Materials Research Bulletin 87 (2017) 92–101

Contents lists available at ScienceDirect

Materials Research Bulletin

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

3D hierarchical flower-like nanostructure of Bi_2MoO_6: Mechanochemical synthesis, the effect of synthesis parameters and photocatalytic activity

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ARTICLE INFO

Article history:
Received 18 May 2016
Received in revised form 7 September 2016
Accepted 14 November 2016
Available online 15 November 2016

Keywords:
A. Inorganic compounds
A. Nanostructures
A. Oxides
B. Optical properties
D. Catalytic properties

ABSTRACT

In this work, we successfully prepared 3D hierarchical flower-like nanostructure of Bi_2MoO_6 by a facile mechanochemical reaction followed by heat treatment at 450 °C for 2 h. The used all chemicals were low-cost and environmentally benign compounds. Acetamide/NH_4NO_3 was used as driving/oxidizer agent to direct the solid phase reaction towards producing special morphology in nanoscale. Characterization results revealed that the resulting compound has been arranged from a 3D hierarchical structure with an ornamental cabbage-like shape composed of nanoparticles. The influence of milling time on the morphology growth was studied *via* running mechanochemical reaction in the milling time from 30 to 120 min. The photocatalytic property of this product was studied for the removal of some organic dye pollutants in water under light irradiation. The results revealed a high degree of photodegradation capability, which can be related to its special structure, more active sites and high light-harvesting capacity.

1. Introduction

In recent years, the considerable growth of different industries and discharge of wastes to the environment has increased the pollution of water bodies as a very serious environmental crisis. Therefore, the formulation of policies for developing and producing efficient catalysts or photocatalysts is of great importance to open new pathways for dealing with such problems. There are many reports on the photocatalytic treatment of wastewaters, however some of them indicate low degree of catalytic performance and often cause the increase of the energy requirement and so the cost for wastewater treatment [1–6]. Amongst reported photocatalysts, Bismuth-containing semiconductors have been attracted a lot of attention due to the special electrical and optical properties [7,8]. Bi_2MoO_6 is an active member of Bismuth-containing compounds with a layered Aurivillius structure consisting of perovskite layers between bismuth oxide layers. It possesses good performances in photocatalytic, catalytic, gas sensing and ion conducting fields due to the excellent intrinsic electrical and optical properties and high oxygen storage capacity. This compound with a band gap about 2.5 eV is well capable for capturing visible light and can be a proper candidate for photodegradation of organic pollutants in water under visible light irradiation [9–12]. With attention to the influence of morphology and particle size on the photocatalytic properties, the synthesis of the photocatalysts with special morphologies *via* facile, safe and low-cost methods is favorable [7,13]. Amongst common reported methods for synthesis of this compound such as hydrothermal [14,15], microwave [16], citrate complex [9], ultrasonic [17] co-precipitation methods [10,18], mechanochemical technique has been presented in a few paper but no special morphology [19–21]. Mechanochemical reaction is a promising and simple technique for synthesis of nanomaterials in solid phase due to the safety, simplicity and cheapness. Because such technique is operated in solid state without any organic solvent, it can be introduced as an environmentally friendly method. On the other hand, when the reactants are suitably selected, this method can be a usable way for production of nanostructures with special morphologies but it has very less attended. The use of capping agents with functional groups of carboxyl and or amine effectively directs orientation of the building blocks towards arranging special morphology. Amongst various introduced agents, acetamide is a low-cost and useful reactant with a high reactivity for trapping of metals in solid reactions [22–24]. To the best of our knowledge, the

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http://dx.doi.org/10.1016/j.materresbull.2016.11.021
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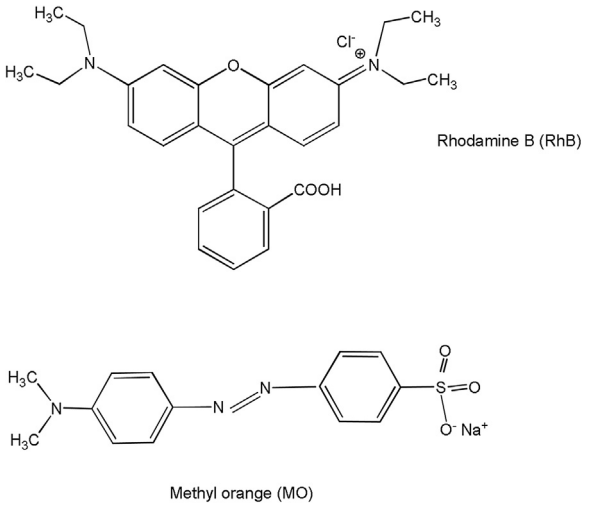

Scheme 1. The molecular structures of Rhodamine B (RhB) and Methyl orange (MO).

synthesis of flower like Bi_2MoO_6 nanostructure by mehcanochemical reaction using acetamide and ammonium nitrate as driving agents has not been reported yet.

