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High-efficient one-pot synthesis of carbon quantum dots decorating Bi₂MoO₆ nanosheets heterostructure with enhanced visible-light photocatalytic properties

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ABSTRACT

In this study, we reported a one-pot hydrothermal synthesis method for the preparation of nano-heterostructured composite carbon quantum dots (CQDs)/Bi₂MoO. Carbon quantum dots were in-situ synthesized and grafted onto Bi₂MoO₆ nanosheets via hydrothermal oxidation of glucose. For comparison studies, carbon quantum dots and Bi₂MoO₆ were also synthesized by the same way. The structures and compositions of the photocatalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV—vis diffuse reflectance spectroscopy and Raman spectroscopy. The photocatalytic activity of the photocatalysts was evaluated by degradation of Rhodamine B (RhB) and methylene blue (MB) under visible light irradiation. The resulting (CQDs)/Bi₂MoO₆ composites possess excellent photocatalytic activity and stability towards the degradation of Rhodamine B (RhB) and methylene blue (MB) in aqueous solution under visible light irradiation. When the mass ratio of Bi₂MoO₆ to glucose is 1:1, the composite showed the highest photocatalytic activity for RhB and MB degradation. A possible charge transfer and the degradation mechanism of CQDs/Bi₂MoO₆ materials were proposed to understand the relationship between structure and performance of the photocatalysts. The present work proposed a new method for the preparation of CQDs modified Bi₂MoO₆ using a facile method, which provided a new insight into the design and fabrication of advanced photocatalyst for energy and environmental application.

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1. Introduction

The rapid development of the industry in recent years has made the issues of environment pollution and energy crisis become increasingly prominent [1—3]. Realizing the seriousness of the problem, many researchers are dedicated to the studies on eco-friendly technologies in the areas of energy production and pollutants degradation. As a green technology, semiconductor photocatalysis are considered to be a promising technology in treating environment pollutants, especially the treatment of environmental organic contaminants [4]. In the past few years, the traditional semiconductor TiO₂ has been widely studied [5—7]. However, the application of TiO₂ semiconductor is great limited because it responds to only UV light (only around 4% of the solar spectrum) for the reason of its relatively wide-band gap (3.2 eV). Therefore, the development of visible light active photocatalysts became a current challenge and the focus of research [8—12].

Bi₂MoO₆ is the simplest Aurivillius oxide and shows excellent visible photocatalytic activity for degradation of organic pollutants and water splitting [13,14]. However, the quick recombination of photo-generated electrons and holes greatly reduces the quantum yield, which is the major limitation to achieve a high photocatalytic efficiency of the pure Bi₂MoO₆ [15]. In order to improve the photocatalytic activity of Bi₂MoO₆, researchers have done much work, including coupling with various semiconductors like TiO₂ [16], MoS₂ [17], BiPO₄ [18], BiOI [19] and Bi₂O₂CO₃ [19], loading of noble metal Ag [20], and incorporation with Carbon-based materials such

as g-C$_3$N$_4$ [21], RGO [22] and C$_{60}$ [23].

It should be noted that carbon quantum dots (CQDs), as a kind of novel nanostructured carbon-based materials, have recently drawn increasing research attention due to their enormous potential for a wide range of technical applications [24,25]. In comparison to the traditional semiconductor quantum dots, CQDs offer certain advantages on aqueous solubility, photostability, nontoxicity, biocompatibility, cheaper cost and good electrical conductivity [24,26,27]. Therefore, CQDs can be applied in various fields, such as energy storage [24], nanomedicine, chemical imaging, Photocatalysis, electrocatalysis [28] and fluorescent sensor [29]. Besides, CQDs possess excellent up-conversion luminescence properties (absorb visible light and convert it to shorter wavelength light) and have unique property that can trap and transfer the photo-induced electrons [27], which have been applied to design a series of photocatalytic nanocomposites to enhance their photocatalytic properties, such as CQDs/TiO$_2$ [30], CQDs/SiO$_2$ [31], CQDs/CdS [32], CQDs/Fe$_2$O$_3$ [33], CQDs/ZnO [34], CQDs/Cu$_2$O [35].

