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Facile synthesis, electronic structure and photocatalytic activity of a novel Bi-based hydroxyl oxalate $Bi(C_2O_4)OH$

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ABSTRACT

A novel Bi-based hydroxyl oxalate $Bi(C_2O_4)OH$ has been successfully synthesized via a facile aqueous precipitation route, and its photocatalytic activity was investigated for the first time. The as-prepared $Bi(C_2O_4)OH$ nanorods were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–vis diffuse reflectance spectra (DRS) and photoluminescence (PL) spectra. It possesses an indirect-transition optical band gap of 3.73 eV. The electronic structure, density of states as well as light absorption of $Bi(C_2O_4)OH$ were studied by the first principle calculations. The photocatalytic performance of the samples was determined by photodegradation of Rhodamine B (RhB) in aqueous solution. The results revealed that RhB can be effectively decomposed by $Bi(C_2O_4)OH$, and the sample with reactant molar ratio of 1:2 exhibits the highest photocatalytic activity. The active species trapping experiments over $Bi(C_2O_4)OH$ indicated that the hydroxyl radicals (•OH) are the most important active species in the process of RhB photodegradation.

Nowadays, semiconductor photocatalysis technique offers great potential for pollutant purification and energy generation due to its advantages of low cost, unlimited resources and environmental friendliness [1–4]. Apart from the intense researches on traditional photocatalysts, e.g. TiO_2, ZnO, development of novel photocatalysts with strong oxidation and reduction ability has generated ever increasing interest [5–9]. Bismuth containing compounds as a new type of photocatalytic materials have received considerable attention due to their incomparable oxidation ability. BiOX (X = Cl, Br, I) [10,11], Bi_2MoO_6 [12], Bi_2WO_6 [13], $BiVO_4$ [14], $Bi_2O_2CO_3$ [15,16] and other newly found photocatalysts [17–21] all exhibit highly efficient photodegradation efficiency for removing contaminants in aqueous solution or gaseous pollutants. So it is of significance to discover other bismuth compounds as photocatalysts. Bismuth hydroxyl oxalate $Bi(C_2O_4)OH$ is a typical multiple Bi-based oxidate with double anions [22]. Nevertheless, few investigations were carried out on $Bi(C_2O_4)OH$ and its photocatalytic activity has been not been studied so far. On the other hand, facile preparation process endows the material with a promising application prospect. Thus, synthesis of new Bi-based photocatalysts by a simple preparation approach is challenging and highly desirable.

In this work, we for the first time systematically synthesized $Bi(C_2O_4)OH$ via a facile aqueous precipitation route. Its microstructure, optical property, electronic structure and photocatalytic activity were investigated in details. The photocatalysis experiment for decomposition of RhB indicated that $Bi(C_2O_4)OH$ can be used as an efficient photocatalyst under UV light irradiation. To the best of our knowledge, this is the first investigation of the photocatalytic performance of $Bi(C_2O_4)OH$.

$Bi(C_2O_4)OH$ was prepared via a facile precipitation route with bismuth nitrate and oxalic acid as raw materials. It crystallizes in the orthorhombic space group *Pnma* with unit parameters a = 6.0853(2) Å, b = 11.4479(3) Å and c = 5.9722(2) Å [22]. The crystal structure of $Bi(C_2O_4)OH$ is mainly composed of BiO_6 polyhetra and $[C_2O_4]$ groups (Fig. 1a). The BiO_6 polyhetra and $[C_2O_4]$ groups alternatively connected through two bridging O atoms along [010] direction to form the three-dimensional structure. It can also be seen that $Bi(C_2O_4)OH$ displays a zigzag configuration along [100]. Fig. 1b shows the X-ray diffraction (XRD) patterns of the as-prepared samples with different molar ratios of $Bi(NO_3)_3 \cdot 5H_2O$ and $H_2C_2O_4 \cdot 2H_2O$. The diffraction peaks of $Bi(C_2O_4)OH$ samples with reactant molar ratios of 1:1, 1:1.5 and 1:2 all can be indexed into the orthorhombic $Bi(C_2O_4)OH$ (ICSD #419313), and no other peaks can be found, indicating the successful synthesis of pure phase of sample. When the molar ratio is lower than 1:2, several impurity peaks at 13.8°, 21.8°, 27.75, etc. were observed in the XRD pattern. Thus, the products are sensitive to the relative ratio of reactants. The typical scanning electron microscope (SEM) images of pure $Bi(C_2O_4)OH$ are shown in Fig. S1. It can be seen that the $Bi(C_2O_4)OH$ products consist of uniform rod-like nanostructures. The crystal sizes of these nanorods are approximately 1–2 μm in length and 200 nm in width, respectively.

