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In situ construction, photocatalytic performance, and mechanism speculation of plasmonic binary Bi/β-Bi_2O_3 hybrids

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ABSTRACT

A facile synthetic route was adopted in this study to construct plasmonic binary Bi/β-Bi_2O_3 hybrids through a solvothermal-incomplete calcination process. As-synthesized samples were systematically characterized by X-ray diffraction patterns, X-ray photoelectron spectroscopy, UV–Vis diffuse reflectance spectroscopy, scanning electron microscopy, transmission electron microscopy, and N_2 adsorption-desorption. The calcination temperature exerted an important effect on the surface phase composition variation and binary Bi/β-Bi_2O_3 hybrids were formed at the suitable temperature with an intimate contact between both components. These hybrids showed enhanced photocatalytic degradation efficiencies over dyes Rhodamine B and methyl orange, mainly attributing to the enlarged specific surface areas, favorable morphology and optical property, and the involvement of semimetal Bi with the surface plasmon resonance effect by means of improved visible-light absorption and efficient charge carries separation. In addition, active species entrapping experiments was eventually conducted for the sake of the possible photocatalysis mechanism speculation.

1. Introduction

Because of satisfactory photocatalytic capabilities of bismuth (Bi)-based metal oxides such as Bi_2O_3 [1], $CaBi_2O_4$ [2], Bi_2MoO_6 [3], $BiVO_4$ [4], Bi_2WO_6 [5], Bi_3NbO_7 [6], $Bi_{12}TiO_{20}$ [7], $Bi_2Fe_4O_9$ [8], $NaBiO_3$ [9], and $Bi_4Ti_3O_{12}$ [10] under the visible-light illumination resulted from the well-dispersed valence bands by the hybridization of Bi 6 s and O 2p orbitals [11], research studies regarding these semiconductors attract numerous attentions. Among abovementioned candidates, Bi_2O_3 is the structurally simplest and extensively researched one, gaining widespread concerns due to the unique physiochemical properties such as the suitable band structure, nontoxicity, sufficient stability, and commercial availability at a low cost [12]. In addition, it was reported that β-Bi_2O_3 possessed better photocatalytic performance than other crystallographic polymorphs counterparts for the decomposition of organic pollutants in the visible-light region [13]. Therefore, a great number of research investigations have been reported by adopting β-Bi_2O_3 as a photocatalyst [14].

To achieve enhanced photocatalytic capabilities and extended light-response range, the single-phased semiconductors generally need to hybrid with other semiconductors or elements to modify electronic structures for the sake of boosting catalytic outcome by means of efficient separation of photoinduced charge carriers. Some elemental noble metals (Au, Ag, Pt, and Pd) of the surface plasmon resonance (SPR) effect are favorable candidates to meet above requirements, which attract tremendous interests in academic communities. The SPR effect, generated by the resonant photon-generated free electrons collective vibration, makes these noble metals as excellent cocatalysts and significantly contributes to the photocatalytic performance [15–18]. Bismuth, as a typical semimetal, possesses unique features, like the small effective mass, the large mean free path, the nano-confinement effect, and the SPR effect. Recently, Dong reported the photocatalytic performance toward the removal of NO under UV-light in a “memory” manner and relevant mechanism of semi-metallic Bi nanostructures by using the SPR effect [19]. Then numerous references using semi-metallic Bi as catalysts or cocatalysts emerged in the photocatalysis field. Generally, the incorporation of elemental Bi onto semiconductors surface was accomplished by an in-situ reduction with appropriate reagents under suitable conditions.

In the current investigation, a facile and simple solvothermal-incomplete calcination procedure was adopted to in situ fabricate a series of plasmonic binary Bi/β-Bi_2O_3 hybrids in absence of any additive reagents. The surface phase composition could be tuned by the variation of calcination temperatures. These binary hybrids were characterized

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by a collection of analytic techniques and hierarchical lamellar microstructure containing heterojunction domains ensured enhanced photocatalytic capabilities over the degradation of dyes RhB and MO under visible-light illumination, revealing the crucial role of semimetal Bi with SPR effect on both the enhanced visible light adsorption and the efficient photoinduced charge carriers separation and transfer. Basing upon active radicals trapping experiments, a primary photocatalysis mechanism was eventually speculated.

2. Materials and methods

2.1. Reagents

Those reagents such as bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), triethanolamine (TEA), isopropanol alcohol (IPA), vitamin C (VC), and ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd. Both methyl orange (MO) and rhodamine B (RhB) were supplied by Shanghai SSS Reagent CO., Ltd and Shanghai Mstar Technology Ltd., respectively. All chemical regents abovementioned were of analytic grade and without further purifications prior to use.

2.2. Construction of metallic Bi and plasmonic binary Bi/β-Bi_2O_3 hybrids

The metallic Bi was prepared according to a previous reference with a minor revision [20]. Typically, a mixture of 4.366 g $Bi(NO_3)_3{\cdot}5H_2O$ and 70 mL ethylene glycol was magically stirred for 1 h to make a clear solution. The resultant solution was then poured into a 100 mL stainless-steel Teflon-lined autoclave for a solvothermal reduction process at 160 °C for 15 h. After naturally cooling down, the suspension was filtered, washed with water and ethanol for three times, and dried at 60 °C for 12 h in a vacuum drying oven to give a black solid metallic Bi.

