Carbon Quantum Dots/BiPO$_4$ Nanocomposites with Enhanced Visible-light Absorption and Charge Separation

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Abstract: In this study, a CQDs/BiPO$_4$ nanocomposite with enhanced visible-light absorption and charge separation was fabricated via a one-step hydrothermal reaction. The photocatalytic activity of the CQDs/BiPO$_4$ nanocomposite was evaluated by degradation of rhodamine B (RhB). The result showed that the CQDs/BiPO$_4$ composite exhibited superior photocatalytic performance to pure BiPO$_4$ under simulated solar light, as well as under visible light irradiation. Its enhanced photocatalytic performance could be ascribed to the excellent light harvesting properties, which increased utilization rate of solar energy, electron transfer efficiency and reservoir ability of the nanocomposites, facilitating the charge separation efficiency of the composite.

Key words: photocatalysis; carbon quantum dots; BiPO$_4$; electron transfer

As a new member of carbon family, carbon quantum dots (CQDs) have attracted much attention due to their unique properties such as strong photoluminescence (PL) emission, broadband optical absorption, chemical stability, good biocompatibility, non-toxicity and facile synthesis$^{[1-3]}$. As a result, they have been extensively used in many fields such as bioimaging, sensors, photodynamic therapy, drug delivery, and energy storage and conversion$^{[4,5]}$. Recently, CQDs are attracting more and more attention in the field of photocatalysis. Researchers find that besides the traditional down-converted photoluminescence, CQDs also display excellent up-converted photoluminescence (UCPL) properties, which allows for fully exploitation of the solar light$^{[7,8]}$. Moreover, photoexcited CQDs can also act as electron acceptors and electron donors, since the photoluminescence of CQDs can be quenched efficiently by either electron donor or electron acceptor molecules in solution$^9$. Therefore, considering the unique PL behavior and photo-induced electron transfer property, CQDs can perform as an efficient component in the design of high-performance photocatalysts. Up to date, many impressive composite photocatalysts based on CQDs (CQDs/TiO$_2$, CQDs/ZnO, CQDs/Cu$_2$O, CQDs/Fe$_2$O$_3$, CQDs/Ag$_3$PO$_4$, CQDs/C$_3$N$_4$) with enhanced photocatalytic activity have been constructed$^{[10-17]}$.

BiPO$_4$ as a new type of oxy-acid salt photocatalyst, is found to exhibit higher photocatalytic activity than TiO$_2$ under UV light and has attracted increasing interest in the past few years$^{[18-22]}$. Besides, it also has many advantages such as low cost, non-toxicity, excellent electronic properties and stable chemical structure, which makes it a promising photocatalyst in environmental purification. However, similar to TiO$_2$, BiPO$_4$ is also a wide band-gap semiconductor (ca. 3.85 eV) and suffers from the drawback of narrow photo-response range, which seriously limits its quantum efficiency and practical application. In order to extend the absorption range of BiPO$_4$, various methods have been adopted, including coupling with a narrow band-gap semiconductor$^{[23-26]}$, adjusting the surface oxygen vacancy$^{[27-28]}$ and doping with fluorine$^{[29]}$ or Ag$^{[30,31]}$. These attempts have successfully extended the photo-absorption range of BiPO$_4$ and enhanced its photocatalytic activity.

In this study, with the purpose of broadening the photo-response and promoting the charge separation of BiPO$_4$ simultaneously, a CQDs/BiPO$_4$ nanocomposite has been designed and fabricated via a facile hydrothermal route. Due to the photo-induced electron transfer and electron reservoir properties, as well as the light harvesting abilities of CQDs, the CQDs/BiPO$_4$ composite exhibited enhanced photocatalytic activity in the photo-degradation of RhB under both simulated solar light and...
visible light ($\lambda > 420$ nm). Based on the transient photocurrent response and radicals trapping experiments, a possible mechanism of the improved photocatalytic activity was proposed.

1 Experimental procedures

1.1 Synthesis

CQDs were synthesized according to a procedure reported by Reisner, et al\textsuperscript{32}. For the synthesis of CQDs/BiPO\textsubscript{4} nanocomposite, in a typical process, 4 mmol of Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O was added into 80 mL distilled water to obtain a white suspension. Then 14.4 mmol of Na\textsubscript{2}H\textsubscript{2}PO\textsubscript{4}·2H\textsubscript{2}O was added into the suspension under magnetic stirring. After that, desired amount of CQDs solution (20 mg/mL) was added into the above mixture and stirred continuously for several hours. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at 160°C for 24 h. After it was cooled to room temperature naturally, the products were washed with distilled water for several times and then dried at 60°C for 12 h. The loading amount of CQDs were 1.6wt%, 2.4wt% and 3.2wt%, respectively.

