Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

# One-step synthesis of in situ reduced metal Bi decorated bismuth molybdate hollow microspheres with enhancing photocatalytic activity

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ARTICLE INFO

*Article history:*
Received 31 July 2016
Received in revised form 22 October 2016
Accepted 26 October 2016
Available online xxx

*Keywords:*
Photocatalytic activity
Bismuth molybdate
In situ reduction
Degradation

ABSTRACT

In this feature work, in situ metal Bi are successfully modified bismuth molybdate hollow spheres using an effective one-pot solvthermal reduction without any temple. In order to deeply understand the influence of reduction conditions on the texture, surface state, and photocatalytic performance of the resulting samples, a series of products were synthesized by tuning the temperatures. The similar morphology, surface area of photocatalysis (BMO-160 and BMO-170) were synthesized, only with the different composition. The detailed characterization and analysis distinctly suggested that increasing solvothermal reduction temperature led to $Bi^{3+}$ was in situ reduced to elementary substance $Bi^0$ by ethylene glycol gradually and dispersed very uniform in bismuth molybdate. Benefiting from the enhanced charge separation, transfer, and donor density resulting from the formation of Bi decorated bismuth molybdate where Bi as cocatalyst, the photocatalytic performance of the reductive $Bi/Bi_{2-x}MoO_y$ hollow spheres (BMO-170) is higher than that of the untreated $Bi_{2-x}MoO_y$ hollow spheres (BMO-160) for Rh6G degradation under visible light irradiation. Additionally, the reductive BMO-170 has a superior stability after five cycles.



## 1. Introduction

Water pollution mainly caused by development of industry is the most rigorous environmental issues in our modern society [1,2]. Utilization of solar energy to purify waste water has been generally considered as the ultimate solution due to the fact that solar light is clean and renewable [3,4]. However, highly efficient and low cost photocatalyst is a key point to realize above process. $TiO_2$ [5–7], ZnO [8], ZnS [9] and other analogous kinds of materials, usually semiconductor, have been comprehensively served as photocatalyst. Unfortunately, most of these semiconductor show high photocatalytic activity only under the help of ultraviolet light irradiation, which greatly hinder their applications in real.

Recently, more and more attention has been forced on seeking visible-light driven photocatalysts in order to effectively utilize solar energy [10,11]. Bismuth molybdate ($Bi_2MoO_6$), a kind of visible light respond and Bi-based Aurivillius oxide, has narrow bandgap (2.66 eV) [12–16]. Some of published paper show an increasing interest for $Bi_2MoO_6$ [17–19]. Actually, it has been proved that the property of photocatalysts go hand in hand with its morphology and structure. Therefore, various porous and hollow textures have been made great efforts to improve it photocatalytic activity and achieve a certain purpose. Nevertheless, its photocatalytic efficiency still not good enough due to the very fast photo-generated charge-carrier's recombination in photocatalytic process [20]. Modifying semiconductor photocatalyst via utilizing nano-metal is regarded as a good way to solve this problem. Noble metals [21,22], such as Ag [23–28], Pt [29], Au [30,31], Pd [32,33] have been used to boost the performance of semiconductors. Moreover, most of the metal/semiconductor composites were synthesized by using two-step, which is difficult to guarantee the metal evenly dispersed in the semiconductor photocatalysts.

Metal Bi is a low cost metal, whose fermi level is −0.17 eV and also shows surface plasmon resonance (SPR), which is similar with the effect of noble metal [34–37]. Based on this purpose, a kind of metal Bi modified bismuth molybdate hollow microspheres was synthesized through utilizing a simple and in situ solvothermal reduction by one step. It found that $Bi^{3+}$ could be in situ reduced to $Bi^0$ by ethylene glycol gradually and dispersed very uniform in bismuth molybdate with the increasing of temperature. By carefully controlling the temperature, it is very interesting that

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http://dx.doi.org/10.1016/j.apsusc.2016.10.173

the Bi/bismuth molybdate and pure $Bi_2MoO_6$ with the analogous microstructure and surface area were successfully synthesized. However, there is a very big difference in photocatalytic activity of two materials. In order to figure out why metal Bi modified bismuth molybdate make significant progress in the photocatalytic activity, a series of experiments were designed and investigated in detail.

## 2. Experimental section

### 2.1. Preparation of photocatalysts

$Bi(NO_3)_3 \cdot 5H_2O$ (3.480 mmol) and $Na_2MoO_4 \cdot 2H_2O$ (1.740 mmol) were dispersed in 15 mL EG under vigorous stirring, respectively. Waiting for solid dissolution, $Na_2MoO_4$ solution was drop wised into $Bi(NO_3)_3$ solution slowly. Then the clear solution was transformed into steel autoclave, and maintained at different temperature (120 °C, 140 °C, 160 °C, 170 °C, 180 °C) for 20 h. Followed, the autoclave was naturally cooled to room temperature. Catalysts were centrifuged, washed with water for several times and dried at 80 °C for 12 h. Photocatalysts synthesized at different temperature

