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Article

Heterostructure TiO_2 polymorphs design and structure adjustment for photocatalysis

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ABSTRACT

Atomic composite-structure materials play an important role in energy generation and storage application fields for their advanced performance. Constructing heterostructured semiconductors is a promising strategy to devise photocatalytic systems with high activity. However, most studied hererostructures are those semiconductors with different materials formed by multi-steps, researches on in-situ formed hererostructure originated from the same precursor are few reported, and the effects of different structure ratios on photocatalytic performance are ambiguous. Here, according to in-situ temperature X-ray diffraction and transmission electron microscope techniques, a nano-sized in-situ formed heterostructure of TiO_2 semiconductors with anatase and TiO_2-B crystalline structures were designed, their structure ratios were adjusted, the heterostructure interface and photocatalytic reaction mechanism were also detected. Results show that high-quality heterojunction and optimum structure ratios have vital influence on photocatalytic performance, there is an obvious synergetic effect between anatase and TiO_2-B structure, degradation reactions on methyl orange (MO) under ultraviolet light irradiation prove that the highest activity toward MO removal can be obtained for material with 82.5% anatase structure.

1. Introduction

As a renewable energy source, solar energy is an alternative option for paying more attention to energy and environment issues. Using solar energy to generate photocatalytic reactions such as water splitting, CO_2 reduction, and organic pollutant degradation have been widely investigated. As a conventionally photocatalytic material, TiO_2 has gotten intensive studies since 1972 [1]. Its physical and chemical properties have been summarized in many excellent reviews including surface structure analysis [2], dimensional control [3–5], synthesis methods [6], photocatalytic mechanism [7], applications and so on [8–12]. There are four common polymorphs of TiO_2 including anatase, rutile, brookite and TiO_2-B. Usually, nano-sized anatase is easy to obtain, especially with a diameter less than 14 nm, while rutile presenting in bulk are considered as a thermodynamically stable form. Brookite and TiO_2-B are both metastable phases, which are less used for photocatalytic reactions compared to anatase and rutile. Besides, these two metastable polymorphs are not easy to prepare, especially in pure phase [13,14]. All these polymorphs are made up by TiO_6 octahedral units and connected in different ways, resulting in different morphology and surface chemistry. Among these polymorphs, anatase usually exhibits the highest photocatalytic activity [15], while rutile is more active toward water splitting with certain particle size. TiO_2-B could be obtained by heating layered hydrate titanate [16]. Its application on electrochemical and photocatalytic reactions has also been investigated [17–22].

However, two major flaws of TiO_2 limit it from wide application. One is the wide band gap, which confines the absorption threshold below 400 nm, indicating only 4% of solar light can be used. The other is the fast recombination of photo-generated charges (in femtosecond), resulting in low photocatalytic efficiency. Solutions for the above matters include doping [23,24], sensitization [25,26], heterostructure design and so on. Heterostructured photocatalyst built up from two or more different semiconductors is one of the effective modification methods to improve the photocatalytic activities. There are mainly five typical types based on the band alignment models [27]. By suitable band gap construction and intimate contact, effective electron-hole pair separation can be expected.

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Previous works show that multiple steps are often required to devise heterostructured photocatalysts. For example, type-II TiO_2/$SrTiO_3$ heterostructured thin film for water splitting is prepared through two-step hydrothermal treatments [28]. Z-scheme of CdS-Au-TiO_2 can be synthesized by consecutive calcination and ultraviolet (UV) light irradiation [29]. Besides, heterostructures formed by different polymorphs of TiO_2 are less studied and few concentrate on anatase and rutile structures. For example, heterogeneous anatase and rutile composite can be prepared by depositing rutile on tubular anatase surface [30]. Using TT-2 TiO_2 as precursor, anatase and rutile heterostructure can be synthesized by calcination [31]. In addition, few groups have considered the synergetic effect of different structures and structure ratios on photocatalytic performance.

In this study, a novel simultaneous formation of heterostructure composing anatase and TiO_2-B was designed. A wide range of structure ratios were adjusted by facile calcination process and their structure ratio was identified carefully by Rietveld refinement method. The corresponding photocatalytic efficiency was measured by degradation reactions. Furthermore, the synergetic effects of two crystalline structures with adjusted structure ratios were investigated in detail.

2. Experimental

2.1. Sample preparation

2.1.1. Synthesis of hydrate titanate (HTO)

In a typical process, P25 (Degussa, 1 g) was dispersed into NaOH solution (40 mL, 10 mol/L), which was sonicated and stirred for 30 min, respectively. The mixed solution was transferred into a 50 mL Teflon-lined autoclave and held at 180 °C for 18 h, then cooled down to room temperature. In order to get HTO, firstly the product was filtered by ultrapure water three times, and then mixed with HCl (0.1 mol/L) and stirred for 24 h to exchange Na^+ ions by H^+. The hydrate titanate was filtered and dried at 60 °C, which is named as HTO.