As noted, Bi_2MoO_6 is a good semiconductor photocatalyst and can be introduced as one of the effective catalysts due to its special structure and properties [12,25]. In present work, we reported a simple mechanochemical technique for the synthesis of this compound with flower-like nanostructure. The effect of some parameters e.g., milling time and presence/absence of the employed driving agent on the product morphology was also studied. The obtained precursor before calcination treatment was characterized and discussed in detail and a probable synthesis mechanism was also proposed. As another objective of this work, the optimal product was employed to remove Rhodamine B (RhB) and Methyl orange (MO) as the model of organic dye pollutants from aqueous solution using photocatalytic process at room temperature and neutral pH.

2. Experimental details

2.1. Materials and synthesis procedure

Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$), acetamide ($CH_3CONH_2$) and ammonium nitrate ($NH_4NO_3$) were purchased from Merck Co. and were used without further purification.

To synthesize γ–Bi_2MoO_6 nanostructure, the stoichiometric amounts of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and $Bi(NO_3)_3{\cdot}5H_2O$ as initial materials in the presence of acetamide/ammonium nitrate as driving/oxidizer agent with a molar ratio of 1:2 were mixed and ground together in solid phase in a ball milling (Retsch MM-400) apparatus with 1800 rpm (30 Hz) for 60 min. The resulting powder was collected, calcined at 450 °C for 2 h in a furnace and then, the obtained yellowish product was analyzed. The effect of milling time by programming from 30 to 120 min, the presence and absence of driving agent and also the molar ratio of capping agent to oxidizer on the morphology of final product were also discussed in detail.

2.2. Photocatalytic test

To study the photocatalytic performance of the prepared product on the removal of dye pollutants, the toxic organic dyes of RhB and MO were selected as the models of water contaminations. These experiments were performed under the following conditions: 0.05 g of the prepared optimal Bi_2MoO_6 nanostructure as photocatalyst was introduced to 100 mL of dye aqueous solutions with the initial concentration of 10 mg L^{-1} accompanied by 0.05 mM H_2O_2 as accelerator agent at room temperature and neutral pH. The reactions were performed into Pyrex glass vessel

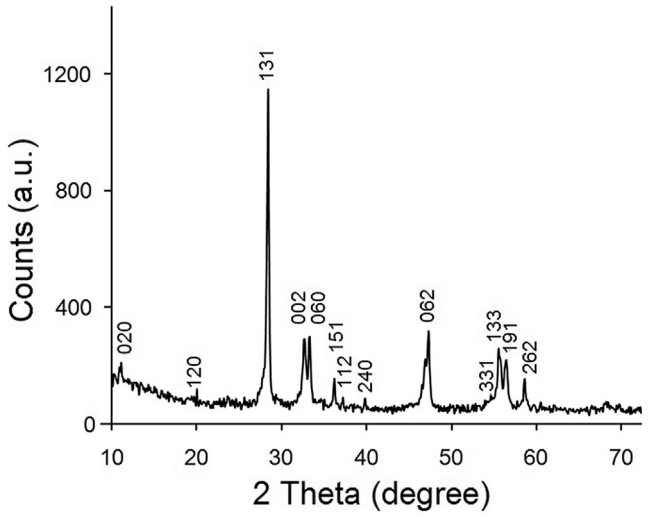

Fig. 3. XRD pattern of the prepared product.

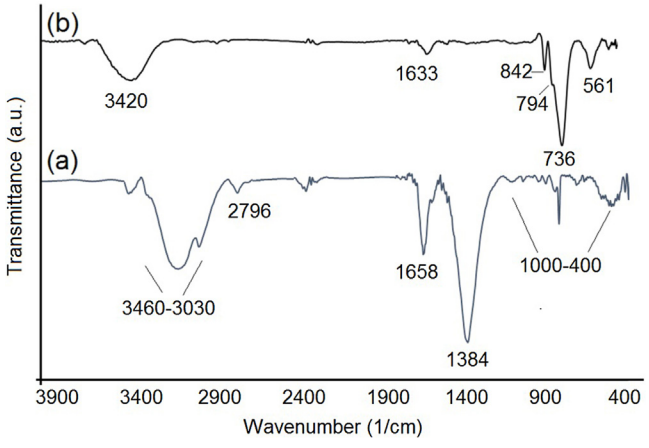

Fig. 1. FT-IR spectra of the precursor (a) after mechanical milling reaction and the product after calcination (b).

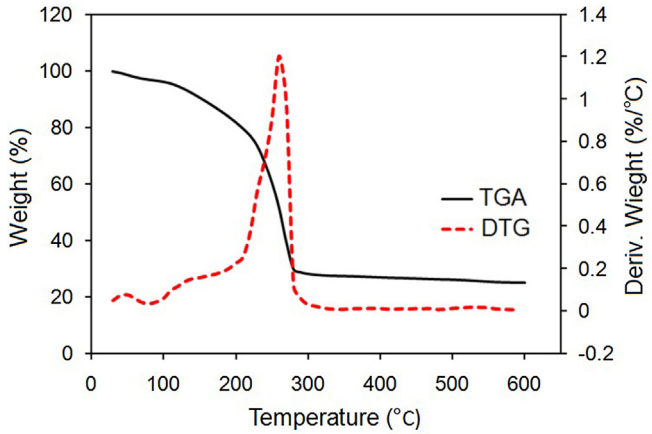

Fig. 2. TGA-DTG curves of the prepared precursor.