Materials Letters 205 (2017) 173–177

Contents lists available at ScienceDirect

Materials Letters

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

The effect of surface heterojunction between (001) and (101) facets on photocatalytic performance of anatase TiO_2

Xiao Zhou, Jiang Wu *, Jing Zhang, Ping He, Jianxing Ren, Jinjing Zhang, Jia Lu, Pankun Liang, Kai Xu, Fei Shui

College of Energy and Mechanical Engineering, Shanghai University of Electric Power, Shanghai 200090, People's Republic of China

ARTICLE INFO

Article history:
Received 10 June 2017
Received in revised form 18 June 2017
Accepted 19 June 2017
Available online 20 June 2017

Keywords:
Semiconductors
Anatase TiO_2
Nanoparticles
(001) and (101) facets
Surface heterojunction
Elemental mercury

ABSTRACT

To explore the effect of surface heterojunction between (001) and (101) planes on photocatalytic activity of anatase TiO_2, the anatase TiO_2 photocatalysts with different ratio of (001) and (101) planes were prepared via a facile hydrothermal method. The as-prepared photocatalysts were characterized by XRD, TEM, HRTEM, UV–vis, and PL to explore the optimal ratio of these facets. Meanwhile, the as-prepared samples were used to photocatalytically remove elemental mercury under UV lamp irradiation. The results indicated that the removal efficiency was different and the percentage of (001) was 32% exhibiting the best photocatalytic activities. It can be attribute to the surface heterojunction between (001) and (101) planes and the optimal ratio of these facets, which can suppress the recombination of photoexcited electron-hole pairs.

1. Introduction

As well-known, in the anatase, rutile, and brookite polymorphs of TiO_2, anatase usually shows the best photocatalytic performance [1]. The surface energies of low-index planes of the three exposed planes in anatase nanocrystals, i.e., (001), (010), and (101) planes, are 0.90, 0.53, and 0.44 J/m^2 respectively [2–4]. Generally the higher surface energy usually exhibit better reactivity in photocatalytic reactions [5], so high-energy (001) facet exposure has become a goal. Lu et al. reported the preparation of anatase with exposed 47% percentage of (001) facets [6], and afterwards, Chen et al. synthesized the anatase microspheres with nearly 100% (001) facets [7]. However, the photoactivity does not continually increase with the percentage of (001) facets [8], for instance, Cheng et al. found that clean (001) planes show lower photoactivity than (101) planes for hydrogen evolution [9]. Moreover, some researches show that the microstructure of surfaces and interfaces in metal oxide nanoparticles can be controlled by the chemical parameters of synthesis process and influence their chemical and physical properties [10,11]. Some researches demonstrate that the synergistic effects of different planes is a promising method for improving photoactivity [12].

Herein, we report anatase TiO_2 with co-exposed (001) and (101) facets and explore the optimal ratio of these facets to reach the best photocatalytic performance. The surface heterojunction between (001) and (101) planes is formed, which is propitious to the separation of photoinduced electron-hole pairs [13]. Furthermore, the as-prepared materials are used for removal of elemental mercury (Hg^0), which is difficult to be removed by photocatalysis because of high oxidation-reduction potentials. Meanwhile, the possible reaction mechanism is elaborated on the basis of characterization and experimental results.

2. Materials and methods

2.1. Preparation of anatase TiO_2

In typical synthesis, 5 mL of tetrabutyl titanate and x ml (x = 0, 0.25, 0.5, 0.75, and 1) hydrofluoric acid (HF) solution (with concentration 40 wt%) were added into 40 ml deionized water. The above solution was continuously stirred for 30 min and then transferred into 50 mL Teflon-lined autoclave with 160 °C for 24 h. After hydrothermal process, the obtained white sediment was gathered and cleaned with absolute alcohol and deionized water for three times. Afterwards, the washed materials was desiccated in ventilation oven overnight at 80 °C. The as-prepared materials were named as A-HF-0, A-HF-0.25, A-HF-0.5, A-HF-0.75, and A-HF-1 respectively.

* Corresponding author at: No. 2103 Pingliang Road, Shanghai 200090, People's Republic of China.
E-mail address: wjcfd2002@sina.com (J. Wu).

http://dx.doi.org/10.1016/j.matlet.2017.06.095
0167-577X/

2.2. Photocatalytic activity test

The experimental equipment comprises simulated flue gas (nitrogen), photocatalytic reactor, and on-line mercury analyzer, which is similar to that used in our previous studies [14]. Two branches of nitrogen are released from cylinders and controlled by mass flow meters (MFC, CS200) with 200 and 1000 mL/min flow rates respectively, one of which with 200 mL/min passed through mercury generator (PSA, UK) with stated temperature (50 °C). Afterwards, the branch carrying mercury (Hg^0) vapor is mixed with another branch in a mixing tank, then introducing into photocatalytic reactor. The gas-phase Hg^0 concentration is measured by an on-line mercury analyzer (RA-915-M, Lumex, Russia). After analyses, the exhaust gas is introduced into the activated carbon and $KMnO_4$ solution bottle before being expelled into the atmosphere.

