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Effect of acetic acid on morphology of Bi_2WO_6 with enhanced photocatalytic activity

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ABSTRACT

Hierarchical bismuth tungstate (Bi_2WO_6) with various morphologies was successfully prepared by a simple hydrothermal method. The hierarchical Bi_2WO_6 are all assembled from nanosheets. However, with increase of acetic acid the morphology of Bi_2WO_6 transformed regularly according to the following order: clew-like, clew-like and flower-like, flower-like, dish-like with crisscross, dish-like with incomplete crisscross, and dish-like ones. Therefore, the effect of acetic acid on the morphology transformation of the Bi_2WO_6 was investigated and a plausible formation mechanism was proposed. Owing to the larger specific surface area and pore diameter, the clew-like Bi_2WO_6 exhibited enhanced photocatalytic activity for the degradation of Rhodamine B (RhB). Furthermore, the possible mechanism of photocatalytic degradation was discussed.

1. Introduction

In the past few years, the environmental problems caused by toxic organic wastewater have become one of the severe challenges to the sustainable development of modern human society. Dyes are a serious organic pollutant because they are not automatically degraded [1]. Their release as wastewater in the ecosystem is a source of environmental pollution, eutrophication and aquatic bioturbation. In order to solve the problem of organic pollution, photocatalysts have drawn a lot of attentions [2,3].

Bismuth tungstate, one of the perovskite semiconductor catalysts, has caused widespread concern due to its potential applications in ion conductive, dielectric, luminescent, and photocatalytic fields [4,5]. Bi_2WO_6 ($E_g = 2.75$ eV) crystallizes with perovskite-type $[WO_4]^{2-}$ layers sandwiched between $[Bi_2O_2]^{2+}$ layers [6,7], which is considered to be in favored of the efficient separation of photo-generated carriers during the photocatalytic process [8]. As a promising light-driven photocatalyst, various approaches for synthesizing Bi_2WO_6 have been developed, including solid-state metathetic reaction [9], ionic liquid-assisted hydrothermal [10], sol-gel [11], hydrothermal or solvo-thermal treatment [12,13], and low-temperature combustion synthesis [14]. However, hydrothermal method in liquid phase technique is one of the most widely used preparation methods because of its simple operation, easy control, as well as low cost. In addition, different morphologies of Bi_2WO_6 have been widely explored, such as nanoplates [15], flower-like structure [16], particles [17], clew-like microspheres [18], etc. However, as far as we know, the effects of acetic acid on the morphology of Bi_2WO_6 and its mechanism have not been systematically studied.

Herein, we report the preparation of hierarchical Bi_2WO_6 assembled from nanosheets via a simple hydrothermal method. Importantly, the influences of acetic acid on the morphology transformation of Bi_2WO_6 were discussed systematically. In the paper, a possible formation mechanism of the morphology transformation of Bi_2WO_6 was proposed. The photo-degradation activity and mechanism of RhB also was investigated.

2. Experimental

2.1. Material and synthesis

Bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$) was purchased from Kemiou chemical reagents Co., Ltd, and sodium tungstate ($Na_2WO_4{\cdot}2H_2O$) and *p*-benzoquinone (BQ, $C_6H_4O_2$) were supplied from Aladdin Industrial Corporation. Nitric acid (HNO_3) was supplied by Laiyang Chemical Industry Co. Ltd. Rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$) was obtained from Tianjin Guangcheng Chemical Industry Co. Ltd. Acetic acid ($C_2H_4O_2$) and isopropyl alcohol (IPA, $(CH_3)_2CHOH$) were purchased from Tianjin Fuyu Chemical Industry Co. Ltd. Ethylenediamine tetraacetic acid disodium salt (EDTA-2Na, $C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$) was obtained from Sinopharm Chemical Reagent Co. Ltd. The water used during the experiment was deionized water (DI, 18.2 MΩ cm^{-1}), and all chemicals

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Table 1
Experimental parameters of Bi_2WO_6 prepared by hydrothermal method.