In this work, we combined the merits of CQDs and Bi$_2$MoO$_6$, and synthesized the nano-heterostructured CQDs/Bi$_2$MoO$_6$ by a simple one-pot hydrothermal method characterized by the decoration of two-dimensional (2D) Bi$_2$MoO$_6$ nanosheets with Zero-dimensional (0D) CQDs. As expected, the obtained composite showed a significant improvement of photocatalytic activity under visible light and excellent cycling stability for removal of organic pollutants compared with the pure Bi$_2$MoO$_6$ nanosheets.

2. Experimental

2.1. Materials preparation

The Bi$_2$MoO$_6$ nanosheets were synthesized by solvothermal synthesis method. All chemicals were analytical grade and used without further purification. The bismuth molybdate materials were also synthesized by solvothermal method. In a typical synthesis, 1 mmol of Bi(CH$_3$COOH)$_3$·5H$_2$O (J&K Scientific) and 0.071 mmol of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (Sinopharm Chemical Reagent Co., Ltd) were dissolved in 20 ml of deionized water and stirred for 30 min. Then 0.3 g of urea was dissolved in 20 ml of ethanol under magnetic stirring for 10 min, and the obtained solution was added to the former solution. The mixture was dispersed by ultrasonication for 10 min and then to hydrothermal treatment in a 50 ml Teflon-lined stainless steel autoclave at 160 °C for 10 h in an oven. After cooling to room temperature, the solid product was separated by centrifuge at 10000 rpm, and then washed several times with water and ethanol, successively. The resultant powder was dried at 60 °C for 6 h under ambient pressure.

CQDs were synthesized by the "bottom-up" method via hydrothermal process taking glucose (Sinopharm Chemical Reagent Co., Ltd) as molecular precursors. 0.1 g of glucose was dissolved in 100 mL of DI water to form a solution of 1 g/L. After that, 40 ml of above aqueous solution was transferred to a 50 ml Teflon-lined stainless steel autoclave and kept at 160 °C for 6 h. The obtained solution was then centrifuged to remove large particles. The resultant dark yellow solution was water soluble CQDs.

CQDs modified Bi$_2$MoO$_6$ were prepared by a hydrothermal method. Specifically, certain amount of glucose (0–0.15 g) was dissolved in 40 ml of distilled water. Then 0.1 g of Bi$_2$MoO$_6$ was added to the above mixture. After being stirred for 30 min at room temperature, the mixture was subject to ultrasonic treatment for 10 min. The resulting solution was transferred to a 50 ml Teflon-lined stainless steel autoclave and kept at 160 °C for 6 h. After cooled down to room temperature, the solid product was collected by centrifugation at 10000 rpm. The obtained precipitation was washed several times with water and ethanol and dried at 60 °C for

10 h. After that, the resulted product was milled into powder. Finally the as-prepared sample was calcined at 300 °C for 4 h in air with the heating rate of 2 °C/min. Depending on the mass of glucose, The as-prepared catalysts were denoted to BMOCX, where "X = 1–3" represent 0.05 g, 0.1 g, and 0.15 g of glucose, respectively, and the BMO represents the pure Bi$_2$MoO$_6$.

2.2. Characterization

The morphology and microstructure was examined by a scanning electron microscopy (SEM, FEI, Holand) in a secondary electron scattering mode at 15 kV and transmission electron microscopy (TEM; JEOL JEM-2100F) that was operated with accelerating voltage of 200 kV. The crystal phase was investigated by X-ray diffraction (XRD, Rigaku, RINT 2000) using Cu Kα ($\lambda = 0.15418$ Å) radiation in the 2θ range of 5°–80° at a scan rate of 4°/min. Raman spectra were conducted on a laser Raman spectrometer with a back scattering con-figuration, and an Ar$^+$ laser (20 mW, 532 nm) was used as excitation source. The Brunauer-Emmett-Teller (BET) surface area of samples was measured by means of N$_2$ adsorption/desorption at 77 K over a NOVA 2000e (Quantachrome) equipment. The chemical status and surface chemical composition of Bi, Mo, O and C elements were analyzed by X-ray photo-electron spectroscopy (XPS). The measurements were carried on an X-ray photoelectron spectrometer (ESCALAB MK II) using MgKa (1253.6 eV) X-rays as the excitation source and C1s (284.6 eV) for calibration.

