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Photocatalytic study of a novel crystal facets sensitive heterojunction between $Sb_8O_{11}Cl_2$ and anatase TiO_2 with different exposed facets

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ABSTRACT

In this work, $Sb_8O_{11}Cl_2$ was composited with TiO_2 with different exposed facets to construct heterostructure and related photocatalytic activity was studied. The results reveal that this $TiO_2/Sb_8O_{11}Cl_2$ heterostructure is crystal facets sensitive. When $Sb_8O_{11}Cl_2$ was loaded on the {001} facets of TiO_2 nanosheets with coexposed {101} and {001} facets, the photo-induced carriers' separation efficiency is enhanced and related photocatalytic activity is improved with a ratio of 74% under optimal composited ratio. However, the carriers' separation efficiency and related photocatalytic activity almost had no variation when $Sb_8O_{11}Cl_2$ was composited with P25 which is mainly constituted by anatase TiO_2 with exposed {101} facets. Pure anatase TiO_2 nanooctahedrons with mainly {101} facets were also composited with $Sb_8O_{11}Cl_2$ and related composites displayed persistent decline in the carriers' separation efficiency and photocatalytic activity. The results can be explained by the different energy band structure of $TiO_2/Sb_8O_{11}Cl_2$ heterostructures. When $Sb_8O_{11}Cl_2$ was composited on the {101} facets of anatase TiO_2, an *n-n* type heterostructure will be constructed and the photo-induced electrons can hardly transform between N-type TiO_2 and $Sb_8O_{11}Cl_2$. But as $Sb_8O_{11}Cl_2$ was composited on the {101} facets of anatase TiO_2 nanosheets with coexposed {101} and {001} facets, a novel *n-p-n* dual heterojunction will form. In this *n-p-n* dual heterojunction, photo-induced electrons produced in the conduction band of $Sb_8O_{11}Cl_2$ will flow into the conduction band of P-type {001} facets and finally flow into the {101} facets of TiO_2. In this way, the photo-induced carriers will separate into different semiconductors and the photocatalytic activity of $TO/Sb_8O_{11}Cl_2$ heterostructures is enhanced.

1. Introduction

Energy and environment have attracted more and more attention for their important site in the human development. To solve the energy and environment crisis, photoelectrochemistry semiconductors have been studied widely for the materials can transform solar energy to be electric energy or chemical energy. These energy transitions only use solar energy and almost have no pollutant, so it is a green and continual route. Photocatalyst is a kind of semiconductors which can transform solar energy to be chemical energy for organic pollutant degradation or hydrogen production. TiO_2 is an ideal photocatalyst for its stabilization, low cost, safety and high efficiency [1]. However, due to the wide band gap and low quantum efficiency, TiO_2 also need to be modified to achieve higher photocatalytic activity. Semiconductors compositing to construct heterojunction with TiO_2 has be confirmed to be an effective approach to improve the photo-induced carriers separation efficiency [2]. In the semiconductors heterojunction, photo-induced carriers can transfer between the heterojunction interfaces to obtain a longer life.

On the other hand, photocatalytic reaction is not only an energy transition, it also includes a surface chemical reaction. The chemical reaction largely depends on the exposed crystal facets of photocatalysts. For TiO_2, the photocatalytic activities of different crystal facets are very different [3]. TiO_2 with some exposed high energy facets have been successfully obtained such as {001} and {111} facets [4–11]. Other facets such as {100} and curved surface have also been reported through controlling the precursor in the hydrothermal progress [12–16]. Moreover, except different photocatalytic activity, the crystal facets also have large influence in the heterojunction between TiO_2 and

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other semiconductors. In our previous research, it has been found that the photocatalytic activity of heterojunction depends on the compositing facets. Mainly speaking, {001} facets of anatase TiO_2 are more suitable to load other semiconductors for improving the photocatalytic property [17–23]. $Sb_8O_{11}Cl_2$ is a novel material which has been rarely studied [24–26]. The photocatalytic property of $Sb_8O_{11}Cl_2$ has not been reported.