1.2 Characterization

The crystal structure of the products were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (Rigaku Co. Ltd., Tokyo, Japan). UV–Vis diffuse reflectance spectra of the samples were measured using a PE Lambda 900 UV-Vis spectrophotometer. Morphologies of the as-prepared products were examined by a FEI tecnaiG2F30 electron microscope. The photocurrents were measured on an electrochemical system (CHI 650E, Shanghai Chenhua) using a standard three-electrode cell.

1.3 Photocatalytic test

In order to evaluate the photocatalytic activities of the CQDs/BiPO\textsubscript{4} composites, photo-degradation of Rh\textsubscript{B} was performed under simulated solar light using a 500 W Xe lamp as the light source. In a typical procedure, 50 mg of the photocatalyst was dispersed in 50 mL of Rh\textsubscript{B} solution (10\textsuperscript{-5} mol/L), which was magnetically stirred in dark for 60 min to establish the adsorption–desorption equilibrium between Rh\textsubscript{B} and the photocatalyst powders. Upon illumination, 3 mL of suspension was sampled every time intervals and centrifuged to remove the photocatalyst. The concentration change of Rh\textsubscript{B} was analyzed by recording the variations of the absorption band maximum (552 nm) through a UV-Vis PE Lambda 900 spectrophotometer.

2 Results and discussion

2.1 Crystal structure

The XRD patterns of CQDs/BiPO\textsubscript{4} nanocomposites with different contents of CQDs are shown in Fig. 1. The XRD profiles of the BiPO\textsubscript{4} and CQDs/BiPO\textsubscript{4} nanocomposites could be indexed to the pure monoclinic phase (space group P21/n, JCPDS 15-0767). The peaks at 2θ= 27.1°, 29.1°, and 31.2° could be assigned to (200), (120) and (012) crystal planes of monoclinic BiPO\textsubscript{4}, respectively. No characteristic diffraction peak of carbon is detected for the CQDs/BiPO\textsubscript{4} composites, which could be due to the low contents and low crystallinity of CQDs in the CQDs/BiPO\textsubscript{4} nanocomposites.

2.2 Morphology

The TEM image of the CQDs/BiPO\textsubscript{4} composite (2.4wt%) is exhibited in Fig. 2(a), which reveals that the particles are crystallites with different sizes ranging from 50 nm to several hundred nanometers. The HRTEM image in Fig. 2(b) displays the excellent crystalline structures of BiPO\textsubscript{4} nanoparticles and CQDs. The lattice fringe with an interplanar distance of 0.466 nm agrees well with the (011) plane of BiPO\textsubscript{4}, and the lattice spacing of 0.321 nm and 0.230 nm correspond to the (002) and (100) planes of carbon, respectively.

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Fig. 1  XRD patterns of pure BiPO\textsubscript{4} and CQDs/BiPO\textsubscript{4} composites with different amounts of CQDs

Fig. 2  TEM image of the CQDs/BiPO\textsubscript{4} composite (2.4wt%) (a) and high resolution TEM image of the CQDs/BiPO\textsubscript{4} composite (b)
2.3 UV-Vis diffuse reflectance spectra

The optical properties of the samples are characterized by UV-Vis diffuse reflectance spectra (DRS) spectra, as shown in Fig. 3. The DRS spectrum of pure BiPO₄ clearly displays the band gap absorption onset located at about 320 nm, while the DRS spectra of the CQDs/BiPO₄ composites show a slight red shift of the absorption edge. In addition, with increase in the amount of CQDs in the composites, the absorption intensity slightly increases, which can be attributed to the addition of CQDs and can be considered as one of the main factors for the improvement of the photocatalytic performance.