To determine the band gap of the materials, ultraviolet–visible (UV–Vis) diffusion reflectance spectra were measured with a SHIMADZU UV-2550 spectrophotometer using BaSO$_4$ as background at room temperature. Valence band (VB) XPS spectra for CQDs/Bi$_2$MoO$_6$ heterostructures were also obtained by using the same XPS system. Measurements were performed using an ultrahigh vacuum chamber with a base pressure below 5×10^{-9} Torr. The VB spectra were recorded in the binding energy range from −5 to 20 eV with analyzer pass energy of 20 eV and step size of 0.1 eV.

2.3. Measurement of photocatalytic activity

Photocatalytic activity of the materials was evaluated in the degradation of Rhodamine B (RhB) and methylene blue (MB) under visible light. A 300 W Xe lamp (PLS-SXE300, Perfect Light Company, Beijing, China) with a cut-off filter ($\lambda > 420$ nm) was used as light source, and the light intensity was 100 mW/cm^2. In each experiment, 50 mg of photocatalyst was added in an aqueous solution of RhB (50 ml 10 mg/L), MB(50 ml 10 mg/L), respectively. Before irradiation, the mixture was kept in the dark under magnetically stirring for 1 h to establish adsorption–desorption equilibrium between the model pollutants and photocatalyst. After that, the mixture was irradiated under visible light for 120 min. During the reaction process, 3 ml solution were sampled at 20 min intervals and centrifuged to remove photocatalyst nanoparticles. The concentration was monitored by measuring the maximum absorbance at 554 nm for RhB and 664 nm for MB through a Shimadzu UV-2550 UV–vis spectrophotometer.

2.4. Characterization

The photocurrent measurements were examined by a standard three-electrode, single-compartment quartz cell on a CHI660D electrochemical workstation. The as prepared samples electrode with an active area of 1 cm^2 were used as the working electrode. The working electrode was prepared by dip-coating method. The as-prepared Bi$_2$MoO$_6$ and CQDs/Bi$_2$MoO$_6$ samples were thoroughly dispersed in deionized water, and then cast onto 3 cm × 1 cm FTO

substrates, respectively. The films were sufficiently dried under room temperature to obtain the Bi_2MoO_6 and $CQDs/Bi_2MoO_6$ thin film electrodes. A graphite electrode and a standard calomel electrode were used as the counter electrode and reference electrode, respectively. 0.5 M sodium sulfate was used as the electrolyte solution for photocurrent measurement. A 300 W Xe lamp (PLS-SXE300, Perfect Light Company, Beijing, China) was utilized as light source and was positioned 10 cm away from the photo-electrochemical cell, and the light intensity was turned to 100 mW/cm^2.

3. Results and discussion

3.1. Crystal phase and textural properties

The microscopic morphologies of Bi_2MoO_6 and $CQDs/Bi_2MoO_6$ were initially studied by SEM. As depicted in Fig. 1a–b, SEM images of pure Bi_2MoO_6 showed a sheet-like morphology with the length in the range of tens to hundreds nanometers and thickness of about 14 nm. Fig. 1c–h shows the morphology of Bi_2MoO_6 modified by CQDs with different ratios. The CQDs are too small to see from the SEM images, and we can see that there is no obvious change of morphology of Bi_2MoO_6 after modified process.

TEM was used to further study the morphologies of CQDs and $CQDs/Bi_2MoO_6$ composites. As shown in Fig. 2a–b, the formed CQDs are mostly spherical dots with a size of approximately 9–20 nm and uniformly dispersed. Fig. 2c–d shows that the pure Bi_2MoO_6 is consisted of many irregular nanosheets with a smooth surface. Fig. 2e–j shows the TEM images of CQDs modified Bi_2MoO_6 materials with different ratio. It can be seen that there are few CQDs on the surface of the Bi_2MoO_6 in the sample of BMOC1 (Fig. 2e–f). In contrast, it can be easily seen from the pictures (Fig. 2e–f) that

Fig. 1. SEM images for (a–b) pure Bi_2MoO_6, (c–d) the sample BMOC1, (e–f) the sample BMOC2, (g–h) the sample BMOC3.

