Catalysis Today xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Cu_2O NPs/$Bi_2O_2CO_3$ flower-like complex photocatalysts with enhanced visible light photocatalytic degradation of organic pollutants

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ARTICLE INFO

Article history:
Received 22 November 2016
Received in revised form 11 January 2017
Accepted 18 January 2017
Available online xxx

Keywords:
Interfacial self-assembly
$Cu_2O/Bi_2O_2CO_3$
Photocatalytic
Degradation

ABSTRACT

A facile and feasible interfacial self-assembly approach was developed to synthesize flower-like $Cu_2O/Bi_2O_2CO_3$ micro-composites. Degradation of methylene blue (MB) was used to evaluate the photocatalytic activity of composite under visible light. When compared to $Bi_2O_2CO_3$, the flower-like $Cu_2O/Bi_2O_2CO_3$ micro-composites show higher photocatalytic activity. Additionally, our results indicate that the photocatalytic activity of $Cu_2O/Bi_2O_2CO_3$ composites is dependent on Cu_2O loading. The highest photocatalytic performance of $Cu_2O/Bi_2O_2CO_3$ micro-composites is 94% after irradiation for 20 min, which is 3–5 times that of pure Cu_2O (calculated based on the equivalent Cu_2O content in $Cu_2O/Bi_2O_2CO_3$) and pure $Bi_2O_2CO_3$ respectively. Photocatalytic mechanism for the degradation of MB over $Cu_2O/Bi_2O_2CO_3$ was proposed based on the above. Our results provide an invaluable methodology for designing high visible-responsive photocatalysts based on Cu_2O/bismuth and related functional materials, which is promising for semiconductor composites and new energy applications.

1. Introduction

In recent years, various semiconductor photocatalytic oxidation technologies have been widely used in wastewater treatment due to their simple operation, mild reaction conditions, and lack of secondary pollutants [1–4]. Among these semiconductor photocatalysts, bismuth subcarbonate ($Bi_2O_2CO_3$) was found that it displays excellent photocatalytic performance in the degradation of organic pollutants [5–7]. $Bi_2O_2CO_3$ is typically found in a Sillen phase, in which $(Bi_2O_2)^{2+}$ and $(CO_3)^{2-}$ layers are intergrown such that the plane of the $(CO_3)^{2-}$ group is positioned orthogonal to the plane of the $(Bi_2O_2)^{2+}$ layers [8–10]. The use of $Bi_2O_2CO_3$ as a photocatalyst was first reported by Cheng et al. [11] It was used to degradated methyl orange (MO) in aqueous solution. The photocatalyst was also used in the degradation of dye wastewater [12,13]. However, $Bi_2O_2CO_3$ possesses a broadband gap and can only absorb Ultraviolet light (less than 5% of solar light), leading to restriction of its practical application for the solar light [14]. In order to solve this problem, combining $Bi_2O_2CO_3$ with narrow band gap semiconductors has been focused through an enormous amount of research effort to extend the absorption range.

As an important class of metal oxide semiconductor, cuprous oxide (Cu_2O) represents a *p*-type semiconductor with a narrow band gap of 2.0 eV [15,16]. Cu_2O has many advantageous characteristics including nontoxicity, low cost, and unique optical and electrical properties, all of which make the metal oxide a promising photocatalyst for the degradation of organic wastewater [17–19]. For example, Zhang et al. [20] loaded polyhedral Cu_2O particles on TiO_2 nanotube arrays through electrodeposition and found significant improvement in the visible-light activity as compared to pure Cu_2O. Lin et al. [21] reported Cu_2O/TiO_2 composite photocatalyst of Cu_2O nanoparticles deposited on TiO_2 and the visible light photocatalytic for degrading RhB was significantly enhanced due to broadened absorption in the visible light region and improved separation of photogenerated h^+-e^-.

In the present study, we first prepared a series of Cu_2O nanoparticle (NPs) modified flower-like $Bi_2O_2CO_3$ photocatalysts via a simple interfacial self-assembly technique. The photochemical performance of the resulting $Cu_2O/Bi_2O_2CO_3$ heterojunction composite was systematically explored under visible light radiation as a function of the amount of Cu_2O loaded on $Bi_2O_2CO_3$. The

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http://dx.doi.org/10.1016/j.cattod.2017.01.032
0920-5861/

as-synthesized samples were characterized by various methods including X-ray powder diffraction (XRD), scanning electron microscope (SEM), UV–vis diffuse reflection spectra (DRS), and others. The measurements revealed that $Cu_2O/Bi_2O_2CO_3$ exhibited a more effective photoconversion capability than $Bi_2O_2CO_3$ alone. High photocatalytic activity of $Cu_2O/Bi_2O_2CO_3$ composite was achieved with an appropriate loading of Cu_2O nanoparticles. The correlated mechanisms of photocatalytic degradation of Dye wastewater under simulated sunlight irradiation were examined. Different from other and numerous photocatalytic dye degradation studies, in this study, the flower-like $Cu_2O/Bi_2O_2CO_3$ photocatalysts possess large surface areas, plenty of *meso*-pores with ordered open pore frameworks, within which the flower-like photocatalysts can effectively harvest visible light due to multiple scattering [22]. Moreover, it is considered that the large surface areas and ultrathin thick nano-plate of the flower-like structure could decrease the recombination efficiency of the photo-excited electron-hole pairs and favour their transfer to the surface to react with organic pollutants [23]. It is widely believed that the coupling of Cu_2O with $Bi_2O_2CO_3$ to form a heterojunction is an effective way to enhance the photocatalytic performance, which would lead to a more efficient photoelectron-hole separation or expanding the spectral absorption range for degrading methylene blue (MB) under visible light.

