Inorganic Chemistry Communications 40 (2014) 55–58

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Direct hydrolysis preparation for novel bi-based oxysalts photocatalyst $Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O$ with high photocatalytic activity

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ARTICLE INFO

Article history:
Received 16 October 2013
Accepted 21 November 2013
Available online 28 November 2013

Keywords:
Hydrolysis
Photocatalyst
Bi-based oxysalts
pH value

ABSTRACT

$Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O$ was successfully prepared by a very facile direct hydrolysis process. The as-prepared samples were characterized by XRD, SEM, DRS and PL. $Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O$ has an indirect-transition optical band-gap of 3.45 eV, and the E_{CB} and E_{VB} are estimated to be 0.75 eV and 4.20 eV, respectively. The as-prepared $Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O$ products showed different morphologies and microstructures with the change of pH value. The photocatalytic activities of the samples were determined by photooxidative decomposition of rhodamine-B (RhB) in aqueous solution. The results revealed that the sample obtained at pH 5 exhibited the highest photocatalytic activity, which is much better than P25 and Bi-based photocatalyst $Bi_2O_2CO_3$.

As a potential solution to the severe problems of energy shortages and environment crises, photocatalysis has attracted increasing attention because it has a great deal of advantages such as unlimited resources, low cost, and environmental friendliness. The effective photocatalytic treatment for all kinds of organic contaminants requires that the photocatalyst should have high efficiency and long life. Therefore, a tremendous effort was made to develop new photocatalysts.

During the last two decades, besides the focused work on TiO_2 modifications, many efforts were made to develop other novel efficient photocatalysts. The reported photocatalyst systems, to the best of our knowledge, can be generally classified as oxides [1–4], sulfides [5–7], oxysulfides [8], nitrides [9] and oxynitrides [10–13]. Among the numerous semiconductors, for the merits of simple, low-cost and low toxicity, bismuth-containing materials have received a lot of attention [14–17], especially in environmental remediation over the past few years. Bi-based oxysalt photocatalysts, such as Bi_2WO_6 [18], $Bi_2O_2CO_3$ [19], $BiPO_4$ [20], Bi_2MoO_6 [21], Bi_2GeO_5 [22], BiOX (X = Cl, Br, I) [23], $BiVO_4$ [24] and $BiFeO_3$ [25] have received a lot of attention in environmental remediation over the past few years. These Bi-based photocatalysts all exhibit high efficiency in the degradation of organic pollutants.

So far, at least 15 bismuth basic nitrates have been reported in the Bi_2O_3–N_2O_5–H_2O system [26]. While in the large family of bismuth compounds, rare reports are published on the photocatalytic performance about basic bismuth nitrates. In this work, $Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O$ were prepared by a simple hydrolysis process at room temperature only using $Bi(NO_3)_3 \cdot 5H_2O$ as raw materials. Its photocatalytic activity was evaluated by the photodecomposition of RhB in aqueous medium under UV lamp. To our knowledge, this is the first investigation of photocatalytic activity of $Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O$.

Fig. 1 shows the projection of the structure of BION-3 along the [*a–c*] plane. The bismuth basic nitrate $Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with the parameters a = 17. 152 (1), b = 9.181 (1), c = 17.752 (1). The structure mainly consists of polycations, in which pairs of cage-like groups $[Bi_6O_5(OH)_3]$ are joined around the symmetry centres through two bridging O atoms, together with nitrate anions and water molecules. Fig. 1c shows that the diffraction peaks of BION-3 products obtained at pH 1 can be indexed to the pure $Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O$ (ICSD #2460). No other peaks are found, suggesting the high purity and crystallinity of the samples. Moreover, the distinct peaks at 13.06°, 19.64°, 25.05°, 42.52° match with the (200), (300), (−123), (−627) crystal planes of BION-3, respectively. As shown in Fig. 1d, the BION-3 products synthesized at pH 1 and 3 are in good crystallization. It is known that a slightly alkalic solution is beneficial to the formation of BINO-3 according to the hydrolysis equation of $Bi(NO_3)_3 \cdot 5H_2O$:

$$6Bi(NO_3)_3 \cdot 5H_2O \rightarrow Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O + 13HNO_3 + 19H_2O \quad (1)$$

However, the crystallization of BION-3 obtained at pH 5 is worse than the BION-3 prepared at pH 1 and 3 (Fig. 1d), and sample synthesized at pH 7 is amorphous. The hydrolysis product of $Bi(NO_3)_3 \cdot 5H_2O$ will become Bi_2O_3 when pH is 12. Thus, further enlargement of pH values will go against the formation of BION-3 and crystal growth.

Fig. 2 depicts typical SEM images of BION-3 products. It clearly demonstrates that there are differences in the morphology and size of the BION-3 products. Fig. 2a shows the BION-3 obtained at pH 1 that consists of micro-strips with length 5–20 μm. Plenty of nanosheets are

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http://dx.doi.org/10.1016/j.inoche.2013.11.030