Photocatalytic activity test was implemented with photocatalyst (50 mg) spread on the glass plates. At the beginning of each test, the nitrogen was passed through the bypass then switched to the photocatalytic reactor till the Hg^0 concentration was reached the setting value and the on-line mercury analyzer was calibrated. The Hg^0 removal efficiency under UV lamp irradiation was following equation:

$$\eta_{Hg}(\%) = \frac{Hg^0_{in} - Hg^0_{out}}{Hg^0_{in}} \times 100\% \quad (1)$$

where Hg^0_{in} and Hg^0_{out} represented Hg^0 concentration (μg/m3) at the inlet and outlet of the photocatalytic reactor respectively.

3. Results and discussions

The XRD patterns (Fig. 1(a)) show that the peaks at 25.28, 37.80, 48.05, 53.89, and 55.06° are observed, which are responded to (101), (004), (200), (105), and (211) facets of anatase TiO_2 agreeing with JCPDS card (NO. 21-1272) respectively [15]. Amusingly, all of the as-prepared samples are indexed to anatase TiO_2 excepting for A-HF-0, which exists brookite. Obviously, the (004) diffraction peak of as-prepared samples are broadened, which indicates that the percentage of (001) planes is increased [16]. Meanwhile, the intensity of the (200) peak is enhanced and the (200) diffraction peak are narrowed, which indicates that the side length of the (001) direction is increased with adding the HF.

The transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) are carried out, and the results are shown as Fig. 1. Fig. 1(b) and (d) illustrates the TEM images of A-HF-0.25 and A-HF-0.75, which shows the

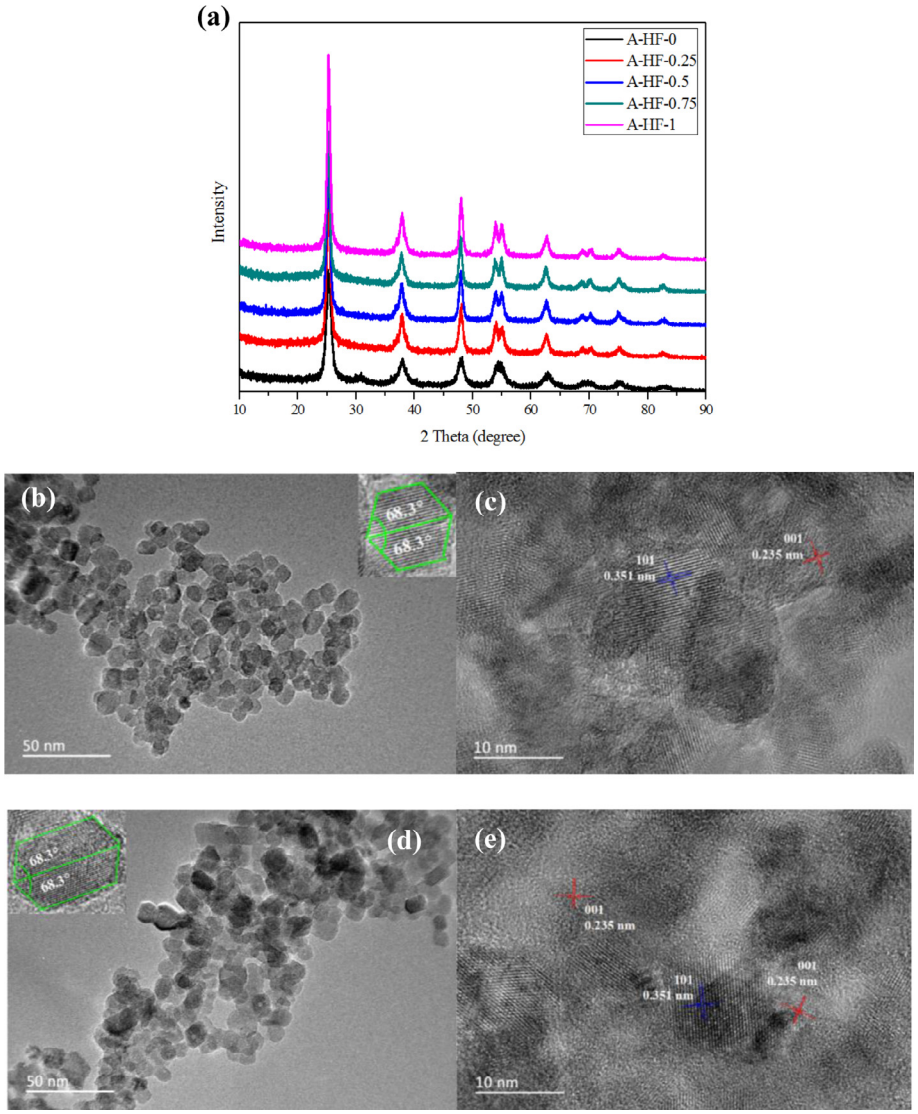

Fig. 1. (a) XRD patterns of as-prepared samples; TEM images of (b) A-HF-0.25; (d) A-HF-0.75; HRTEM images of (c) A-HF-0.25; (e) A-HF-0.75.