Sample	$Bi(NO_3)_3{\cdot}5H_2O$/M	$Na_2WO_4{\cdot}2H_2O$/M	Type of acid	Volume of acid/ml	Temperature /°C	Time /h
S1	0.05	0.025	HNO_3	8	160	24
S2	0.05	0.025	$C_2H_4O_2$	8	160	24
S3	0.05	0.025	$C_2H_4O_2$	8	180	3
S4	0.05	0.025	$C_2H_4O_2$	6	180	3
S5	0.05	0.025	$C_2H_4O_2$	4	180	3
S6	0.05	0.025	$C_2H_4O_2$	10	180	3
S7	0.05	0.025	$C_2H_4O_2$	12	180	3
S8	0.05	0.025	$C_2H_4O_2$	14	180	3
S9	0.05	0.015	$C_2H_4O_2$	8	180	3

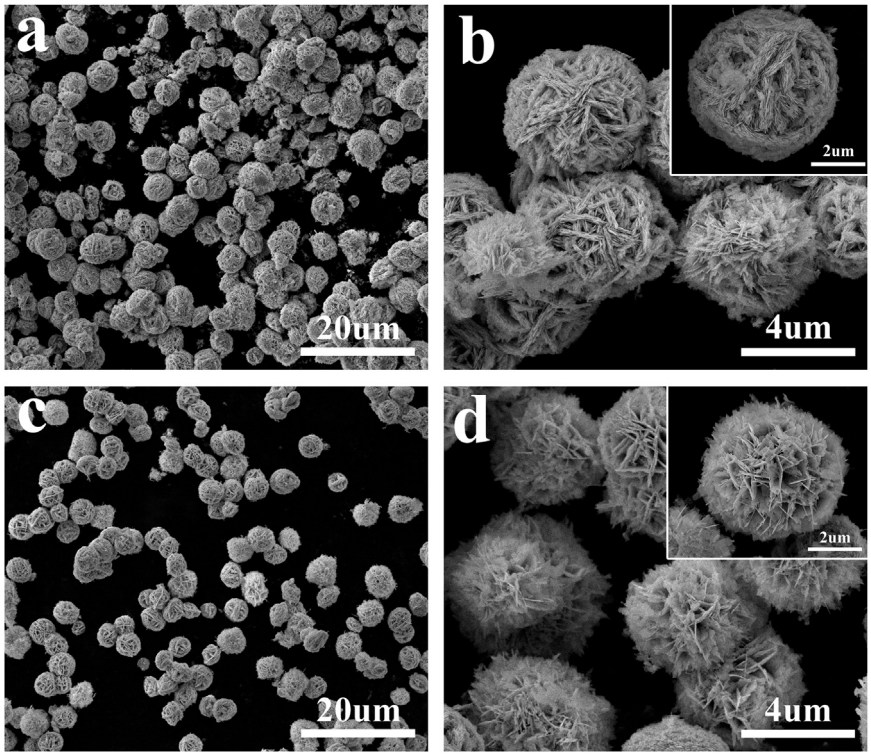

Fig. 1. SEM images of samples prepared with different acid at 160 °C for 24 h. (a, b) nitric acid, S1; (c, d) acetic acid, S2. The insets are the corresponding SEM images with high magnification.

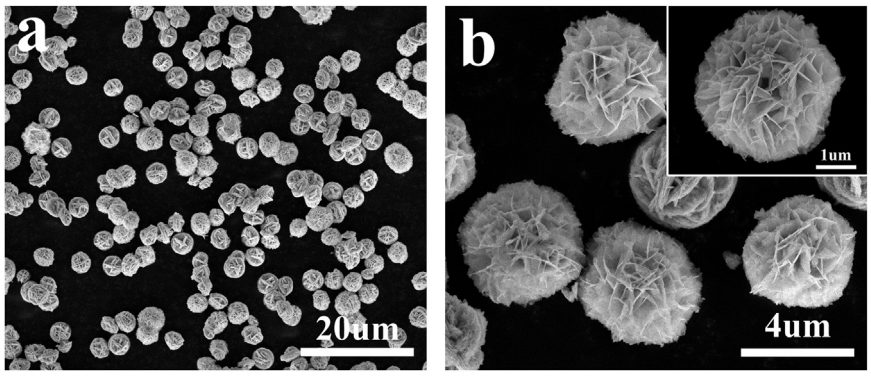

Fig. 2. SEM images of S3.

were of analytical grade and used directly without any further purification.

In the paper, Bi_2WO_6 samples were prepared by a simple hydrothermal reaction. In a typical procedure, 0.05 M of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved into the mixed solution (8 ml of acetic acid and 22 ml of DI water) and stirred for 10 min. Then 10 ml of 0.025 M of $Na_2WO_4{\cdot}2H_2O$ solution was added dropwise into the above mixture and stirred for 30 min. The as-obtained mixture solution (maintained at 40 ml) was transferred into a Teflon-lined autoclave with capacity of 80 ml and kept at 180 °C for 3 h. After the autoclave was cooled down to room temperature naturally, the resulting sample was collected by centrifugation and washed with DI water and ethanol. Subsequently, the