Fig. 2. TEM images for (a–b) CQDs, (c–d) the sample BMO, (e–f) the sample BMOC1, (g–h) the sample BMOC2, (i–j) the sample BMOC3.

the a number of CQDs show black and gray contrast dots with diameter of approximately 7–10 nm and are evenly distributed on the surface of Bi_2MoO_6 nanosheets in the sample of BMOC2. The TEM images of the BMOC3 sample (Fig. 2i–j) show that much CQDs accumulate on the surface of Bi_2MoO_6 nanowires, which may lead to a decrease in photocatalytic efficiency. The TEM images of all the samples confirmed that Bi_2MoO_6 was effectively and completely coupled with CQDs and the introduction of CQDs to Bi_2MoO_6 doesn't affect the main morphology of Bi_2MoO_6.

3.2. Crystal phase and textural properties

Fig. 3a shows the XRD pattern of the as-prepared Bi_2MoO_6 and a series of CQDs/Bi_2MoO_6 nanocomposites. As indicated by XRD patterns in Fig. 3a, the diffraction peaks can be indexed to the Bi_2MoO_6 without any impurity phase (PDF No.21–0102). The diffraction peaks of pure Bi_2MoO_6 at $2\theta = 10.98°$, $19.56°$, $23.50°$, $28.36°$, $32.64°$, $33.18°$, $34.40°$, $36.12°$, $39.58°$, $39.64°$, $43.02°$, $44.68°$, $46.86°$, $47.24°$, $55.62°$, $56.32°$ and $58.52°$ can match well with the (020), (120), (111), (131), (002), (060), (220), (151), (240), (042),

(142), (080), (202), (062)/(260), (133)/(331), (191) and (262) crystal planes of the orthorhombic phase Bi_2MoO_6. The diffraction peaks of pure Bi_2MoO_6 have no significant change after thermal treatment at 300 °C for 4 h, indicating that the thermal treatment process doesn't change the phase composition. After coupling with CQDs, similar XRD pattern are obtained from CQDs/Bi_2MoO_6 samples. All these diffraction peaks still exist, suggesting that the heterogeneous process doesn't affect the crystal structure of Bi_2MoO_6. Moreover, no distinctive peaks of CQDs can be observed, and this can be attributed to the low content of CQDs in the samples. Such phenomenon also appeared in other similar systems [27,36].

The Raman analysis was used to further characterize the crystal structure of obtained samples. The Raman spectrum of as-prepared samples proved the presence of Bi_2MoO_6. As shown in Fig. 3b, the A1g peak at 791 cm^{-1} could be assigned to the symmetric stretch of a MoO_6 octahedron, while the peak at 710 and 841 cm^{-1} (A_{2u} mode) showed the characteristics of orthorhombic distortions of the MoO_6 octahedron in Bi_2MoO_6 with Aurivillius structure of layered slabs ($Bi_2O_2^{2+}$) connected through the corner sharing of distorted MoO_6 octahedra. The presence of peaks below 400 cm^{-1} resulted from

Fig. 3. (a) XRD patterns and (b) Raman spectra for CQDs loaded on Bi_2MoO_6 nanosheet with different ratios.

Fig. 4. Nitrogen absorption–desorption isotherm of the as-prepared CQDs/Bi2MoO6 with different CQDs loading amounts (a) and the corresponding pore size distributions curves (b).

the bending modes of the MoO_6 octahedra merging with stretching and bending modes of the Bi−O polyhedra [37,38]. Additionally, bands at 398, 350, 323, 289, 279, 192 and 134 were found, which correspond well to those reported for Bi_2MoO_6 in the literature [37,39]. Moreover, the spectrum peaks of CQDs/Bi_2MoO_6 samples showed slight shift with the modification of CQDs. This change indicated that there existed some electron interactions between the surface of Bi_2MoO_6 and CQDs, which may be beneficial to the enhancement of the photocatalytic efficiency of Bi_2MoO_6, which will be discussed subsequently.

