE, respectively.

### 3.3 Photocatalytic properties

Fig. 5 (a) presents the photocatalytic performance for the degradation of MB over g-C$_3$N$_4$ nanoparticles, bare BiFeO$_3$, and g-C$_3$N$_4$/BiFeO$_3$ composites under simulated sunlight irradiation. To clarify the effect of adsorption and direct photolysis of dye on the photocatalytic result, the photolysis and adsorption experimental were performed. It can be seen from Fig. 5 (a) that only ~ 17 % of MB is degraded after 9 h simulated sunlight irradiation without catalyst, and the dye is slightly adsorbed on the photocatalyst. When BiFeO$_3$ microspheres are employed as photocatalyst, about 35 % of MB is degraded with 9 h irradiation, indicating its weak photocatalystic activity. After combination with g-C$_3$N$_4$ nanoparticles, the g-C$_3$N$_4$/BiFeO$_3$ composites exhibit enhanced photocatalytic activity compared with bare BiFeO$_3$ under the same conditions. In the case of composites, the photocatalytic efficiency gradually increases with the increase of the content of g-C$_3$N$_4$ nanoparticles, achieving the highest degradation percentage of ~ 60 % at the g-C$_3$N$_4$ nanoparticles content of 16 %. However, further increasing the content of g-C$_3$N$_4$ nanoparticles leads to the decrease of
photocatalytic efficiency. This is mainly attributed to the fact that the excessive g-C$_3$N$_4$ nanoparticles may cover the surface of BiFeO$_3$ and decrease the photon absorption by the BiFeO$_3$ microspheres, and moreover, the large amount of g-C$_3$N$_4$ nanoparticles tend to self-agglomerate, consequently making it difficult to form heterojunction in the composites.

As a consequence, there exists an appropriate ratio of g-C$_3$N$_4$ nanoparticles to achieve optimal photocatalytic activity. The experimental data in Fig 5 (a) were fitted by first-order kinetic equation $\ln(C_0/C_t) = k_{app}t$, where $k_{app}$ is the apparent first-order reaction rate constant (Fig 5 (b)). The reaction rate constant of samples are shown in Fig 5 (b). It can be seen that the 16CN/BFO sample exhibits the highest reaction constant, which is almost 2.1 times as that of bare BiFeO$_3$.

For comparison, the photocatalytic performances of the physical mixture sample M16CN/BFO and the bulk g-C$_3$N$_4$/BiFeO$_3$ composite (16bulkCN/BFO) toward the degradation of MB were also investigated, as shown in Fig.5 (c). It is seen that the photocatalytic activities of the two samples are much lower than that of 16CN/BFO sample. Compared with physical mixture, the hydrothermal treatment in this work is more likely to promote the formation of the heterojunction between g-C$_3$N$_4$ and BiFeO$_3$. This is beneficial to the migration of the photogenerated charge between the two materials.

On the other hand, it is generally accepted that the g-C$_3$N$_4$ nanoparticles exhibit much higher surface area than bulk g-C$_3$N$_4$, thus offering more available surface active sites for the photocatalytic reaction. The above results illustrate that the nanoscaled g-C$_3$N$_4$ in the composite and strong heterojunction between g-C$_3$N$_4$ and BiFeO$_3$ are necessary for the efficient improvement of photocatalytic activity.

To exclude the dye sensitization effect during the photocatalytic process, phenol is used as another colorless target pollutant to test the photocatalytic activity of BiFeO$_3$ microspheres and 16CN/BFO sample under simulated sunlight irradiation, as shown in Fig.6 (a). The blank experiment indicates that the direct photolysis of phenol is about 5% for 9 h without photocatalyst. Bare BiFeO$_3$ can only degrade ~ 13% of phenol after 9 h irradiation. The 16CN/BFO sample exhibits improved photocatalytic activity for the degradation of phenol compared with bare BiFeO$_3$ and about 25% of phenol is degraded after 9 h.
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Exposure. The photocatalytic degradation kinetics of phenol is also investigated (Fig. 6(b)), indicating that the reaction rate constant of 16CN/BFO (0.0202 $\text{h}^{-1}$) is higher than that of bare BiFeO$_3$ (0.0111 $\text{h}^{-1}$). The result demonstrated that the degradation of dye over g-C$_3$N$_4$/BiFeO$_3$ composites is caused by its intrinsic photocatalytic property rather than dye sensitization.

In addition to the catalytic activity, the recyclability of photocatalysts is another important parameter for their photocatalytic application. The recycling runs for the photocatalytic degradation of MB over 16CN/BFO sample under simulated sunlight illumination were carried out, as presented in Fig. 7. It can be seen that the degradation percentage of dye still reaches ~ 53 % after five successive runs. This indicates that g-C$_3$N$_4$/BiFeO$_3$ composites exhibit good photocatalytic stability for the dye degradation.

