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Design and synthesis of multistructured three-dimensionally ordered macroporous composite bismuth oxide/zirconia: Photocatalytic degradation and hydrogen production

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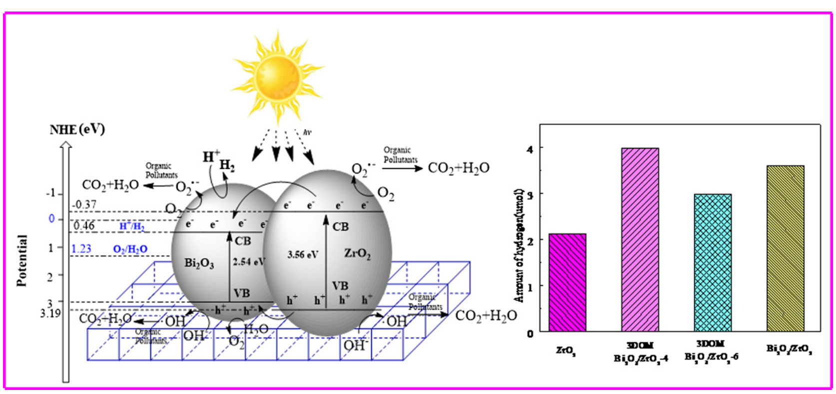
GRAPHICAL ABSTRACT

Using polystyrene spheres (PS) microspheres and $EO_{20}PO_{70}EO_{20}$ (P123) as templates, 3DOM Bi_2O_3/ZrO_2 composites owned a tetragonal "fishing net" or a hexagonal "honeycomb" structure were synthesized by the sol-gel combined with the decompression filling method, in which 3DOM Bi_2O_3/ZrO_2 with tetragonal "fishing net" structure exhibited well photocatalytic degradation and enhanced activity in splitting water into hydrogen than that of 3DOM Bi_2O_3/ZrO_2 showing hexagonal "honeycomb" one.



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ABSTRACT

Two types of three-dimensionally ordered macroporous (3DOM) Bi_2O_3/ZrO_2 composites were prepared by the sol–gel method combined with the decompression filling method using polystyrene (PS) microspheres and $EO_{20}PO_{70}EO_{20}$ (P123) as the templates. The crystal structure, morphology, and surface physicochemical properties of Bi_2O_3/ZrO_2 composites were well characterized by X-ray diffraction, UV–visible diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, high-resolution transmission electron microscopy, and N_2 adsorption–desorption measurements. The results show that 3DOM Bi_2O_3/ZrO_2 composites possessed mixed crystal phases including the monoclinic bismuth oxide and mixed zirconia phases, and moreover exhibited a regular arrangement and pure tetragonal (or hexagonal) macroporous structure. Moreover, compared to Bi_2O_3/ZrO_2, the specific surface areas of 3DOM Bi_2O_3/ZrO_2 composites were ca. 2.7–2.8 times. In addition, the properties of 3DOM Bi_2O_3/ZrO_2

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composites with the tetragonal "fishing net" and hexagonal "honeycomb" structure were compared, and the relationship between the structure and activity of 3DOM Bi_2O_3/ZrO_2 composites was determined. The results show that in the UV photocatalytic degradation of pollutants and splitting of water into hydrogen using 3DOM Bi_2O_3/ZrO_2 composite, the tetragonal "fishing net" structure exhibited better activity than the hexagonal "honeycomb" structure. This can be attributed to different photocatalytic properties of the composites with different structures (tetragonal "fishing net" and hexagonal "honeycomb" structures).

1. Introduction

In recent years, environmental pollution and energy shortages have stimulated much effort in developing more effective visible-light-driven photocatalysts [1–4]. Production of hydrogen as the secondary energy from water has many advantages such as high efficiency, cleanliness, storage capacity, transportability, and safety. This is considered as one of the most ideal green energy.

Hydrogen production by solar photoelectrochemical decomposition of water is an important way to solve human energy and environmental problems from a long-term perspective. Therefore, currently solar-energy-driven water splitting to provide hydrogen energy has attracted much interest. As an efficient technology for dealing with environment pollution, photocatalysis is widely used because of its high efficiency and environmentally friendly and catalytically generated products without pollution [5]. Moreover, studies on nanocomposite photocatalysts have also attracted much interest [6,7]. ZrO_2 is a transition-metal oxide with a broad band gap and excellent mechanical, chemical, electrical, and physical characteristics. As a semiconductor photocatalyst, ZrO_2 has both redox and acid/base properties; when ZrO_2 has a nanometer size, special morphology, and channel structure, it has a large specific surface area, rich surface oxygen vacancy, and strong ion exchange capacity.