N_2 physical adsorption was carried out to study the specific surface area of the samples. Fig. 4 showed the N_2 adsorption-desorption isotherms and pore size distributions (PSDs) of all the samples. It could be seen from Fig. 4a, All of them displayed typical type-IV isotherms with a type H_3 hysteresis loop at high relative pressure (0.6−1.0), suggesting the existence of the mesoporous structure. The BET specific surface area of pure Bi_2MoO_6 was 15.81 m^2/g. After decorating by CQDs, the BET specific surface area of the sample BMOC1, BMOC2 and BMOC3 were measured to be 16.27, 16.83 and 12.73 m^2/g, respectively. The BET specific surface area firstly increased and then decreased with the increase of mass ratio of carbon quantum dots, which was because the aggregation phenomenon of CQDs caused by loading excessive CQDs on Bi_2MoO_6, and the agglomeration could cause the decrease of BET specific surface area. The pore size distribution curves of all the

samples were shown in Fig. 4b, we can see that all of them showed a wide distribution of the pore size, including small mesopores of 10 nm and some lager mesopores about 30 nm, which were likely originated from the space between the packed nanosheets. Thereby, this hierarchical porous structure and higher specific surface areas of the BMOC2 sample make it possessed more active sites and fully contacted with contaminants, and it was favorable to the photocatalytic performance. The above results implied that the sample of BMOC2 may show the highest photocatalytic activity among all the samples.

3.3. Band gap and chemical state analysis

The optical properties of the Bi_2MoO_6 and a series of CQDs/Bi_2MoO_6 nanocomposites were investigated using UV−vis diffuse reflectance spectra (DRS) measurement. As shown in Fig. 5a, all the samples possess a similar light absorption edge. Some research has shown that the absorption of some photocatalysts were enhanced in visible region after coupling with CQDs [27,36,40]. But in the present study, CQDs show a small effect on the optical trapping capability of Bi_2MoO_6. As shown in Fig. 5a, the absorption intensity of visible light of CQDs modified Bi_2MoO_6 materials were increased slightly. The reason for this could be the fact that some CQDs are partially oxidized during heat treatment, which present weak

at about 159.1 eV, which was assigned to Bi $4f_{7/2}$. The higher binding energies peak at about 164.4 eV was ascribed to Bi $4f_{5/2}$. Meanwhile, the binding energies (BE) of 232.4 and 235.6 eV in Mo 3d high-resolution XPS spectra of pure Bi_2MoO_6 sample (Fig. 6c) were attributed to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ of Mo^{6+}, respectively [45]. The O1s high-resolution XPS spectra of pure Bi_2MoO_6 (Fig. 6d) presented one peak at 530.0 eV, indicating the O species in the pure Bi_2MoO_6 sample were present in O^{2-} state and originated from Bi_2MoO_6 crystal [46]. When loading CQDs on Bi_2MoO_6, it was noted that the peaks of O 1s, Bi 4f and Mo 3d high-resolution XPS spectra in the CQDs/Bi_2MoO_6 samples showed apparent shift in contrast with pure Bi_2MoO_6, The peaks corresponding to Bi 4f ($4f_{7/2}$ and $4f_{5/2}$) in the spectras of BMOC1, BMOC2 and BMOC3 lightly shifted (about 0.1, 0.2 and 0.2 eV) toward higher binding energies as compared to pure Bi_2MoO_6. The binding energies of Mo $3d_{5/2}$, Mo $3d_{3/2}$ and O1s peaks in BMOC1, BMOC2 and BMOC3 were also slightly higher than those of pure Bi_2MoO_6. The above results indicated that there existed some electron interactions between Bi_2MoO_6 and CQDs. Furthermore, it can be seen that the main peaks of C1s high-resolution XPS spectra of the CQDs/Bi_2MoO_6 samples (Fig. 6e) were at about 285.0 eV, 289.0 eV and 289.2 eV, which corresponded to the C—C bond with sp^2 orbital, C—O—C bond, and C=O bond, respectively [33]. The above results demonstrate the coexistence of CQDs and Bi_2MoO_6 in the CQDs/Bi_2MoO_6 hybrid material.

Moreover, the VB value of Bi_2MoO_6 was investigated by XPS valence spectra. As shown in Fig. 8d, the Bi_2MoO_6 displayed the maximum energy edge of VB at about 2.40 eV and the result is consistent with the estimated value as before.

