

Carbon quantum dots/BiVO₄ composite with enhanced photocatalytic activity

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Received June 21, 2018; accepted September 18, 2018; published online January 14, 2019

In this study, we report the facile fabrication of a carbon quantum dots (CQDs)/BiVO₄ composite with efficient photocatalytic activity. Due to the excellent upconversion photoluminescence, as well as the photo-induced electron transfer and reservoir properties of CQDs, the CQDs/BiVO₄ composite exhibited superior photocatalytic performance in the degradation of rhodamine B (RhB) under the irradiation of simulated solar light. This study provides a strategy for the development of high-performance catalysts based on CQDs.

carbon quantum dots, BiVO₄, photocatalysis, composite, electron transfer

Citation: Zhang Z J, Huang H R, Xu J Y, et al. Carbon quantum dots/BiVO₄ composite with enhanced photocatalytic activity. *Sci China Tech Sci*, 2019, 62: 356–360, <https://doi.org/10.1007/s11431-018-9361-6>

1 Introduction

Since the accidental discovery during purification of single-walled carbon nanotubes through preparative electrophoresis in 2004 [1], carbon quantum dots (CQDs) have gradually become a rising star in the nanocarbon family. Compared to traditional semiconductor quantum dots (QDs), CQDs have the advantages of low cost, low toxicity, good biocompatibility, facile functionalization, chemical inertness, tunable fluorescence emissions and high resistance to photobleaching [2,3]. Therefore, CQDs are attracting considerable attention as a promising alternative to semiconductor QDs in various applications such as biological labeling, bioimaging, and drug delivery [4–7].

On the other hand, with the urgent environmental concerns and increasing energy demand, semiconductor-based photocatalyst has attracted much attention in the past few decades. As visible light accounts for a large proportion of the solar spectrum, great interests in photocatalysis have been focused on the exploitation of visible-light-driven photo-

catalysts. Monoclinic scheelite bismuth vanadate (m-BiVO₄), with a narrow band gap of 2.4 eV, is attracting much attention as a visible-light responsive photocatalyst and has been widely used in photocatalytic evolution of O₂ and degradation of organic pollutants [8–12]. However, its practical applications are still hindered by the poor quantum yield due to rapid recombination of photo-generated electrons and holes [13]. It has been reported that CQDs exhibit photo-induced electron-transfer and electron reservoir properties, which can hinder the electron/hole pair recombination probability [14]. Therefore, enhanced photocatalytic performance can be achieved through the construction of CQDs/semiconductor composites. For example, CQDs/TiO₂, CQDs/C₃N₄, CQDs/BiOCl, CQDs/Bi₂WO₆, and CQDs/BiPO₄ composites are reported to show enhanced charge separation efficiency and photocatalytic activities [15–19]. Considering such remarkable properties of CQDs and the limitations of the BiVO₄ photocatalytic system, the combination of CQDs and BiVO₄ may be regarded as an ideal strategy to construct an efficient composite photocatalyst.

In a previous report, Tang et al. [20] have demonstrated that CQDs/BiVO₄ nanocomposite showed enhanced photo-

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catalytic activity in the degradation of methylene blue dye under visible light irradiation. However, the mechanism for the improved photocatalytic performance needs to be further revealed. In this paper, CQDs/BiVO₄ nanocomposite has been fabricated via a facile hydrothermal route, which exhibited enhanced photocatalytic activity in the degradation of rhodamine B (RhB) under simulated solar light irradiation. Based on the transient photocurrent response and radicals trapping experiments, the crucial roles of CQDs in the enhancement of photocatalytic activity of BiVO₄ is discussed in detail.

2 Experimental procedures

2.1 Synthesis

CQDs were synthesized according to the ref. [21]. CQDs/BiVO₄ nanocomposite was synthesized by a hydrothermal process as follows: in a typical process, 4 mmol of Bi(NO₃)₃·5H₂O and 4 mmol of NH₄VO₃ were added into 40 mL of deionized water, respectively. Then the two solutions were mixed together under magnetic stirring. Subsequently, desired amount of CQDs solution (20 mg/mL) was added into the above mixture. After stirring for 1 h, this precursor suspension was poured into a Teflon-lined stainless steel autoclave and heated at 160°C for 24 h. After the autoclave was cooled to room temperature, the precipitate was separated by filtration, washed with distilled water for several times, and then dried at 60°C for 12 h. CQDs/BiVO₄ composites prepared by adding 0.5, 1.0, and 1.5 mL of CQDs solution were denoted as C 0.5/BiVO₄, C 1.0/BiVO₄, and C 1.5/BiVO₄, respectively.

