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Multi-layer three-dimensionally ordered Bismuth trioxide/Titanium dioxide nanocomposite: Synthesis and enhanced photocatalytic activity

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ABSTRACT

Taking polystyrene latex spheres (PS) and $EO_{20}PO_{70}EO_{20}$ (P123) as dual templates, and TiO_2 was used as substrate, a series of multi-layer three dimensionally ordered macroporous (3DOM) composites Bi_2O_3/TiO_2 were successfully synthesized with sol–gel method and post-processing calcination. The fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), UV–vis diffuse reflectance (UV–vis/DRS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM) and nitrogen adsorption–desorption measurements were employed to analyze the crystalline phase, chemical composition, morphology, and surface physicochemical properties of as-synthetized samples. The results showed that as-composites were provided with obvious crystalline phase structure and periodically highly uniform ordered macroporous structure with mesoporous walls; moreover, of which was multi-layer three dimensionally ordered structure. As a result of unique optical properties of Bi_2O_3 and composite material structural characteristic being propitious to reactant molecular transmission and diffusion, the photocatalytic activities of 3DOM Bi_2O_3/TiO_2 were enhanced, and the sample 3DOM Bi_2O_3/TiO_2-2 was significantly higher than that of direct photolysis, P25, Bi_2O_3, and other 3DOM Bi_2O_3/TiO_2-*X* (*X* = 1, 3, 4) during the photocatalytic degradation of crystal violet under multi-modes such as UV, visible light, simulated solar light, and microwave-assisted irradiation. The centrifugal samples water solution phase of TOC analysis indicated that water solution products formed with continued ultraviolet radiation, the intermediates eventually mineralized, volatilized, or were converted to other products. In addition, the photocatalytic activity of 3DOM Bi_2O_3/TiO_2-2 composite was basically kept even after three cycles. Meanwhile, the possible photocatalytic reaction mechanism of as-synthesized material based on the experimental results was proposed.

1. Introduction

In recent years, the semiconductor photocatalyst technology shows potential application value owing to that is applied to environmental cleaning, solar energy conversion and H-energy production [1–5]. Almost all difficult to degrade organic pollutants have been ultimately completely mineralized into CO_2 and H_2O under the action of semiconductor photocatalyst with light especially in the field of degradation of organic pollutants. At present, the semiconductor photocatalyst has been wide application such as anatase TiO_2 and wurtzite ZnO. Although these kinds of semiconductor photocatalyst are cheap, non-toxic and high activity, they can only be excited under ultraviolet light, limiting their application at the same time [6–10]. Thus, a variety of approaches have been explored to develop the visible light photocatalytic materials for the sake of absorbing maximum solar to photocatalytic degradation, including phase/morphological control, ion doping, surface sensitization, noble metal loading, and heterostructure constructing. Among them, one of the most effective methods is that using narrow band gap semiconductor compounds with visible light catalyst material. Bi_2O_3 is an important non-poisonous narrow band gap photosensitizer with a direct band gap of 2.1–2.8 eV, and the high oxidation ability of electron holes of Bi_2O_3 is regarded as an important condition for a kind of good photocatalytic materials.

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However, too many opportunities for the recombination of photoformed electrons and holes owing to the narrow band gap of Bi_2O_3 semiconductors and then application is limited [11–14]. Accordingly, catalyst is prepared by the TiO_2 compounds with Bi_2O_3, exploiting the synergy to improve the utilization rate of catalyst for the light, so then to solve the aporia of Bi_2O_3 electron holes easily recombination have been deserves special attention [15,16].

Furthermore, to further improve the photocatalytic activity by controlling morphological has been turned into the focus of studies in recent years, and more investigators have paid attention to the synthesis of three-dimensionally ordered macroporous (3DOM) structure [17–24]. This is mainly that taking PS colloidal crystal template method to complete in the paper. 3DOM materials are synthesized by the following steps: (i) a colloidal crystal template is synthesized by ordering monodisperse PS into a face-centered, close-packed array (opal structure), (ii) interspace of the colloidal crystal is then filled with the precursor of the destination product, either neat or in solution, that solidify in voids of the sphere templates, and (iii) the orderly structure is produced after removing template by calcination method. The macropores are interconnected through windows that form as a result of contact between the template spheres prior to the infiltration of precursor solution [25]. Due to the formation of three-dimensional macroporous materials caused by the precursor which is from transition process of liquid to solid, therefore, the level of order degree of the PS template and the physicochemical properties, dynamic viscosity, fluidity and operating conditions of precursor play very important roles in the preparation of three dimensionally ordered macroporous material.