The UV–vis diffuse reflectance spectra of the as-prepared samples were presented in Fig. 2. The optical absorption edge of $Bi(C_2O_4)OH$ is roughly estimated to be 345 nm. Band gap (E_g) of a semiconductor

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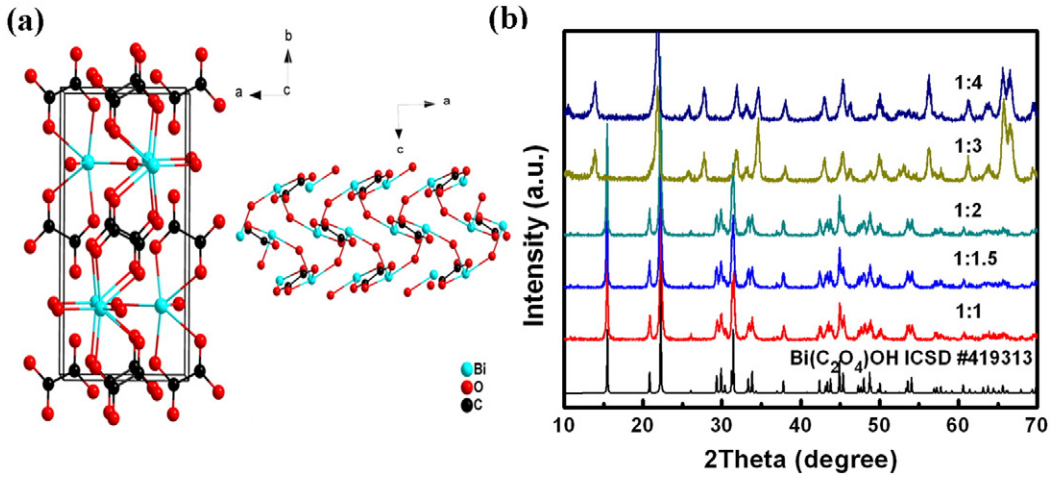

Fig. 1. (a) Crystal structure $Bi(C_2O_4)OH$. (b) XRD patterns of $Bi(C_2O_4)OH$ samples with molar ratios of $Bi(NO_3)_3 \cdot 5H_2O$ and $H_2C_2O_4 \cdot 2H_2O$ 1:1, 1:1.5, 1:2, 1:3 and 1:4.

can be determined by the formula $\alpha h\nu = A(h\nu - E_g)^{n/2}$ [23,24], where α, h, ν, E_g and A are absorption coefficient, Planck constant, light frequency, band gap energy, and a constant, respectively. Herein, the n value is determined by the type of optical transition of $Bi(C_2O_4)OH$ (n = 1 and 4 for direct and indirect transition, respectively). Data plots of absorption$^{1/2}$ versus energy in the absorption edge region are nearly linear, indicating the indirect-optical-transition property of $Bi(C_2O_4)OH$. Accordingly, the E_g of $Bi(C_2O_4)OH$ was estimated to be 3.73 eV (inset of Fig. 2). Besides, the conduction band (CB) and valence band (VB) positions of $Bi(C_2O_4)OH$ can be calculated to be 0.47 and 4.20 eV, respectively [25].

The brillouin zone path and corresponding energy band structure of $Bi(C_2O_4)OH$ are shown in Fig. 3(a) and (b), respectively. The valence band maximum (VBM) is located at the G point, and the conduction band minimum (CBM) is at D point, confirming the indirect band gap of $Bi(C_2O_4)OH$. The theoretical band gap is 2.65 eV which is smaller than that of experimental value of 3.73 eV because of the underestimation of density functional calculation. Fig. 3(c) presents the total and partial density of states projected on *s* and *p* orbitals of Bi, C, H, O for one unit cell of $Bi(C_2O_4)OH$. The top of the VB is mainly dominated by 2*p* orbitals of O and the bottom of CB is mainly occupied by O 2*p*, C 2*p* and a slight of Bi 6*p* orbitals. We also calculated the optical property of $Bi(C_2O_4)OH$ as shown in Fig. 3(d). Three polarization directions of photon electric field, namely 1 0 0, 0 1 0, and 0 0 1 were considered. It can be seen that it is optically anisotropic. In the range of short-wavelength from 170 to 300 nm, the photon absorption for the polarization direction of 0 1 0 is stronger than that of 1 0 0 and 0 0 1 directions.