2.2 Characterization

The crystalline phases of the products were identified by X-ray diffraction (XRD) using an X-ray diffractometer with Cu K α radiation (Rigaku Co. Ltd., Tokyo, Japan). The morphologies of the samples were investigated by transmission electron microscopy (TEM, FEI tecnaiG2F30). UV-vis diffuse reflectance spectra (DRS) were obtained using a PE Lambda 900 UV-vis spectrophotometer. Specific surface areas were determined following the Brunauer-Emmet-Teller analysis. The photoelectrochemical measurements were carried out on an electrochemical workstation (CHI 650, China) using a three-electrode system (with CQDs/BiVO₄, Pt wire and a standard calomel electrode (SCE) as the working, counter and reference electrode, respectively).

2.3 Photocatalytic test

The photocatalytic activities of the photocatalysts were evaluated by photo-decomposition of rhodamine B (RhB) under simulated solar light using a 500 W Xe lamp as the

light source. 50 mL of RhB aqueous solution (10⁻⁵ mol/L) was mixed with 0.05 g of photocatalyst. The mixture was magnetically stirred in the dark for 1 h before conducting the photocatalytic reactions to allow the system to reach an adsorption/desorption equilibrium. The concentration of RhB solution was evaluated by UV-vis spectrophotometer (PE Lambda 900) at 552 nm.

3 Results and discussion

3.1 Crystal structure

To investigate the phase structures of the products, their X-ray diffraction patterns are measured. As shown in Figure 1, the characteristic diffraction peaks of each XRD pattern can be perfectly indexed to a monoclinic BiVO₄ phase (JCPD file no: 14-0688). All composites exhibit the same characteristic diffraction peaks of BiVO₄ and no characteristic diffraction peak of carbon is observed, which can be ascribed to the low contents and crystallinity of CQDs.

3.2 TEM observation

The morphology and microstructure of the CQDs/BiVO₄ composite (C 1.0/BiVO₄) is revealed in Figure 2. As shown in Figure 2(a), the as-prepared CQDs/BiVO₄ composite exhibits nanosheet structure. The high resolution TEM (HRTEM) of the CQDs/BiVO₄ composite further confirms the existence of CQDs (Figure 2(b)), which has a crystal lattice spacing of 0.321 nm, corresponding to the (002) lattice planes of graphitic carbon [22].

3.3 UV-vis diffuse reflectance spectra

Figure 3 shows the UV-vis diffuse reflectance absorption (DRS) spectra of CQDs, pure BiVO₄ and CQDs/BiVO₄ composites with different CQDs amounts. It can be seen that

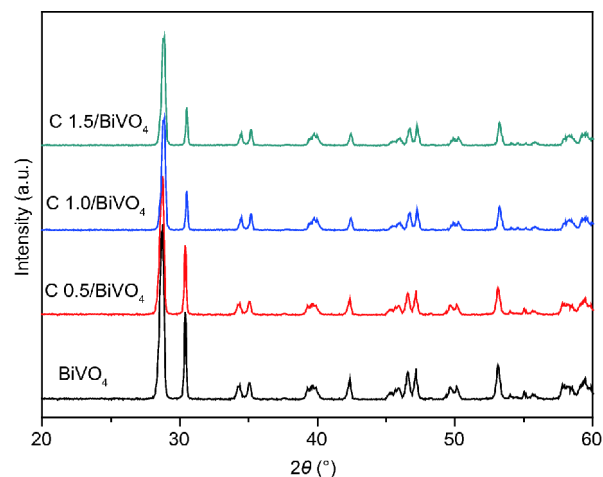


Figure 1 (Color online) X-ray diffraction patterns of the CQDs/BiVO₄ composites with different amounts of CQDs.

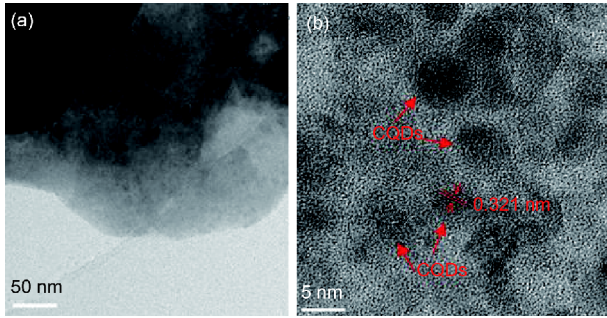


Figure 2 (Color online) (a) TEM image of the CQDs/BiVO₄ composite (C 1.0/BiVO₄); (b) high resolution TEM image of the CQDs/BiVO₄ composite.