Zirconia is used as a photocatalyst because of its unique properties including a p-type semiconductor structure and acid/base amphoteric and redox properties [8–12]. Bismuth-containing photocatalytic materials are one of the non-TiO_2 semiconducting photocatalytic materials with unique electronic structure, and its valence band is formed by the hybridization of Bi-6s and O-2p orbitals [13]. This unique structure provides a more steep absorption edge within the visible range, and the antibonding between anions and cations is more conducive to the formation and flow of electron holes. Thus, photocatalytic reactions can be easily carried out. Bismuth has a very broad application prospect as a photocatalytic material owing to its visible-light absorption ability and high catalytic activity [14].

Three-dimensionally ordered macroporous (3DOM) materials have the characteristics of a strong periodic arrangement of pore structure, uniform large pore size, and narrow pore size distribution, resulting in a good application potential in many aspects such as catalysis or macromolecular catalysis, catalyst carrier, electrode material, virus isolation and refinement, secondary templates, photosensitive materials, and other aspects [15–17]. 3DOM materials not only can enhance substance diffusion and mass-transfer efficiency during the reaction, but also have important significance and application due to controllable and adjustable pore size and pore wall. Li et al. [18] prepared a 3DOM material, 3DOM Gd/TiO_2, using the colloidal crystal template (CCT) method, and 3DOM Gd/TiO_2 showed excellent photocatalytic properties for the degradation of methyl orange under UV and visible light compared to pure 3DOM TiO_2 and P25. Jiao et al. [19] synthesized 3DOM TiO_2 using the CCT method and tetrabutyl titanate as the precursor solution, and 3DOM TiO_2-supported CeO_2 nanolayers with different weight ratios of CeO_2 to TiO_2 were successfully prepared by the gas bubbling-assisted membrane precipitation (GBMP) method. The 3DOM CeO_2/TiO_2 photocatalysts exhibited a high catalytic activity in the photocatalytic reduction of CO_2 with H_2O under simulated solar irradiation.

By preparing 3DOM composites, the inherent physical properties and structure of 3DOM materials can be combined with the unique chemical properties of composites to obtain new composites with a novel structure, high specific surface area, high chemical sensitivity, chemical activity, and regular network pore structure [20–23]. Previous studies on 3DOM materials from our group showed that 3DOM materials exhibit excellent performances [16,17,24]. In this study, 3DOM Bi_2O_3/ZrO_2 composites were prepared by combining the 3DOM structure with composite materials, thus utilizing the strong light absorptivity of Bi_2O_3 in the visible region to establish the synergetic effect of photocatalytic degradation and photocatalysis of water between Bi_2O_3 and ZrO_2. On this basis, 3DOM Bi_2O_3/ZrO_2 composites with different morphologies, namely, tetragonal "fishing net" and hexagonal "honeycomb", were also designed.

Previous studies in our group mainly focused on a series of composites synthesized using polystyrene (PS) microspheres arranged in the form of hexagon as the template. In these studies, the arrangement of template and activities of composite correlated; therefore, the photocatalytic activities of two different composites in water splitting were compared to systematically study the effect of template morphology on the 3DOM samples to prepare a series of desired photocatalysts to solve the energy and environmental problem. In this paper, the 3DOM Bi_2O_3/ZrO_2 composite with a tetragonal "fishing net" structure exhibited a higher photocatalytic activity in UV light, visible light, and simulated solar photocatalytic degradation; moreover, the composite had a certain ability to produce H_2 from water.

2. Experimental section

2.1. Reagents

Zirconium *n*-butoxide ($C_{16}H_{36}O_4Zr_2$) was purchased from Shenzhen Meryer; $EO_{20}PO_{70}EO_{20}$ (P123) was purchased from Sigma-Aldrich Company, USA; bismuth nitrate pentahydrate ($Bi(NO_3)_3\cdot 5H_2O$), NaOH, anhydrous ethanol, and potassium persulfate ($K_2S_2O_8$) were purchased in Tianjin Kai Chemicals Co., Ltd.; isopropanol was purchased from Tianjin Chemical Reagent factory; commercial photocatalyst (Degussa P25) was purchased from Aldrich, USA; styrene was purchased in Tianjin City Guangfu Chemical Research Institute; crystal violet (CV), malachite green (MG), congo red (CR), methylene blue (MB), salicylic acid (SA) were purchased from Beijing Chemical Plant, all experimental water was distilled.

2.2. Preparation of 3DOM Bi_2O_3/ZrO_2 composite

Monodispersed and tightly packed PS microspheres were synthesized by emulsification-free polymerization [25–27], and two