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Review

Multifarious roles of carbon quantum dots in heterogeneous photocatalysis

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ABSTRACT

As a new member of carbon material family, carbon quantum dots (CQDs) have attracted tremendous attentions for their potentials in the heterogeneous photocatalysis applications. Due to the unique microstructure and optical properties, the roles of CQDs played in the CQDs-based photocatalytic systems have been found to be diverse with the continuous researches in this regard. Herein, we provide a concise minireview to elaborate the multifarious roles of CQDs in photocatalysis, including photoelectron mediator and acceptor, photosensitizer, photocatalyst, reducing agent for metal salt, enhancing adsorption capacity and spectral converter. In addition, the perspectives on future research trends and challenges are proposed, which are anticipated to stimulate further research into this promising field on designing a variety of efficient CQDs-based photocatalysts for solar energy conversion.

1. Introduction

Solar energy conversion by photocatalysis has been attracting much interest as a promising technology for a sustainable future in the context of the aggravating energy and environmental problems such as fossil fuel depletion, pollution, and global warming [1–9]. Photocatalysis is generally based on the light absorption of semiconductor, such as ZnO, TiO_2 and CdS, to excite the electrons to conduction band and leave a hole in the valence band, thus creating photogenerated electron–hole pairs, which in turn trigger photoredox reaction [10–12]. Unfortunately, many of the present photocatalytic systems still suffer from low-usage of sunlight and high recombination rate of the photoinduced charge carriers, which seriously limits the overall quantum efficiency of photocatalysis [2,13–15]. Thus, it is of considerable interest to design novel photocatalyst to increase the capacity to utilize visible light and improve the quantum efficiency of conventional semiconductors-based photocatalysis [16,17].

Carbon quantum dots (CQDs) are a new class of carbon nanomaterials composed of discrete, quasi-spherical carbon nanoparticles with sizes below 10 nm, first obtained during purification of single-walled carbon nanotubes through preparative electrophoresis in 2004 [18]. CQDs have gradually become a rising star in the carbon material family and have shown great potentials in the photocatalysis applications because of their low cost, low toxicity, chemical inertness, superiority in water solubility, ease of functionalization and simple synthetic routes [19–23]. Recent years have witnessed the explosion of CQDs-based photocatalysis research with improved solar-to-energy conversion efficiency [23–27]. Due to the unique microstructure and optical properties, the roles of CQDs played in the CQDs-based photocatalytic systems have been found to be diverse. For instance, similar to the other members of carbon material family (e.g., carbon nanotube, graphene), CQDs have also shown good capability in separating the photogenerated electrons–hole pairs and enhancing adsorption capacity in the composite photocatalysis systems [28,29]. Furthermore, CQDs display excellent optical absorption in the ultraviolet and visible region [24]. More importantly, CQDs have remarkable upconversion ability to convert low-energy photons into high-energy photons and exceptionally long lifetime of hot carriers, which has been successfully applied to serve as spectral converter for efficiently utilizing the full spectrum of sunlight [30–32]. Recent works have also found that the excellent electron donating capability of photoexcited CQDs enables fast reduction of metal salts to corresponding metal nanoparticles [25,33]. Although some reviews related to CQDs have emerged in the past few years [26,34–37], a separate dedicated review with focus only on describing the multifarious roles of CQDs in heterogeneous photocatalysis has been unavailable.

Herein, we provide such a concise minireview to elaborate the multifarious roles of CQDs in the field of photocatalysis application,

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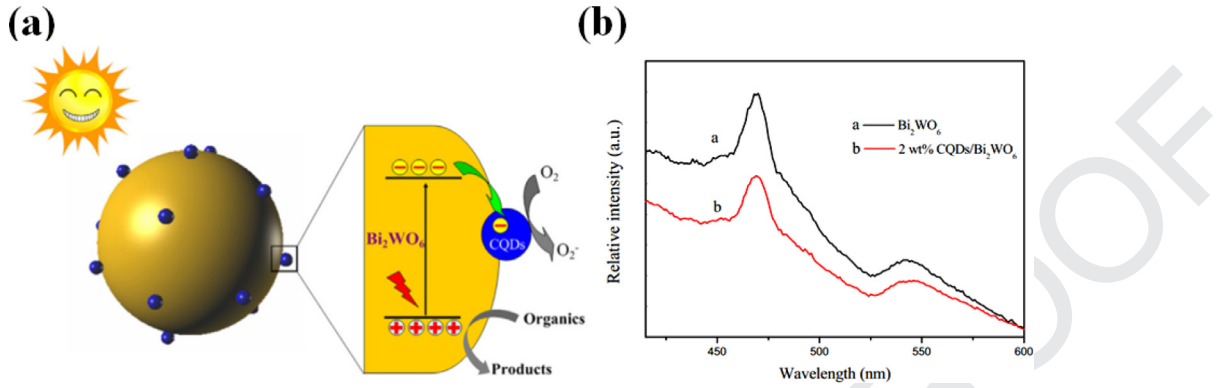

Fig. 1. (a) Schematic of the separation and transfer of photogenerated charges in the CQDs/Bi_2WO_6 hybrid material combined with the possible reaction mechanism of photocatalytic procedure. (b) PL spectra of pure Bi_2WO_6 and 2 wt% CQDs/Bi_2WO_6 hybrid materials. Reprinted with permission [41]. Copyright 2015, Elsevier. Q5

including photoelectron mediator and acceptor, photosensitizer, photocatalyst, reducing agent for metal salt, enhancing adsorption capacity and spectral converter. Furthermore, the perspectives on future research trends and challenges in construction of CQDs-enhanced photocatalytic systems for solar energy conversion are proposed. It is anticipated that this minireview would provide useful information to in depth understand the versatile roles of CQDs in the CQDs-based photocatalytic systems, thereby advancing ongoing interest to rationally harness the unique structure and properties of CQDs to fabricate more efficient CQDs-based photocatalysts toward target applications in solar energy conversion and storage.