CQDs show strong absorption in the visible light region. Pure BiVO₄ shows its fundamental absorption edge located at 550 nm. Moreover, a red shift of the absorption edge is observed for the CQDs/BiVO₄ composites compared with pure BiVO₄, indicating that the introduction of CQDs can increase the utilization rate of solar energy.

3.4 Photocatalytic performance

In order to investigate the photocatalytic activities of the as-prepared samples, photocatalytic decomposition of RhB is performed under simulated solar light irradiation. For comparison, the photocatalytic performance of commercial Degussa P25 was also investigated under the same experimental

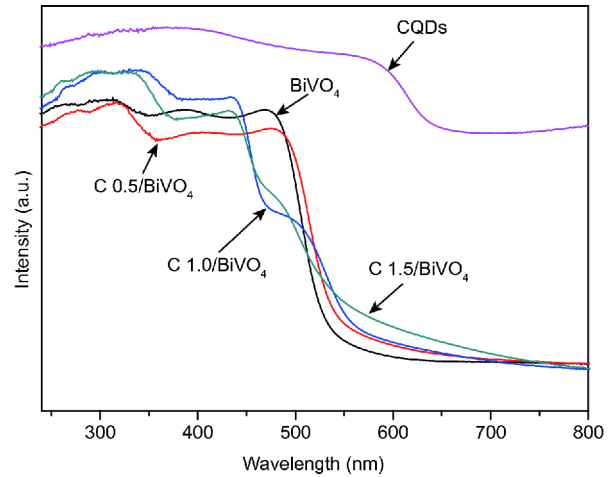


Figure 3 (Color online) UV-vis diffuse reflectance spectra of the CQDs/BiVO₄ composites with different amounts of CQDs.

conditions. **Figure 4(a)** shows the comparison of photocatalytic activities among Degussa P25, pure BiVO₄ and CQDs/BiVO₄ composites with different contents of CQDs. It can be seen that all the CQDs/BiVO₄ composites show superior photocatalytic performance to pure BiVO₄ and Degussa P25. The C 1.0/BiVO₄ sample exhibits the highest photocatalytic activity, which can degrade RhB completely after 40 min of simulated solar light irradiation, while the degradation rate of RhB by pure BiVO₄ is only 48.5% after the same time period. However, when the content of CQDs