3.4. Photocatalytic performance analysis

The photocatalytic activities of as-prepared samples were evaluated by degradation of model pollutants in water under visible light irradiation (using a 300 W Xe lamp with a cut-off filter at $\lambda > 420$ nm). We can see from Fig. 7a, there was almost no degradation of Rhodamine B after irradiation for 120 min in the absence of catalyst, indicating that the Rhodamine B molecules was sufficiently stable under visible light irradiation for a long time and its self photolysis can be ignored in photocatalytic process. Besides, the pure carbon quantum dots only presented an excellent absorption property and have no any photocatalytic activity. The CQDs/Bi_2MoO_6 materials show higher photocatalytic efficiency than that of pure Bi_2MoO_6. It suggested that some heterojunctions should be formed between CQDs and Bi_2MoO_6 nanosheets, which played crucial role in the transfer and separation of photo-generated carriers. When irradiated by visible light, the electrons Bi_2MoO_6 could be excited from the VB to the CB of Bi_2MoO_6. Due to the excellent electronic conductivity of the CQDs, the photo-generated electrons could be easily scavenged by CQDs, leading to efficient separation and reduced possibility of the recombination of photogenerated electron—hole pairs. Moreover, among all these samples, BMOC2 exhibited the highest activity for the degradation of RhB under visible light. After 120min visible light irradiation, about 100% of RhB can be degraded in the presence of the sample BMOC2, whereas the degradation rate is only about 85% over pure Bi_2MoO_6. This result indicates that the photocatalytic activity of composites is closely related to the mass ratio of two components. In other word, suitable mass ratio could form an efficient junction interface between CQDs and Bi_2MoO_6 that is favorable to the photo-generated carriers transfer, and thereby effectively restrains the recombination of photo-generated carriers. In contrary, excess CQDs deposited on the surface of Bi_2MoO_6 would weaken the absorption of Bi_2MoO_6 to visible light. Besides, a number of carbon quantum dots will reunite on the surface of Bi_2MoO_6, which will

Fig. 5. UV—vis spectra (a) and the band gap (b) for CQDs loaded on Bi_2MoO_6 nanosheets with different ratios.

absorption in the range of visible light [41]. The absorption edge of Bi_2MoO_6 were around 479 nm, corresponding to band gaps of 2.73 eV calculated via the Kubelka-Munk function, $(h\nu F(R\infty))2$ vs. Because of the similar band gaps of all the as-prepared samples, the light harvesting capability shouldn't be the most significant factor attributing to the enhanced photocatalytic activity of Bi_2MoO_6.

The valence band (VB) of Bi_2MoO_6 can be calculated according to the following empirical equation: $E_{VB} = X-E^e+0.5E_g$ Ref. [42], where E_g is the band gap of the semiconductor, E^e is the energy of free electron on the hydrogen scale (about 4.5 eV), and X is the electronegativity of the semiconductor (for Bi_2MoO_6, X is 5.55 eV) [43]. Therefore, the E_{VB} values of Bi_2MoO_6 are calculated to be 2.41 eV. Based on the above result, the CB value of Bi_2MoO_6 was calculated by Mulliken electronegativity theory: $E_{CB} = E_{VB}-E_g$ Ref. [44]. Accordingly, the CB value of Bi_2MoO_6 was determined to be -0.32 eV.

XPS was carried out to investigate the surface properties and components of the Bi_2MoO_6 and CQDs/Bi_2MoO_6 samples. As shown in Fig. 6, the XPS survey spectra (Fig. 6a) indicating that the Bi, Mo, C and O elements were detected on the surface of Bi_2MoO_6 and CQDs/Bi_2MoO_6 samples. The Bi 4f and Mo 3d spectra of all samples showed that all the Bi and Mo species were present in Bi^{3+} and Mo^{6+} state, respectively. Fig. 6b showed the Bi 4f high-resolution XPS spectra of the pure Bi_2MoO6 and CQDs/Bi_2MoO_6 samples. In the Bi 4f spectra, The existence of Bi (III) in the samples of pure Bi_2MoO_6 was evidenced by a shoulder observed on the main peak

Fig. 6. (a) XPS spectra of the samples BMO and BMOC1; High-resolution XPS spectra of (b) Bi 4f, (c) Mo 3d, (d) O 1s for all the samples and high-resolution XPS spectra of (e) C 1s for the samples BMC1, BMOC2and BMOC3.