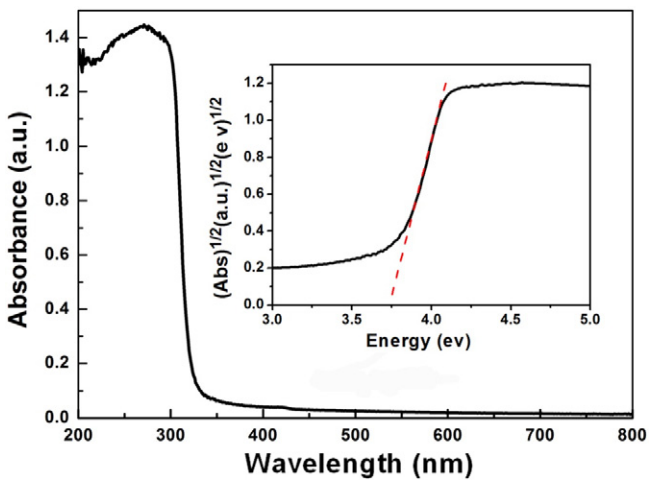

Fig. 2. UV–vis diffuse reflectance spectra and Band gap (inset) of $Bi(C_2O_4)OH$.

The photocatalytic activity of $Bi(C_2O_4)OH$ was evaluated by degradation of RhB molecules in aqueous solution under UV light irradiation. As shown in Fig. 4a, the self-degradation of RhB by UV light can be neglected. RhB molecules can be effectively decomposed by $Bi(C_2O_4)OH$. The $Bi(C_2O_4)OH$ sample with reactant molar ratio of 1:2 exhibited the highest degradation efficiency, and over 81% of RhB was degraded within 1 h irradiation. Fig. 4b presented the time-resolved absorption spectra of RhB. It can be observed that the maximum absorbance of the solution at 554 nm was gradually decreased with prolonging the illumination time. Fig. 4c showed the photoluminescence (PL) spectra of $Bi(C_2O_4)OH$ samples under excitation wavelength of 248 nm. As indicated, $Bi(C_2O_4)OH$ exhibits an emission band at around 410 nm, which is consistent with that of other bismuth compounds. Besides, the separation efficiency of the photogenerated electrons and holes can be investigated by PL [26]. Generally, lower PL emission intensity indicates the lower recombination efficiency of photogenerated charge carriers, and thus the higher photocatalytic activity. From Fig. 4c, the $Bi(C_2O_4)OH$ sample with molar ratio of 1:2 displays an obviously lower emission intensity than other counterparts. This is in good agreement with the order of their photocatalytic activities.

To detect the active species generated in the degradation process, the sacrificial agents, including 4-benzoquinone (BQ), isopropyl alcohol (IPA) and disodium ethylenediaminetetraacetate (EDTA) were used as scavengers of superoxide radicals ($\bullet O_2^-$), hydroxyl radicals (•OH) and holes (h+), respectively [25]. As shown in Fig. 4d, the RhB degradation was moderately affected by the addition of 1 mM of EDTA or 1 mM of BQ, suggesting that $\bullet O_2^-$ and h+ have a slight influence on the photodegradation of RhB. Nevertheless, the decomposition rate of RhB was significantly depressed with adding 1 mM IPA, indicating that •OH plays a critical role in the RhB photooxidation process. Radical trapping experiment revealed that the hydroxyl radical (•OH) is the main active species in the degradation process of RhB over the $Bi(C_2O_4)OH$ photocatalyst.

In summary, bismuth hydroxyl oxalate $Bi(C_2O_4)OH$ nanorods were successfully synthesized via a facile aqueous precipitation route. $Bi(C_2O_4)OH$ possesses an indirect transition optical band-gap of 3.73 eV, and its E_{CB} and E_{VB} were also estimated. Theoretical calculation revealed that the bottom of CB was occupied by O 2*p*, C 2*p* and a slight of Bi 6*p* orbitals, and the top of VB was mainly dominated by O 2*p*. The photodecomposition of RhB experiment demonstrated $Bi(C_2O_4)OH$ can be used as effective photocatalysts under UV light irradiation. In the photodegradation process, the hydroxyl radicals (•OH) serving as the main active species play critical roles, as revealed in the radical trapping experiments.