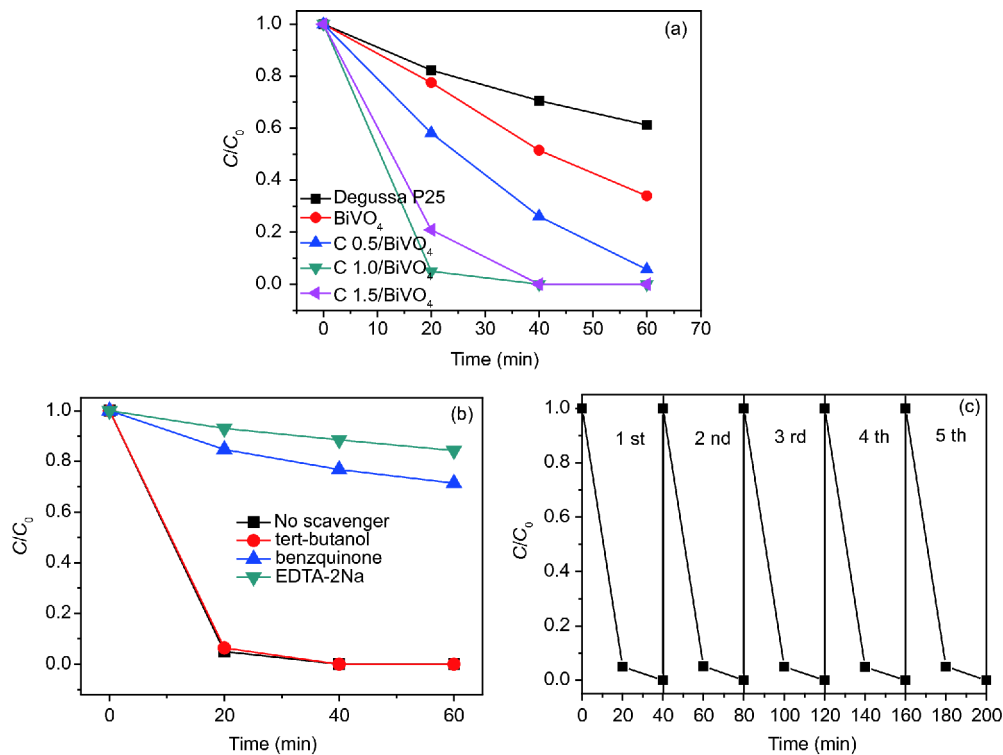


Figure 4 (Color online) (a) Degradation efficiency of RhB as a function of time by the as-prepared samples under simulated solar light irradiation; (b) photocatalytic degradation of RhB by CQDs/BiVO₄ composite with different scavengers; (c) recycling performance of CQDs/BiVO₄ composite towards RhB degradation.

further increases, the photocatalytic activity decreases, which can be explained by the opacity and light scattering of the CQDs decreasing the absorption of incident light, as well as the reduced catalytic active sites [23].

In addition, the trapping experiments of radicals are conducted in order to determine the main oxidative species of the CQDs/BiVO₄ composite, in which tert-butyl alcohol (tBuOH) is used as hydroxyl radical scavenger, benzoquinone as superoxide radical ($\bullet\text{O}_2^-$) scavenger, and EDTA-2Na as holes radical scavenger [24], respectively.

As shown in Figure 4(b), the addition of tBuOH has a negligible influence on the photocatalytic degradation rate of the RhB, which indicates that hydroxyl radicals are not the main oxidative species of the CQDs/BiVO₄ composite. In contrast, after the addition of EDTA-2Na and benzoquinone, the activity is suppressed significantly, implying that both holes and superoxide radicals play important roles in the CQDs/BiVO₄ composite system.

Considering the importance of photocatalyst stability in practical applications, the reusability of the CQDs/BiVO₄ composites for RhB degradation was evaluated. As shown in Figure 4(c), after five consecutive cycles, no obvious deactivation of the photocatalyst was observed, indicating the high stability of the CQDs/BiVO₄ composite during the photocatalytic reaction.

It is well known that the specific surface area of the photocatalysts is an important factor influencing the photocatalytic activity. The specific surface areas of pure BiVO₄, C 0.5/BiVO₄, C 1.0/BiVO₄, and C 1.5/BiVO₄ are 1.91, 2.03, 1.98, and 2.10 m²/g, respectively. The specific surface areas of all the samples are very low and exhibit slight differences. Therefore, the specific surface areas may not influence their photocatalytic activities much.

It has been reported that the upconversion emission of CQDs was responsible for the enhanced photocatalytic activities of CQDs modified composite photocatalysts under visible light [25]. In order to see whether our CQDs have upconversion emission properties, the up-converted PL spectra of CQDs is measured by using excitation wavelengths ranging from 400 to 560 nm. As shown in Figure 5, CQDs display excellent up-converted emissions, which exhibit an excitation-dependent behavior with the emission wavelengths ranging from 330 to 400 nm. When CQDs are introduced into the composites system, a fraction of visible light is transformed into ultraviolet light, which then excites BiVO₄ to produce the photo-generated electron-hole pairs, and the photocatalytic activity of the composite is enhanced.

Another crucial factor that determines the photocatalytic performance is the separation and transfer rate of the photo-generated charge carriers, which can be reflected directly by the photocurrent responses of the photocatalysts [26]. Figure 6 shows the photocurrent responses of pure BiVO₄ and CQDs/BiVO₄ composite after deposition on FTO electrodes.

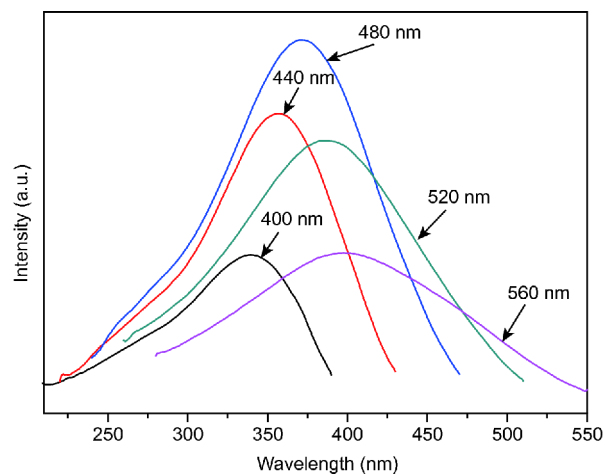


Figure 5 (Color online) Upconversion luminescence spectra of CQDs with excitation of different wavelengths.