Fig. 7. Photocatalytic degradation of (a) Rhodamine B (RhB) and (c) methylene blue (MB) by CQDs loaded on Bi_2MoO_6 nanosheet with different ratios under visible light irradiation; kinetic fit for the degradation of (c) Rhodamine B (RhB) and (d) methylene blue (MB) with CQDs loaded on Bi_2MoO_6 nanosheet with different ratios.

also reduce the photocatalytic efficiency of the catalyst.

In order to study the wider practical application, methylene blue (MB) is chosen as a different kind of degradation object to further evaluate the photocatalytic properties. As shown in Fig. 7c, The CQDs modified Bi_2MoO_6 materials still show more excellent photocatalytic performance on the degradation of methylene blue (MB)

than that of pure Bi_2MoO_6. The sample BMOC2 show the highest photoactivity that was about 100% removal efficiency of MB after 120min visible light irradiation, only 91% of MB can be degraded at the same time for the pure Bi_2MoO_6. Fig. 7e and f showed the temporal UV−vis absorption spectral changes during the photocatalytic degradation of RhB and MB solution in the presence of the

Fig. 8. (a) Photocurrent density of the pure Bi_2MoO_6 and the sample BMOC2 during the UV−vis light on/off cycles; (b) cycling performance of the pure Bi_2MoO_6 and BMOC2 for Rhodamine B (RhB) degradation; (c) effects of different active species scavengers on the degradation of MB over the sample BMOC2 under visible light irradiation; (d) valence band XPS spectra of the Bi_2MoO_6 sample.

sample BMOC2 under visible light irradiation. It can be seen that the intensity of the characteristic absorption peak of RhB and MB at about 554 nm and 664 nm decreased gradually and nearly disappeared after 120 min. All the photocatalytic degradation results imply that loading CQDs on Bi_2MoO_6 can obviously improve the photocatalytic efficiency under visible light and the strategy of CQDs modification is efficient.

In order to further compare the photocatalytic efficiency of these samples, the reaction kinetics of RhB and MB degradation were investigated. The reaction rate constant were calculated by the linear fitting of the degradation time against $\ln(C_0/C_t)$. As shown in Fig. 7b and d, the processes of RhB and MB degradation followed the pseudo-first-order kinetics, and the sample BMOC2 had the maximum reaction rate constants both in degradation of RhB and MB. The reaction rate constants in degradation of RhB and MB are 0.029 min^{-1} and 0.048 min^{-1} for the sample BMOC2, which are almost 2.0 times and 2.4 times as high as that of pure Bi_2MoO_6, respectively. Moreover, Bi_2MoO_6 nanomaterials studied for photocatalysis under visible light irradiation in recent years were also shown in Table S1 [47-52].

The stability and reusability are considerable features of the photocatalyst, which are crucial to the practical application. To test

the stability and reusability of the prepared CQDs/Bi_2MoO_6 hybrid material, the photocatalytic decomposition of RhB was repeated ten times. In this study, BMOC2 after photocatalytic degration of RhB for 80 min under UV−Vis light was collected by the centrifugal and dried for the subsequent photocatalytic reaction cycles. In contrast, the same test conditions were conducted for pure Bi_2MoO_6 and the results are shown in Fig. 8b, from which it can be seen that BMOC2 sample can keep a high efficient and stable photocatalytic performance after ten consecutive cycles, which demonstrates the high stability of the photocatalysts. The stability of pure Bi_2MoO_6, in contrast, performed less well. The degradation rate of RhB was down from initial 92%−75% after ten consecutive cycles. In addition, there exist some evident fluctuations during the cycle experiment for pure Bi_2MoO_6. All the result above indicated that CQDs/Bi_2MoO_6 hybrid material performed extremely well on both the stability and reusability.