3.4 Photocatalytic mechanism

In order to clarify the photocatalytic degradation mechanism, the active species trapping experiments were carried out. As shown in Fig. 8, the degradation percentage of MB decreases obviously by the addition of AO (a scavenger of $h^+$), indicating that the photogenerated $h^+$ plays an important role in this photocatalytic reaction. Nevertheless, the photocatalytic degradation of dye is slightly inhibited with the introduction of ethanol (a scavenger of •OH), implying relatively minor role of •OH responsible for the dye degradation. Besides $h^+$ and •OH, •O$_2$ and H$_2$O$_2$ generated from the reaction between photogenerated electrons and O$_2$ are considered to be another active species for dye degradation. It is generally accepted that the O$_2$ molecules dissolved in reaction solution can be expelled by the N$_2$ purging, and then inhibits the generation of •O$_2$ and H$_2$O$_2$. Upon bubbling with N$_2$, a drastic decrease of the degradation percentage is observed, suggesting that •O$_2$ and/or H$_2$O$_2$ is the major active species in the photocatalysis.

Based on the above experimental results, a possible photocatalytic mechanism of g-C$_3$N$_4$/BiFeO$_3$ composite for the degradation of MB is proposed, as displayed in Fig. 9. When the composite is irradiated by simulated sunlight, the g-C$_3$N$_4$ nanoparticles and BiFeO$_3$ are excited and generated photoinduced electron-hole pairs (Eq (3) and (4)). As mentioned above, the CB (-1.22 V) and VB (1.66 V) potentials of g-C$_3$N$_4$ are negative to the CB (0.33 V) and VB (2.53 V) potentials of BiFeO$_3$, respectively, suggesting that the two photocatalysts exhibit matchable overlapping band-structures. Therefore, the photoinduced electrons in the CB of g-C$_3$N$_4$ can facilely migrate to the CB of BiFeO$_3$, meanwhile the photogenerated holes are prone to transfer from the VB of BiFeO$_3$ to that of g-C$_3$N$_4$. Due to the above charge transfer process, the recombination of the photogenerated electrons-holes pairs is inhibited to a large extent, leaving more photogenerated charges to form active...
Figure 8. Effect of N₂, ammonium oxalate (AO) and ethanol on the photocatalytic degradation of MB over 16CN/BFO sample. Initial conditions: C(MB) = 5 mg/L, C(catalysts) = 0.5 g/L, C(AO) = 2×10⁻³ mol/L, C(ethanol) = 10 % by volume, N₂ flow rate = 0.1 L/min, T = ~ 20°C.

Figure 9. A proposed photocatalytic mechanism of g-C₃N₄/BiFeO₃ composite for the degradation of MB under simulated sunlight irradiation.

species, which is beneficial to improving the photocatalytic activity. It is well known that the photogenerated holes in the VB of g-C₃N₄ possess strong ability to oxidize dyes directly. However, because the VB potential of g-C₃N₄ is negative to the redox potentials of H₂O/•OH (+2.72 V vs. NHE) and OH⁻/•OH (+1.89 V vs. NHE) 37, photogenerated holes cannot oxidize OH⁻ or H₂O to form •OH radicals. On the other hand, the CB potential of BiFeO₃ is more positive than the redox potentials of O₂/•O₂⁻ (-0.13 V vs. NHE) but more negative than that of O₂/H₂O₂ (0.68 V vs. NHE) 38, indicating that the photogenerated electrons in the CB of BiFeO₃ cannot reduce O₂ to generate ‘O₂⁻, but can react with O₂ and H₂ to produce H₂O₂ (Eq (5)). The analysis result confirms the role of H₂O₂ for the dye degradation. This is why N₂ purging exhibit obvious inhibiting effect on the photocatalytic efficiency (Fig 8). Furthermore, the H₂O₂ can also take part in a series of reactions to generate •OH radicals (Eq (6)), which is regarded to be the major route for the production of •OH radicals in this photocatalytic process. As a consequence, the photocatalytic degradation of MB over simulated sunlight irradiated g-C₃N₄/BiFeO₃ composite is mainly caused by the attack of h⁺, •OH and H₂O₂ (Eq (7)). This is consistent with the results of active species trapping experiment.

\[ \text{BiFeO}_3 + \text{hv} \rightarrow \text{BiFeO}_3(\text{e}^- + \text{h}^+) \]  
(3)

\[ \text{C}_2\text{N}_4 + \text{hv} \rightarrow \text{C}_2\text{N}_4(\text{e}^- + \text{h}^+) \]  
(4)

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \]  
(5)

\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\cdot\text{OH} \]  
(6)

h⁺, H₂O₂ or •OH + dye → degradation products  
(7)

4. Conclusion

The g-C₃N₄ nanoparticles were decorated on the BiFeO₃ microspheres through hydrothermal method to obtain g-C₃N₄ nanoparticles/BiFeO₃ composites. The as-prepared g-C₃N₄/BiFeO₃ composites exhibit much higher photocatalytic activity towards the degradation of MB under simulated sunlight irradiation than bare BiFeO₃. Furthermore, the intrinsical photocatalytic property of composite is demonstrated by the degradation of colorless phenol under the same condition. In addition, the composite possess good photocatalytic stability. The enhancement of the photocatalytic activity for the g-C₃N₄/BiFeO₃ composite is mainly ascribe to the photoinduced electron-hole pairs separation derived from the charge migration between g-C₃N₄ and BiFeO₃. The investigation of photcatalytic mechanism of g-C₃N₄/BiFeO₃ composite suggests that the main active species responsible for dye degradation are the h⁺ and H₂O₂, while •OH plays a minor role in the photocatalytic reaction.

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