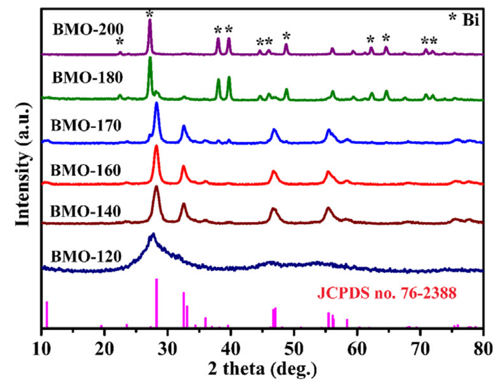


**Fig. 1.** The XRD patterns of photocatalysts.

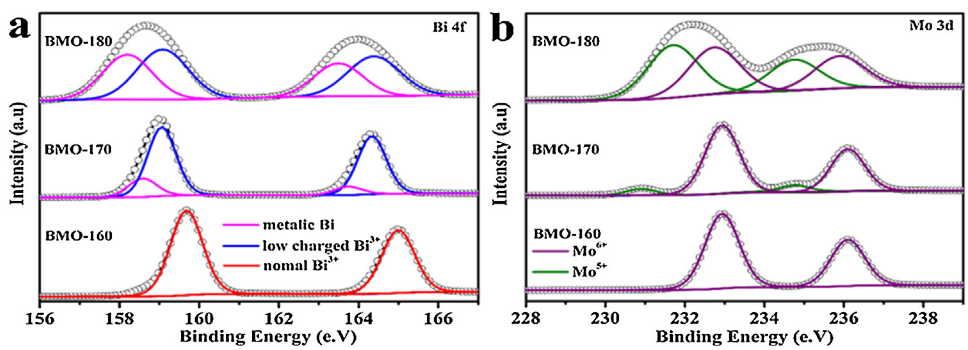


**Fig. 2.** The XPS high-resolution Bi 4f (a), Mo 3d (b) of BMO-160, BMO-170 and BMO-180.

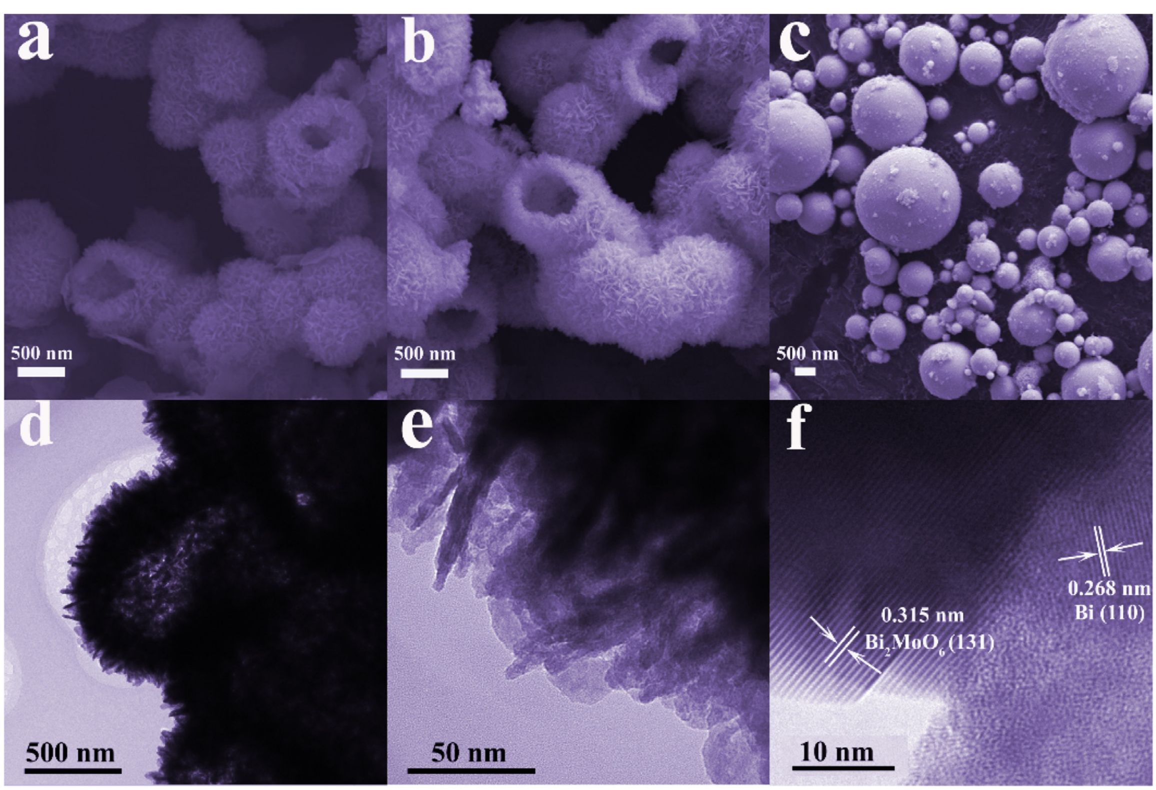


**Fig. 3.** The FE-SEM images of BMO-160 (a), BMO-170 (b) and BMO-180 (c) and the TEM images of BMO-170 (d–f).

Please cite this article in press as: M. Jin, et al., One-step synthesis of in situ reduced metal Bi decorated bismuth molybdate hollow microspheres with enhancing photocatalytic activity, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.10.173