2. The key roles of carbon quantum dots in photocatalysis

2.1. Photoelectron mediator and acceptor

One of the fundamental issues in photocatalysis is the fast recombination of photogenerated electron–hole pairs within the photocatalysts [38–40]. Therefore, suppressing the recombination of electron–hole pairs is one of the key factors to improve the photocatalytic activities. In recent years, a variety of semiconductor photocatalysts have been combined with CQDs to suppress the recombination of electron–hole pairs, therefore enhancing photocatalytic efficiency [28,29,38,41–46]. For example, Di et al. [41] have shown that the hybrids composed of CQDs and Bi_2WO_6 (CQDs/Bi_2WO_6) exhibit a significant photoactivity enhancement toward photodegradation of rhodamine B (RhB), colorless antibiotic agent ciprofloxacin (CIP), tetracycline hydrochloride (TC), and bisphenol A (BPA) under visible light irradiation. The enhanced photoactivities are ascribed to the presence of CQDs, which act as an electron acceptor and transporter to efficiently separate the photogenerated electron–hole pairs in Bi_2WO_6 (Fig. 1(a)). As displayed in Fig. 1(b), when CQDs are anchored on the Bi_2WO_6 surface, the photoluminescence (PL) intensity decreases significantly, which indicates the more efficient inhibition of the recombination of electron−hole pairs photogenerated in the CQDs/Bi_2WO_6 hybrid materials.

Compared with zero bandgap graphene, CQDs have an intrinsic bandgap due to the quantum confinement and edge effect [47], which renders CQDs show unique property in promoting the separation of the photogenerated electron–hole pairs. Chai et al. [38] have reported that the CQDs/CdS heterojunction films prepared by layer-by-layer method show excellent photocatalytic activity for reduction of nitro-benzene derivatives in the aqueous phase under visible light irradiation. As shown in Fig. 2(a), the layer-by-layer alternating deposition method enables the formation of a well-controlled assembly of CQDs/CdS multi-layers with intimate interfacial contact, which facilitates efficient charge transfer from CdS to CQDs [48]. Furthermore, the results of Mott–Schottky plots indicate that the conduction band edges of CdS and CQDs are 0.37 V and 0.04 V (vs. NHE), respectively. The much lower-lying conduction band edge of CQDs would render the electron transfer from CdS to CQDs, thus leading to an efficient charge separated state. As shown in Fig. 2(b), upon visible light irradiation, both CQDs and CdS are excited and the lower-lying conduction band edge of CQDs enables the electron transfer from CdS to CQDs, and concomitant movement of holes in the valence band of CQDs to that of CdS. The type II band structure ensures efficient separation of carriers, thereby enhancing the photocatalytic activity of the CQDs/CdS heterojunction films.

2.2. Photosensitizer

Among different photocatalysts, wide band gap semiconductors such as titanium dioxide (TiO_2) are the widely studied semiconductor photocatalysts because of their relatively low cost, superior photocatalytic performance and environmental friendliness [40,49–51]. However, only the ultraviolet (UV) light response owing to the wide band gap significantly restricts the improvement of solar energy conversion efficiency [12,52]. Coupling with photosensitizers is a facile way to render these wide band gap semiconductors to become visible light photoactive [50,53]. Typical photosensitizers are either expensive (e.g., noble metal, ruthenium-based dyes [54,55]), toxic (e.g., CdSe [56] and CdS [57] quantum dots), or unstable (e.g., organic dyes) [58,59], which limits their practical application. CQDs can be easily and inexpensively synthesized on a multigram scale and they display excellent optical absorption in the ultraviolet and visible region, representing a type of promising photosensitizer for decorating the wide-band gap semiconductors [22,60].

For instance, Li et al. [60] have reported that CQDs can act as visible light photosensitizer for titania nanostructured fibers (TiO_2). As shown in Fig. 3, under visible light irradiation, CQDs can be photoexcited to form holes (h^+) and electrons (e^-). The excited electron is then injected into the conduction band of TiO_2 to initiate the reaction. However, the photosensitive efficiency of CQDs cannot be exactly evaluated in this work, due to the possibility that photogenerated electrons resulting from the RhB photosensitization under visible light irradiation, can transfer to the CQDs or the conduction band of TiO_2, which will enhance the visible light photoactivity for RhB degradation over TiO_2–CQDs composites [61–63]. In other words, it is not appropriate to choose the degradation of RhB dye as a probe reaction to study the photosensitizer role of CQDs because of the complex charge transfer

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