2.1.2. Synthesis of mixed phase of anatase and TiO_2-B

The ratios were controlled by variant calcination temperature, in a typical process, HTO (0.1 g) was placed into a crucible and heated to 680 °C for 1 h in air with a heating rate of 5 °C/min, other ratios were obtained at 620, 640, 660, 700, 720 °C.

2.2. Characterization

Rietveld X-ray diffraction (XRD) patterns were determined by Bruker D8 Advance operating at 40 kV/40 mA with a Cu Kα1 radiation (λ = 0.1541 nm, 1.4 s/step), where the 2θ ranges from 10°–100°. For the high temperature in-situ XRD measurement, the data was collected in 0.4 s/step and heated from room temperature to 1,000 °C then cooled down to room temperature again within 10 min in air. About 20 mg of sample was used, and the heating rate was controlled at 10 °C/min. The Rietveld XRD analysis was performed on Topas software to calculate structure ratios and cell parameters.

Scanning electron microscope (SEM) images were recorded by Hitachi S-8020U, high-resolution transmission electron microscope (HRTEM) images were recorded by FEI Titan™ ETEM equipped with a Cs aberration corrector under 300 kV. The specific areas and pore structures were analyzed by ASAP 2020 at 77 K, the samples were pre-treated by degassing at 150 °C for 8 h. UV–vis diffuse reflectance spectra were carried on Shimadzu-3600Plus UV–vis spectrophotometer. Mott-Schottky measurement was conducted on CHI660E electrochemical workstation with three-electrode system, using TiO_2 as working electrode, Pt wire as the counter electrode, a saturated calomel electrode as the reference electrode and 0.1 mol/L Na_2SO_4 was used as electrolyte.

2.3. Photocatalytic activity measurement

The photocatalytic activity was evaluated by degrading methyl orange (MO) under UV light (365 nm), the light was emitted by a homemade light emitting diode (LED) and set at 3.7 V, 1.0 A. Before irradiation, 50 mg of catalyst, 80 mL of H_2O, and 0.5 mL of MO (1 mg/mL) were mixed thoroughly in a 100 mL beaker, then stirred for 1 h in dark to get adsorption-desorption equilibrium, the ultimate concentration of MO is 6.25 mg/L. The distance between light and liquid level is about 2 cm. 4 mL of the sample was taken out every 15 min and centrifuged at 12,000 r/min for 5 min. Finally, the supernatant was tested by UV–vis spectrophotometer to calculate the degradation rate. The cycling performance was conducted to test catalyst stability. After every cycle, the powder was centrifuged and washed by H_2O for three times, then mixed thoroughly with 80 mL of H_2O and 0.5 mL MO, and kept in dark for 1 h before irradiation.

3. Results and discussion

In order to design the composite structure materials with anatase and TiO_2-B polymorphs for photocatalytic field, the HTO precursor, ascribed to $H_2Ti_8O_{17}$ (JCPDS No. 36-0656) structure in Fig. 1b, is employed, and in-situ time-resolved XRD (TXRD) technique is used for investigating the range of polymorph transformation temperature of HTO. From the two-dimensional (2D) contour plot in Fig. 1a, it is obvious that there are three stages for in-situ HTO TXRD experiment. In the first stage (room temperature to 200 °C), with the increase in temperature, gradual vanish of HTO character peak (11.5°) can be considered as the HTO structure dehydrate process, and the weakened intensity at about 13° is ascribed to the new TiO_2-B crystal nucleus formation. These structure evolution processes can be demonstrated clearly in the magnified contour plot region, which corresponds to the XRD patterns in Fig. 1c. Furthermore, it is worth mentioning that peak is shifted from higher angle (33°) to lower angle (29°) above 300 °C with the gradual crystal nucleus growth of TiO_2-B structure. During the second stage (200–800 °C), the obvious TiO_2-B structure is formed and there is strong evidence that anatase structure nucleation starts above 600 °C, which is illustrated in Fig. 1d, e by the magnified contour plot and a frame line marked in XRD patterns. The third stage (800–1,000 °C) clearly indicates anatase structure with the presence of small amount of TiO_2-B structure. It is surprising to find the structure of TiO_2-B at such high temperature (1,000 °C) because of its metastable state.

After in-situ TXRD treatment, SEM technique has been used to investigate the morphological variation of the designed samples as shown in Fig. S1 (online). The fibrous morphology is maintained with melted edges and macropores compared to HTO in Fig. 2d. Based on the above results, it can be inferred that heating rate and holding time are the important factors that have impact on the structure transition and morphological changes. When a high heating/cooling rate is applied, the metastable TiO_2-B structure can be maintained without significant morphological changes.

In addition, the calcined environment and precursors may also affect the intermediate phases. Previous study of in-situ high temperature TEM technique has shown that reduced titanium oxide (Ti_3O_5, Ti_6O_{11}) can be produced during the transformation process of TiO_2-B structure to the anatase structure under air and vacuum environment [32]. However, these structures were not detected in