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Short communication

Synthesis of Bi/BiOCl-TiO_2-CQDs quaternary photocatalyst with enhanced visible-light photoactivity and fast charge migration

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ABSTRACT

A series of Bi/BiOCl/TiO_2-CQDs(α) (BBTC-α) quaternary photocatalysts with lamellar structure were synthesized via a solvothermal method followed by a hydrothermal process. The BBTC-0.6 photocatalyst exhibited highest visible-light photoactivity in decomposing methyl orange and p-nitrophenol, and it was about 4.8 and 10.3 times of BiOCl/TiO_2 nanosheets. In this system, Bi and CQDs were served as electron donors, and BiOCl and TiO_2 were served as electron trappers to extend the lifetime of photogenerated carriers. The enhanced visible-light photoactivity could be attributed to the strong light absorption and upconversion photoluminescence of the CQDs, and the surface plasmon resonance effect of the surface Bi also played an important role in this system.

1. Introduction

As one of the simplest bismuth based compounds, bismuthoxyhalide-family semiconductor materials (BiOX, X = Cl, Br, I) have attracted much attention due to their high stability, non-toxicity, suitable band gaps and superior photoactivity [1,2]. For instance, Dong et al. [3] investigated the change from nonselective oxidation to selective oxidation in the NO removal on BiOI surface. Zhang et al. [4] studied the oxygen vacancy structure associated photocatalytic water oxidation of BiOCl. Zhao et al. [5] first used the reactable polyelectrolyte, poly (allylamine hydrochloride) to fabricate BiOCl materials via an assisted solvothermal method. However, among the BiOX semiconductors, the photoactivity of the pure BiOCl is limited by its low light absorption efficiency, difficult charge migration and fast recombination of photoexcited electron-hole pairs. To improve its photocatalytic performance, many methods had been attempted, such as the preparation of heterojunctions [6,7], introduction of SPR effect [8,9], crystal plane controlling [10,11], metal doping or nonmetal doping [12,13]. For instance, Liu et al. [6] explored a group of $BiO(ClBr)_{(1-x)/2}I_x$ solid solution with a homogeneous layered tetragonal matlockite structure for visible-light photodegradation of 2-propanol. Rochkind et al. [14] used the synthetic derivatives of flavins as photosensitizers to facilitate the heterogeneous photocatalytic activity of BiOCl particles under visible light by covalently attaching on its surface. Zhang et al. [15] synthesized the BiOCl/BiOBr composite photocatalysts with different Cl-to-Br molar ratios by a simple microwave-assisted coprecipitation method. Obviously, aforementioned modifications to the BiOCl semiconductor could indeed improve its visible-light photocatalytic performance.

CQDs, known as a novel class of recently discovered carbon-based materials, exhibit strong visible-light absorption and upconversion photoluminescence, are typically quasi-spherical nanoparticles comprising amorphous to nanocrystalline cores with predominantly graphitic carbon (sp^2 carbon) or graphene and graphene oxide sheets fused by diamond-like sp^3 hybridized carbon insertions [16]. Due to its representative conjugated π structure, CQDs exhibits the excellent electron transfer/reservoir properties, and open a new way for efficiently utilizing the full spectrum [17,18]. Therefore, the investigation of CQDs in photocatalysis field has attracted many researchers in recent years. For instance, Di et al. [19] prepared a nitrogen-doped carbon quantum dots (N-CQDs) modified atomically-thin BiOI nanosheet nanojunctions. Liu et al. [20] developed a carbon quantum dots-decorated $MoSe_2$ photocatalyst with whole spectrum response. Chen et al. [21] proposed a practical strategy to facilitate the separation of e^--h^+ pairs and enhance the photostability in a semiconductor by the use of a Schottky junction in a noble metal-CQDs-semiconductor stack structure. Fang et al. [22] synthesized the ultrathin g-C_3N_4 nanosheets coupled with carbon nanodots as 2D/0D composites for efficient photocatalytic H_2 evolution. No doubt, the CQDs indeed exhibit prominent superiority for improving the photocatalytic performance of traditional photocatalysts, and is a desired candidate for the modification of other photocatalysts.

In our previous research [23], the BiOCl/TiO_2 composite with lamellar structure was found could be synthesized by a facile one-pot solvothermal method when the proportion of titanium source was

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appropriate. For the formation of the BiOCl-TiO_2 heterojunction, the BiOCl/TiO_2 nanosheets exhibited higher visible-light photoactivity than the pure BiOCl and TiO_2. However, the its photocatalytic performance should be further improved if being used to decompose the hard-degradable organic pollutant in visible-light range. Therefore, some superior BiOCl/TiO_2-based ternary composites had been reported by some researchers, and enhanced performance had indeed been obtained, such as the synthesis of the BiOCl/$Bi_5Nb_3O_{15}$/TiO_2, attapulgite-BiOCl-TiO_2 and TiO_2/$Bi_2(BDC)_3$/BiOCl composites [24–26]. Inspired by other researchers' discoveries, we aim to further improve the visible-light photocatalytic performance of our synthesized BiOCl/TiO_2 nanosheets by the CQDs loading. As known to all of us, the lamellar structure of the BiOCl/TiO_2 composite would be very conducive to the light absorption for the exposed effective absorption surface, and the CQDs with strong light absorption and upconversion photoluminescence can effectively improve the visible-light response of the BiOCl/TiO_2 composite. Besides, the rhombohedral Bi as co-catalyst was found to be generated in the BiOCl/TiO_2 matrix during the followed hydrothermal process, thus the SPR effect would be introduced to this composite. As known to all of us, the SPR effect had been applied by many researchers in photocatalysis field [27,28]. However, no existing report is about the synthesis of the BBTC quaternary composites. Therefore, the structural features and photocatalytic performances of the photocatalysts were invesigated systematically.