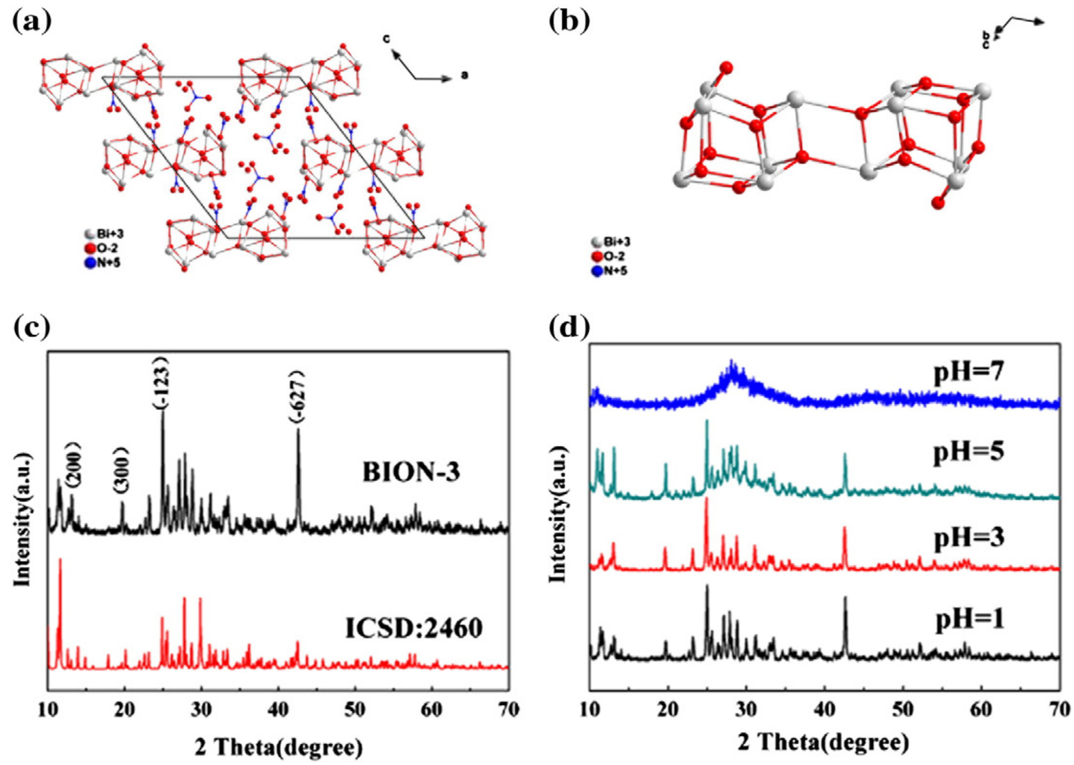

Fig. 1. (a) Projection of the structure of BION-3 along the [*a*–*c*] plane. (b) The structural units of Bi-O groups. (a) XRD pattern of BION-3 obtained at pH 1 (c) and different pH values (d).

observed in BION-3 products prepared at pH 3 (Fig. 2b). Fig. 2c and d revealed that the BION-3 products obtained at pH 5 and 7 are composed of nanoplates with widths of 200 nm–2 μm. With the increase of pH value, it can be seen that the intensity of the (200) and (300) crystal planes diffraction peaks changes as revealed in Fig. 1d. The result demonstrates that the pH has impact on growth of some crystal planes, which lead to the different morphologies of BION-3 products.

On the basis of the above results, we may propose the formation process of $Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O$ at different pH values (Fig. S1). At the early stage of hydrolysis process, the $Bi(NO_3)_3 \cdot 5H_2O$ was hydrolyzed to rectangular nanosheets, which were stacked together in vertical to form micro-strips at pH 1 (Fig. S2a, 2b) and assembled together in horizontal to form wide nanosheets at pH 3 (Fig. S2c, 2d). The $Bi(NO_3)_3 \cdot 5H_2O$ direct hydrolyzed to irregular nanoplates.

UV–vis diffuse reflectance spectra of BION-3 is shown in Fig. 3a. In semiconductors, the square of absorption coefficient is linear with energy for direct optical transitions in the absorption edge region; whereas the square root of absorption coefficient is linear with energy

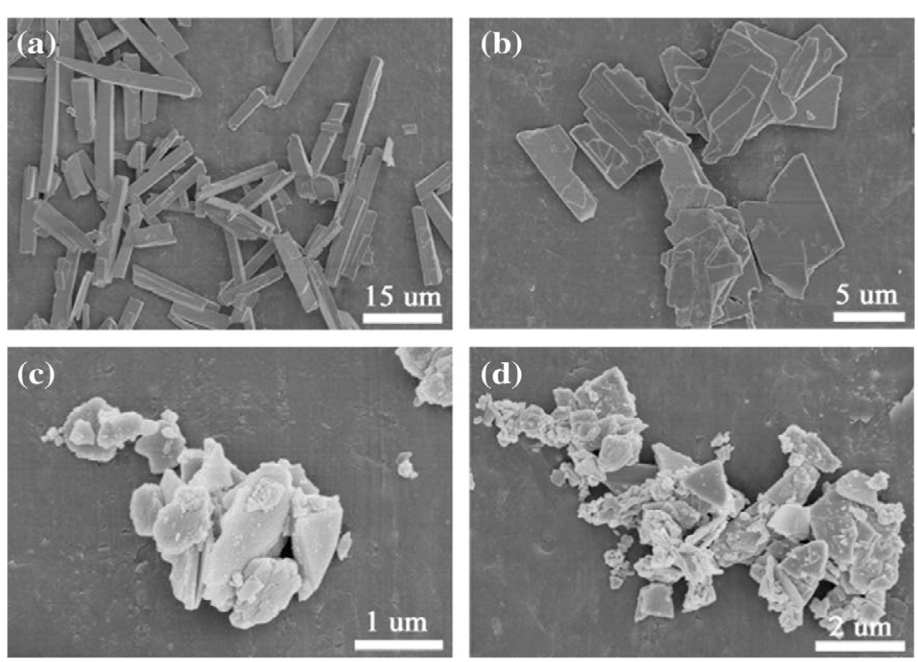

Fig. 2. SEM images of BION-3 obtained at pH 1 (a), pH 3 (b), pH 5 (c) and pH 7 (d).