2.4 Photocatalytic activities

To investigate the photocatalytic performance of the as-prepared CQDs/BiPO₄ composites, photocatalytic degradation of a model pollutant, RhB is performed under simulated solar light irradiation. Figure 4(a) shows the photocatalytic degradation of RhB vs. irradiation time by pure BiPO₄ and CQDs/BiPO₄ composites with different amounts of CQDs. It can be seen that all the composites display higher photocatalytic activity than pure BiPO₄. Moreover, when the mass percentage of CQDs is 2.4wt%, the sample shows the best photocatalytic performance, which can degrade RhB completely after 40 min of irradiation under simulated solar light. In contrast, only 42.8% of RhB is degraded by pure BiPO₄ after the same time period. However, further increasing the amount of CQDs leads to an obvious decrease of photocatalytic activity, which can be due to the reason that the higher content of CQDs in the CQDs/BiPO₄ composites can result in a competition for light absorption, which decreases the availability of light for RhB degradation.

In addition, photo-degradation of RhB is carried out under visible light (Xe lamp with a band pass filter to remove light with wavelength of λ<420 nm) in order to elucidate the roles of CQDs in the composite. As shown in Fig. 4(b), under visible light irradiation, the CQDs/BiPO₄ composite (2.4wt%) exhibits better photocatalytic performance than pure BiPO₄, which can degrade 33.3% and 17.7% of RhB after 80 min of visible light irradiation, respectively. Considering the photo-sensitization effect of dyes, a colorless compound phenol is selected as the model pollutant. As shown in Fig. 4(c), under visible light irradiation, the CQDs/BiPO₄ composite (2.4wt%) exhibits better photocatalytic performance than pure BiPO₄, which can degrade 33.3% and 17.7% of phenol after 80 min of visible light irradiation, respectively. This result demonstrates that CQDs can act as a photo-sensitizer to broaden the photo-absorption range of BiPO₄, which leads to the enhanced visible light photocatalytic activity of the CQDs/BiPO₄ composite.

2.5 Mechanism of enhanced photo-activities

As well known, the photocatalytic performance is closely related to the generation, separation and migration efficiencies of photogenerated electrons and holes\(^{[33]}\), which can be reflected by the photocurrents. Figure 5 shows the photoresponses of pure BiPO₄ and CQDs/BiPO₄ composite after deposition on FTO electrodes under several on/off sunlight irradiation cycles. It can be seen that both samples exhibit stable and reversible photocurrent at light-on and off. Moreover, the photocurrent generated by CQDs/BiPO₄ composite is about 1.9 times as high as that of BiPO₄, which implies higher separation efficiency.
and longer lifetime of the photogenerated charge carriers. This is in good agreement with the enhancement of the photocatalytic activity.

In order to further elucidate the photocatalytic mechanism, the main oxidative species in photocatalytic process are detected through the trapping experiments of radicals using EDTA-2Na as holes radical scavenger, tert-butylalcohol (t-BuOH) as hydroxyl radical scavenger, and benzoquinone as superoxide radical (\(\cdot\)O_2^-) scavenger[^34], respectively. As shown in Fig. 6, with the addition of t-BuOH to the reaction system, the photocatalytic activity decreases slightly. In contrast, the addition of EDTA-2Na and benzoquinone cause a severe suppression of the degradation rate. This result demonstrates that holes and superoxide radicals are the main oxidative species in the CQDs/BiPO_4 composite system, rather than hydroxyl radicals.

On the basis of the above experimental results, a possible mechanism for the superior photocatalytic performance of CQDs/BiPO_4 composite is proposed. Firstly, the introduction of CQDs can extend the photo-response of BiPO_4 into the visible range of the solar spectrum, thus increasing the utilization rate of solar energy. Secondly, CQDs as an electron reservoir can trap electrons emitted from BiPO_4, which can inhibit the recombination rate of the photo-generated charge carriers, as confirmed by the transient photocurrent response shown in Fig. 5. On the other hand, the holes on the valence band of BiPO_4 can oxidize the pollutant directly. Overall, CQDs may act as sensitizer and transporter in the CQDs/BiPO_4 composite, which not only increase the utilization rate of solar energy, but also promote the separation of the photo-induced charge carriers. Therefore, the CQDs/BiPO_4 composite exhibits enhanced photocatalytic activity.

### 3 Conclusion

In summary, a facile hydrothermal route was developed to synthesize CQDs/BiPO_4 composite with high photocatalytic activity for pollutant degradation. The results of UV-Visible DRS spectra, photocurrent measurement, as well as the radicals trapping experiments, show that CQDs can act as a photosensitizer and transporter in the CQDs/BiPO_4 composite. As a result, the CQDs/BiPO_4 composite exhibited enhanced photocatalytic activity in the photodegradation of RhB under simulated solar light, as well as under visible light. Such novel composites may bring new insight into the design of highly efficient visible light photocatalytic systems.

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