2. Experimental section

The detailed experimental process is described in the Supporting Information (SI).

3. Results and discussion

The morphology and microstructure of the BiOCl/TiO_2 nanosheets and BBTC-α hybrid materials were characterized by SEM and TEM, and the corresponding images were shown in Fig. S1. The synthesized BiOCl/TiO_2 composites exhibit the representative lamellar structure (Fig. S1a), and the TiO_2 nanoclusters with the size of about 5–10 nm are uniformly dispersed into the BiOCl matrix (Fig. S1b). At the same time, the obvious crystal lattices with the lattice spacing of 0.34 nm, 0.26 nm and 0.27 nm can be observed in the HRTEM image (Fig. 1a), which can be attributed to the (101), (110) and (102) plane of tetragonal BiOCl, respectively [6,11,29]. Beyond that, the crystal lattices with the lattice spacing of 0.35 nm can also be observed, which can be attributed to the (101) plane of anatase TiO_2 [30]. After the CQDs loading, the surface roughness of the sample is increased significantly (Figs. S1d and S2d, g, m, p), and plenty of dark spots with the size of about 3–6 nm can be observed clearly on the BiOCl/TiO_2 matrix (Fig. S1e). As shown as the HRTEM images in Fig. 1b, the obvious crystal lattices with the lattice

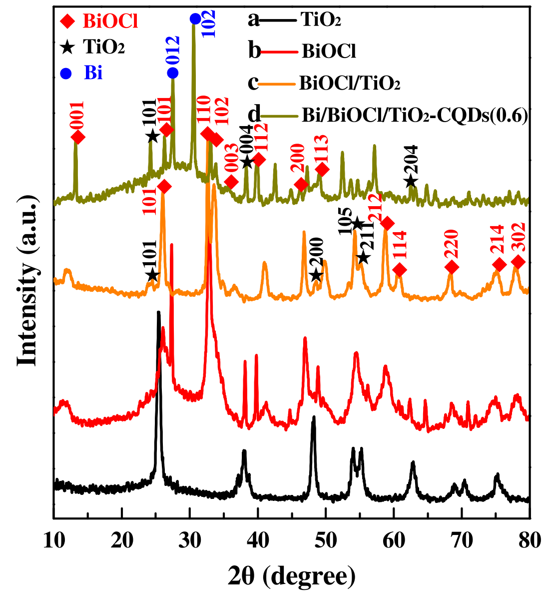

Fig. 2. XRD patterns of anatase TiO_2 (a), tetragonal BiOCl (b), BiOCl/TiO_2 (c), and BBTC-0.6 (d).

spacing of 0.32 nm can be observed, which can be attributed to the (002) plane of CQDs [31]. In addition, the crystal lattices with the lattice spacing of 0.328 nm can also be observed, which can be attributed to the (012) plane of rhombohedral Bi [6]. As shown as the inset in Fig. S1e, the electron diffraction (SAED) pattern of the corresponding selected area indicates that the sample is polycrystalline, and the corresponding FFT image in Fig. 1b also indicates the polycrystalline characteristic, which confirms the successful preparation of the BBTC photocatalyst. The distinct multiple diffraction rings can be indexed with the anatase TiO_2 and rhombohedral Bi. The change of the morphologies and the elementary composition with the change of the CQDs contents was discussed detailedly in the SI. Furthermore, the EDS elemental mapping (Fig. S3) also confirmed the existence of Bi, Ti, O, Cl and C elements in the BBTC-0.6, which proved the successful synthesis of the quaternary photocatalyst.

Subsequently, the crystalline structure of the samples were examined by XRD analysis. As displayed in Fig. 2c, the diffraction peaks corresponding to the tetragonal BiOCl (JCPDS 06-0249) [32] and anatase TiO_2 (JCPDS 21-1272) [33] can be observed clearly by comparing with Fig. 2a and b. For the formation of the BiOCl-TiO_2 hierarchical structure, the diffraction peak corresponding to the (101) plane of anatase TiO_2 shifted to 24.5° from 25.5°. After the CQDs loading (Fig. 2d), a wide diffraction peak corresponding to the amorphous

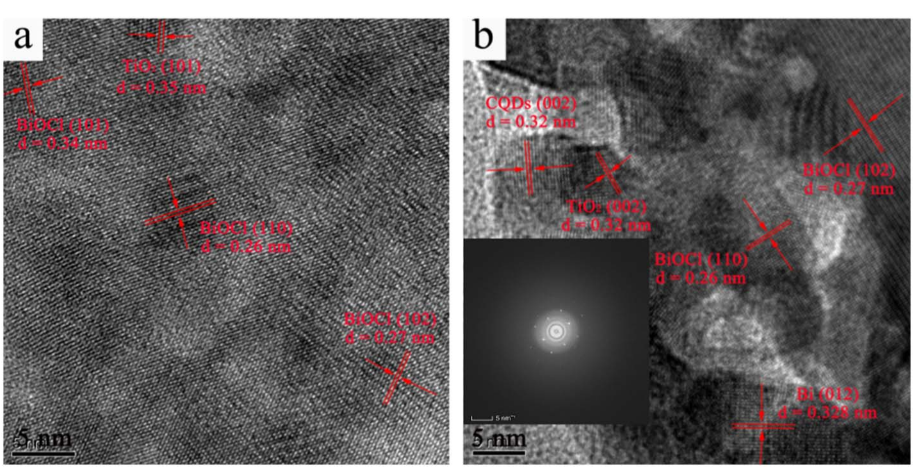

Fig. 1. HRTEM images of BiOCl/TiO_2 nanosheets (a) and BBTC-0.6 photocatalyst (b). The inset of b is the corresponding FFT image.