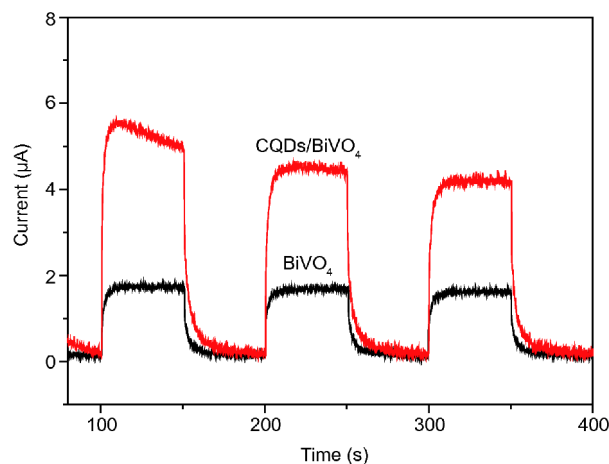


Figure 6 (Color online) Transient photocurrent response curves of BiVO₄ and CQDs/BiVO₄ composite (C 1.0/BiVO₄).

It can be seen that both samples exhibit stable and reversible photocurrents at light-on and light-off, and the photocurrent generated by CQDs/BiVO₄ composite is about 3.0 times as high as that of pure BiVO₄. The higher photocurrent over CQDs/BiVO₄ composite implies more efficient separation of the photo-induced charge carriers, which is especially important for the enhancement of photocatalytic activity.

Based on the above experimental results, the mechanism for the enhanced photocatalytic performance of the CQDs/BiVO₄ composite is proposed, as illustrated in Figure 7. It has been reported CQDs have up-conversion luminescence properties, which can transform longer wavelength light into shorter wavelengths [15]. Under simulated solar light irradiation, CQDs can absorb light beyond the absorption range of BiVO₄ and convert it into shorter wavelength, which then activates BiVO₄ to generate electron-hole pairs. Therefore, the solar light is harvested more effectively. On the other hand, CQDs as an electron reservoir can trap electrons emitted from BiVO₄, which can inhibit the recombination of

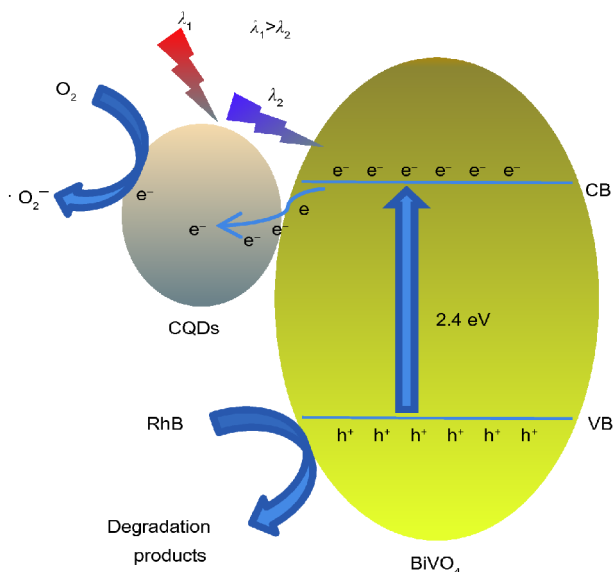


Figure 7 (Color online) Schematic illustration for the photocatalytic mechanism of CQDs/BiVO₄ composite.

electron-hole pairs and prolong the lifetime of photo-generated holes of BiVO₄. The electrons can be shuttled freely in the conducting network of CQDs and react with adsorbed O₂ to produce highly reactive superoxide radicals ($\cdot\text{O}_2^-$). Both the superoxide radicals and the longer-lived holes on the valence band of BiVO₄ are strong oxidative species (as proved by the trapping experiments in Figure 4(b)), and can oxidize the adsorbed pollutants into small molecules.

4 Conclusions

In conclusion, an efficient CQDs/BiVO₄ composite photocatalyst was synthesized by a facile one-step hydrothermal method. It showed enhanced photocatalytic activity in the degradation of RhB under simulated solar light irradiation, which can be attributed to the unique up-converted PL, photo-induced electron transfer and reservoir properties of CQDs. Both the superoxide radicals and holes play key roles in the degradation process for the CQDs/BiVO₄ composite system.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51402194, 51572128).

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