2. Experimental

2.1. Photo-catalyst synthesis

A hydrothermal method was used to synthesize the flower-like $Bi_2O_2CO_3$ precursor. Using a typical course to prepare $Bi_2O_2CO_3$ flower-like precursor, 3 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 20 mL of 1 M HNO_3, 2 mmol of citric acid was added into the solution. After stirred for 10 min, the pH of the solution was controlled to 4-4.2 by NaOH solution. The white precursor that formed was transferred to a Teflon-lined stainless steel autoclave and maintained at 160 °C for 24 h. After cooling to room temperature, the flower-like $Bi_2O_2CO_3$ precursor was separated by centrifugation, and washed several times with distilled water and ethanol, and subsequently dried under vacuum at 80 °C for 8 h.

An interfacial self-assembly method was used to prepare $Cu_2O/Bi_2O_2CO_3$. 0.5 g of $Bi_2O_2CO_3$ powder and ethylenediaminetetraacetic acid (EDTA) were dissolved into deionized water at room temperature under vigorous magnetic stirring for 30 min. After dissolution, 0.0705 g $Cu(Ac)_2$ were then added into the solution and stirred for 30 min 20 mL of NaOH (0.45 mol/L) solution were then added dropwise into the solution resulting in the development of a blue colour, indicating the formation of $Cu(OH)_2$ nanoparticles. After 30 min, 20 mL of cetyltrimethylammonium bromide (CTAB) and ascorbic acid (AA) solution was added dropwise which then slowly turned to orange. The resulting sample containing $Cu_2O/Bi_2O_2CO_3$ was washed with distilled water and anhydrous ethanol to remove the surfactant. The samples were then dried at 80 °C for 8 h.

$Cu_2O/Bi_2O_2CO_3$ photocatalyst with different molar ratios of Cu_2O to $Bi_2O_2CO_3$ were prepared via a similar procedure as described above.

Pure Cu_2O was synthesized in a similar manner using an interfacial self-assembly method with $Cu(Ac)_2$, EDTA, NaOH, AA and CTAB.

2.2. Photo-catalyst characterization

X-ray diffractometry (XRD, Rigaku D/MAX2500 PC Cu Kα radiation, 40 kV, 100 mA) was used to determine the crystal structures and phase data for samples. The morphologies of the samples were investigated with scanning electron microscopy (SEM) (Hitachi, s-4800), energy dispersive X-ray spectroscopy (EDX), as well as by transmission electron microscopy (TEM) (JEOL Ltd., JEM-2010). UV–vis light (UV-vis) diffuse reflectance spectra were recorded on a UV–vis spectrometer (Puxi, UV1901). The photoluminescence of the powdered samples was measured by a spectrofluorometer (Hitachi, f7000). A constructed three electrode quartz cell system was used to perform the electrochemical and photo-electrochemical measurements. The photo-electrochemical experimental results were recorded via a CHI 660 B electrochemical system.

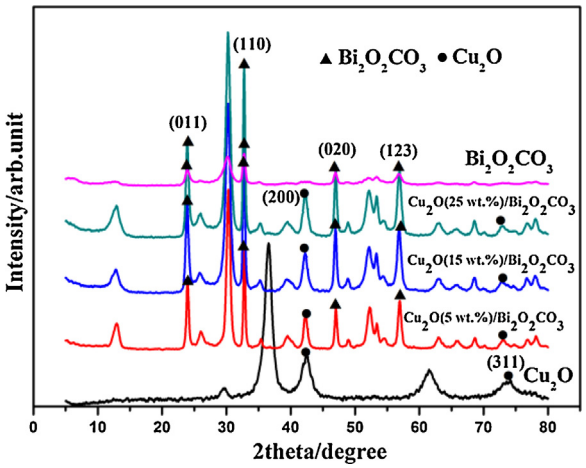

Fig. 1. XRD patterns of the prepared photocatalyst.

2.3. Photocatalytic activity

Photocatalytic activities of $Cu_2O/Bi_2O_2CO_3$ samples were evaluated by the degradation of methylene blue (MB) under the irradiation of a 250 W halide lamp (Philips). The halide lamp with a 420 nm cutoff filter was used at a distance of 10 cm from the top of an unsealed beaker. A glass reactor was employed with circulating water flowing outside to control the temperature to 25 ± 2 °C. For each test, 0.5 g catalyst powder was added to 100 mL 10 mg/L MB solution. Prior to irradiation, the test solution was stirred in the dark for 30 min to ensure adsorption-desorption equilibrium. During irradiation, a 3 mL reaction solution was withdrawn every 3 min and then centrifuged at 10,000 rpm for 6 min to remove the particles. The collected solutions concentration was analyzed by a UV–vis spectrophotometer.

The degradation efficiency (%) was calculated as follows [24,25]:

$$Degradation(\%) = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

Where C_0 is the initial concentration of MB, and C is the concentration of MB at time t.

Control experiments for MB photocatalytic degradation were also performed both in the dark in the presence of the photocatalyst and under visible-light irradiation in the absence of the photo-catalyst [26].

3. Result and discussion

3.1. Catalyst characterization

The crystalline structures of the as-prepared samples were examined by X-ray diffraction (XRD). Fig. 1 shows the typical XRD patterns of Cu_2O, $Bi_2O_2CO_3$ and $Cu_2O/Bi_2O_2CO_3$ composites with

Please cite this article in press as: S. Lin, et al., Cu_2O NPs/$Bi_2O_2CO_3$ flower-like complex photocatalysts with enhanced visible light photocatalytic degradation of organic pollutants, Catal. Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.01.032