The transient photo-current responses measurement was carried out to investigate the effect of CQDs on the recombination of electron-hole pairs of Bi_2MoO_6. As can be seen from Fig. 8a, the photocurrent intensity of CQDs/Bi_2MoO_6 materials were higher than that of pure Bi_2MoO_6, confirming that loading CQDs onto Bi_2MoO_6 nanosheets remarkably enhanced the photocurrent. The

Fig. 9. The scheme of the possible heterostructure of CQDs/Bi$_2$MoO$_6$ nanosheet and the transfer pathway of charge carriers on the CQDs/Bi$_2$MoO$_6$ nanosheet surface heterojunction.

sample BMOC2 has the highest photocurrent of 0.57—0.96 μA/cm^2, obviously higher than that of other samples, and the significant improvement of photocurrent reveals that it could form heterojunction on the interface between CQDs and Bi$_2$MoO$_6$ nanosheets and therefore the photogenerated electrons in Bi$_2$MoO$_6$ could quickly transfer to CQDs, facilitating the photoelectrons and holes separation, which was closely related to the photocatalytic performance.

3.5. Detection of active species

In order to reveal the photocatalytic mechanism, we carried out some experiment to detect the main oxidative species in the photocatalytic process. In the experiment, tert butyl alcohol (TBA) and potassium iodide (KI) as the scavengers of •OH and photogenerated holes were added in the catalytic system, respectively. Besides, experiment was carried out under air-equilibrated and N$_2$-bubbled to investigate the role of •O$_2^-$. The result as shown in Fig. 8c, the addition of TPA (100 μL) only had little impact on the photodegradation of RhB, indicating that there are lesser •OH radicals in the RhB oxidation process. On the contrary, the addition of KI resulted in a significative degree of inhibition of RhB degradation, which demonstrate the indispensable role of photo-generated holes existed. At the same time, the degradation rate of RhB was clearly decreased when bubbled N$_2$ into the solution, which demonstrated the crucial role of •O$_2^-$ evolved produced by dissolving oxygen in the reaction system.

3.6. The proposed photocatalytic mechanism

Based on the above results, a mechanism for the improvement of photocatalytic action of CQDs/Bi$_2$MoO$_6$ hierarchical structure is proposed in Fig. 9. Carbon quantum dots exhibit a synergistic role in the CQDs/Bi$_2$MoO$_6$ hierarchical structure. Upon visible light irradiation, the electron can be excited by the high-energy photon from the valance band (VB) into the conduction band (CB). The photogenerated electrons in Bi$_2$MoO$_6$ can transfer quickly to the CQDs because of their excellent electric conductivity. As a result, the separation of photo-generated electrons from holes can be effectively promoted and the degradation efficiency is further improved.

The valance band (VB) of Bi$_2$MoO$_6$ was calculated to be +2.41 eV (vs. NHE), which was more negative than the VB of •OH/H$_2$O (+2.68eV vs. NHE), indicating that photo-generated holes couldn't oxidize H$_2$O to yield •OH radicals in Bi$_2$MoO$_6$. Nevertheless, the CB potential of Bi$_2$MoO$_6$ was calculated to be −0.32 eV (vs. NHE) that is more negative than E (O$_2$/O$_2^-$) (−0.046eV vs. NHE), which can easily reduce dissolved O$_2$ to produce •O$_2^-$. As is well knew, the •OH radicals also could be generated from photo-generated electrons besides photo-generated holes [53], which is why there exists a slight decrease for the photodegradation efficiency of RhB in the presence of tert butyl alcohol.

4. Conclusions

In summary, this work developed a facile and green thermochemical method for the preparation of easily recycled CQDs/Bi$_2$MoO$_6$ composite. The deposited CQDs enhanced the photocatalytic activity of the Bi$_2$MoO$_6$ nanosheet towards the degradation of RhB and MB under visible light irradiation. It can be mainly attributed to the forming efficient junction interface between CQDs and Bi$_2$MoO$_6$, which inhibits the recombination of charge carriers to enhance photocatalytic activity. The sample BMOC2 exhibited the highest photocatalytic performance among all the samples, which is due to the formation of more efficient heterojunctions between CQDs and Bi$_2$MoO$_6$, the enhancement of light absorption, and the enlarged BET surface area. The findings in this work proposed a new insight into the design and fabrication of CQDs modified Bi$_2$MoO$_6$, which provides novel inspiration in developing CQD modified other semiconductor materials.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2017.06.130.

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