In view of the above, our research group has developed a series of 3DOM macroporous composite in several years. These 3DOM composites mainly used the monodisperse PS sphere which was synthesized by emulsifier-free emulsion polymerization technique as large-hole template. Although the large pore structure characteristics of composites are obvious, and the photocatalytic properties of composites have been improved, the holes on the distribution of the 3DOM composites hole-wall are more general. In this study, a series of multi-layer 3DOM Bi_2O_3/TiO_2-*X* (*X* = 1, 2, 3 and 4) composite materials with different Bi/Ti molar ratios have been synthesized using $EO_{20}PO_{70}EO_{20}$ (P123) as surface active agent via sol–gel method and post-processing calcination at the intrinsic experiment. The purposes of this experimental study are following: on the one hand, the P123 is a kind of common triblock copolymer surface active agent with hydrophilic poly (ethylene oxide) and hydrophobic poly (propylene oxide), which could be formed a containing soluble and insoluble core corona micelles and be able to dispersed precursor solution, and then the precursor solution soak into space of the PS template; on the other hand, under the effect of the template agents of PS spheres and P123, the structure of as-formed 3DOM would be more regular and compact, and the uniform mesoporous wall is beneficial to input and output of the reactant molecules, so that the photocatalytic activities of the composite will be enhanced. In this study, the degradation effect of the as-synthesized 3DOM Bi_2O_3/TiO_2-*X* composite on crystal violet (CV) selected as the model molecule has been investigated, under multiple modes including UV, visible light, microwave-assisted, and simulated solar light irradiation, respectively. The results revealed that the degradation effect of the 3DOM Bi_2O_3/TiO_2-2 composite is higher than that of the other systematic photocatalysts. Moreover, the photocatalytic performance of the 3DOM Bi_2O_3/TiO_2-2 composite for various organic pollutants and its catalytic cyclic process (recyclability of the photocatalyst) has been carried out under UV irradiation. In addition, based on the results of capture experiment, the possible photocatalytic reaction mechanism of 3DOM Bi_2O_3/TiO_2-*X* composite has been speculated.

2. Experimental

2.1. Materials

Titanium isopropoxide (TTIP, 98%) and the triblock poly (ethylene oxide)-block-poly (propylene oxide)-block-poly (ethylene oxide) copolymer (P123) ($EO_{20}PO_{70}EO_{20}$, Mw = 5800) were purchased from Energy Chemical Company. Styrene (St), potassium persulfate ($K_2S_2O_8$), bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), Degussa P25, *p*-benzoquinone (BQ), tert-butyl alcohol (TBA), crystal violet (CV), methyl orange (MO), xylenol orange (XO), and salicylic acid (SA) were purchased from Guangfu testmart, China. All other reagents were analytical grade and used without further purification. Water used in all experiments was deionized.

2.2. Synthesis of polystyrene microsphere template

The synthesis of monodisperse PS microsphere was performed by according to a slightly modified reported procedure [26,27]. Briefly, during a typical experiment, phenylethylene (0.235 mol), $K_2S_2O_8$ (0.33 mmol), and deionized water (240 mL) were taken into a clean three necked bottle equipped with a mechanical stirrer, thermometer with a temperature controller, bubbled with nitrogen, stirred slowly and then placed in a water bath kept at 70 °C for 7 h and nitrogen was also imported continuously for 7 h, $K_2S_2O_8$ was as initiator. The resultant dispersion solution was separated by centrifugation at 1000 rpm for 24 h, and then dried under room temperature.

2.3. Synthesis of 3DOM Bi_2O_3/TiO_2-X

The sample 3DOM Bi_2O_3/TiO_2-*X* was prepared by sol–gel method using PS and P123 as dual templates. In a typical synthesis, TTIP was dispersed in a mixture of ethanol and isopropanol ($n_{ethanol}$:$n_{isopropanol}$ = 4:1) containing P123 (marked as solution A). After stirring for 30 min, Bismuth nitrate solution was added into solution A and then the as-obtained solution was marked as solution B ($n_{Bi(NO3)3{\cdot}5H2O}$:n_{TTIP} = 0.015:1; 0.03:1; 0.06:1 and 0.09:1). Subsequently, the mixed solution was infiltrated into the colloidal crystal template of PS and the sample was obtained by filtration. The obtained sample was dried at 60 °C and calcined in a muffle furnace at 600 °C for 7 h (marked as 3DOM Bi_2O_3/TiO_2-*X*, *X* = 1, 2, 3, and 4).

2.4. Photocatalytic degradation of CV

The 3DOM Bi_2O_3/TiO_2-*X* composite materials' photocatalytic activities were evaluated by photocatalytic degradation of crystal violet dye under multi-modes including UV, visible light, microwave-assisted, and simulated solar light irradiation. A 125 W high pressure mercury lamp (λ = 313.2 nm) was used as UV irradiation source. A 400 W xenon lamp ($\lambda \geqslant 420$ nm) was used as visible source. The microwave discharge electrodeless lamp (MDEL, UV emission wavelength mainly located at 280 nm) had the power of 15 W which was taken as microwave-assisted irradiation light source and the output power of microwave reaction was 600 W. A photochemical reaction instrument equipped with a 1000 W xenon lamp (Shanghai bilon Instruments Co., Ltd.; O_3 could be not produced during the photocatalytic reaction process.) was used for simulated solar light irradiation displaying strong consecutive spectra from UV to near IR region.

CV was used as a model dye. Moreover, the reaction liquid volumes of four modes were 90, 220, 90, and 500 mL, and the dosage of the catalysts was 0.15, 0.30, 0.15, and 0.50 g, respectively.