The obtained metallic Bi was charged into a muffle furnace and then calcined at different temperatures for 1 h to produce a series of binary Bi/β-Bi_2O_3 composites with various contents of elemental Bi. These Bi/β-Bi_2O_3 composites were labeled as Bi-T and T was set as 180 °C, 210 °C, 230 °C, 250 °C, and 270 °C. N-TiO_2 was synthesized through a sol-gel method basing on a previous report [21].

2.3. Characterization

X-ray diffraction patterns (XRD) were recorded on a Bruker D8 Advance X-ray diffractometer using a Cu Kα radiation source (λ = 1.5418 Å) operated at 40 kV and 40 mA to check the phase, crystallinity, and purity of as-synthesized samples. The microstructures and morphology were characterized by a scanning electron microscope (SEM, QUANTA F250) and transmission electron microscope (TEM, Tecnai G2 F20) with an acceleration voltage of 200 kV. The surface chemical composition and valence states were measured on an X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi, USA) combined with an argon ion etching technique, with a monochromator of Al Kα radiation source ($h\nu$ = 1486.6 eV). UV–Vis diffuse reflectance spectra were measured on a Shimadzu/UV2600 UV–Vis spectrophotometer with the pure $BaSO_4$ as a reference. N_2 adsorption-desorption isotherms and specific surface areas of samples were measured on a Micromeritics ASAP2020HD88 apparatus at 77 K and all samples were degassed at 120 °C for 2 h before exposing to measurements. The photocurrent spectroscopy was recorded on an electrochemical workstation (CHI 660E, Chenhua Instrument Company, Shanghai) with and 0.1 M Na_2SO_4 aqueous solution as an electrolyte. The Pt wire, saturated calomel electrode, and samples coated on a copper sheet were adopted as the counter electrode, reference electrode, and working electrode, respectively.

2.4. Photocatalytic capability measurement

Photocatalytic performance of as-synthesized samples was estimated via degrading dye RhB and MO in aqueous solutions. A xenon lamp (300 W, CEL-HXF300, AuLight, Beijing) was employed as an irradiation source and a cut-off filter was equipped to guarantee an incident visible light ranging from 400 to 780 nm. The light was 20 cm apart from the surface of reaction suspension and the light intensity on the surface of reaction was tested as 96.7 mw cm^{-2} by a light optical power meter (CEL-NP2000). 80 mg of as-prepared catalyst was added into an RhB (20 mg L^{-1}, 80 mL) or MO (10 mg L^{-1}, 80 mL) aqueous solution to make a suspension that was continuously stirred in dark for 60 min to reach an adsorption-desorption equilibrium before confronting to the visible-light illumination. During reaction processes, at every 30 min interval 3 mL aliquot was withdrawn from the suspension and centrifuged for 5 min (10,000 rpm) twice to detach catalytic particles. The residue concentrations of RhB and MO aqueous solutions were analyzed by a Purkinje General T6 UV–vis spectrophotometer at 554 nm and 463 nm, respectively.

3. Results and discussion

3.1. XRD patterns and XPS analyses

Fig. 1 exhibits the XRD patterns of all as-synthesized calcined and uncalcined Bi-based samples. Obviously, the calcination temperature exerts a significant effect on the surface phase composition of samples. Diffraction peaks of both samples uncalcined and calcined at 180 °C are in good accordance with the PDF card #85-1329, confirming the presence of rhombohedral phase of metallic Bi [20]. No other peaks was found corresponding to impurities such as bismuth oxide nitrate hydroxide hydrate or other substances. It is generally realized that external semimetal Bi is quite easily to be oxidized to form an amorphous β-Bi_2O_3 thin film with several nanometers coated on surface owning to the oxidizable nature and low melting point of 271.3 °C [22,23]. The resultant amorphous β-Bi_2O_3 thin film cannot show any peaks in XRD patterns but is able to be detected by HRTEM in Fig. S1 with a thickness not exceeding 5 nm. With the raise of calcination temperature up to 210 °C, the formation of another crystalline phase β-Bi_2O_3 occurs, proven by the good agreement of corresponding peaks to the PDF card #78-1793 [20]. The continue increase of calcination temperature induces the complete conversion of external elemental Bi to crystalline β-Bi_2O_3 and a single phase of β-Bi_2O_3 on surface is finally observed in sample calcined at 270 °C. The weight content of each component in a binary-phase composite can be estimated by a relative intensity ratio (RIR) detection method using two formulas as below [24]:

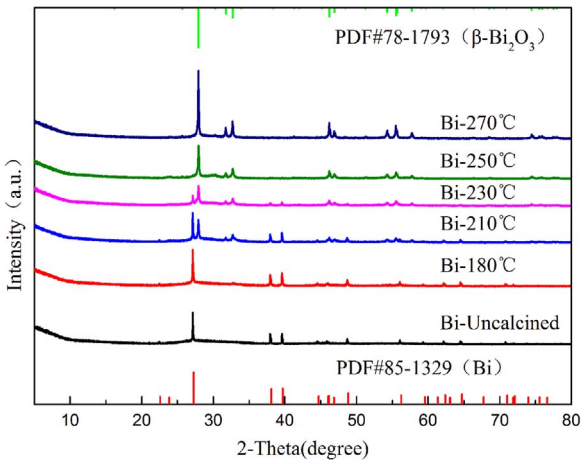

Fig. 1. XRD patterns of calcined and uncalcined Bi-based samples.