In this work, $Sb_8O_{11}Cl_2$ nanoparticles were composited with different TiO_2 with different exposed facets (anatase TiO_2 nanosheets with mainly exposed {001} facets, P25 with mainly exposed anatase {101} facets and anatase TiO_2 nano-octahedron with only exposed {101} facets) to compare the photocatalytic activity. The results showed that the $TiO_2/Sb_8O_{11}Cl_2$ heterojunction had crystal facets sensitive: only when $Sb_8O_{11}Cl_2$ composited on the {001} facets of TiO_2, the $TiO_2/Sb_8O_{11}Cl_2$ heterojunction showed an obvious photocatalytic improvement while the photocatalytic activity became weak when {101} facets of TiO_2 were loaded $Sb_8O_{11}Cl_2$. The work develops a new approach to improve the heterojunction property for photocatalytic application.

2. Experimental section

2.1. Synthesis of samples

1) Synthesis of {001} facets exposed anatase TiO_2 nanosheets (TO). {001} facets exposed anatase TiO_2 nanosheets were prepared through a hydrothermal route. The method was detailedly stated as follows. Approximately 25 mL of $Ti(OBu)_4$ was mixed with 3 mL HF in a 100 mL Teflon-lined autoclave, and then the autoclave were heated at 180 °C for 24 h. A further centrifugation process with 10000 rpm was executed to separate the precipitates from the suspension for 15 min. The obtained samples were dried at 102 °C for 12 h.
2) Synthesis of {101} facets exposed anatase TiO_2 nanooctahedrons (ATO). {101} facets exposed anatase TiO_2 nanooctahedrons were prepared through two hydrothermal processes. At the first step, 2 g P25 was mixed with 60 mL of 10 M KOH solution in a 100 mL Teflon-lined autoclave. The autoclave was heated at 200 °C for 24 h. The product was separated by centrifugation process and washed for 3 times. After dried at 80 °C for 12 h, white K_2TiO_{13} powders were obtained. The K_2TiO_{13} powders were further ion-exchanged with 0.1 M NH_4NO_3 solution to product ammonium-exchange titanate. Finally, 0.2 g obtained ammonium-exchange titanate nanowires was dispersed in 60 mL deionized water in a 100 mL Teflon-lined autoclave. The autoclave was heated at 160 °C for 24 h. White TiO_2 powders were obtained after centrifugation, washing and drying process.
3) Synthesis of $Sb_8O_{11}Cl_2$ nanoparticles (SOC). $Sb_8O_{11}Cl_2$ nanoparticles were prepared through a hydrothermal route. In this process, 300 mg $SbCl_3$ were put into 60 mL deionized water and then stirred until completely dissolved, then the mix solution was put into a 100 mL Teflon-lined autoclave, finally the autoclave was heated at 100 °C for 12 h. The products were deal under the same route as ATO to purify and dry.
4) Synthesis of TO/SOC heterostructures. TO/SOC heterostructures were fabricated via a further hydrothermal route. In this process, 100 mg TO were mixed with relative $SbCl_3$ in 60 mL of deionized water in a 100 mL Teflon-lined autoclave. Then the mix solutions were heated at 100 °C for 12 h. Finally, the products were deal under the same route as ATO to purify and dry. Samples with various Sb:Ti mole ratios were labeled as TSC1 (21.4 mg $SbCl_3$, Sb:Ti = 7.5%), TSC2 (28.5 mg $SbCl_3$, Sb:Ti = 10%), TSC3 (35.6 mg $SbCl_3$, Sb:Ti = 12.5%) and TSC4 (42.8 mg $SbCl_3$, Sb:Ti = 15%).
5) Synthesis of P25/SOC heterostructures. P25/SOC heterostructures were fabricated via a further hydrothermal route. In this process, 100 mg P25 were mixed with relative $SbCl_3$ in 60 mL of deionized water in a 100 mL Teflon-lined autoclave. Then the mix solutions were heated at 100 °C for 12 h. Finally, the products were deal under the same route as ATO to purify and dry. Samples with various Sb:Ti mole ratios were labeled as PSC1 (2.1 mg $SbCl_3$, Sb:Ti = 0.75%), PSC2 (2.9 mg $SbCl_3$, Sb:Ti = 1%), PSC3 (7.1 mg $SbCl_3$, Sb:Ti = 2.5%) and PSC4 (14.3 mg $SbCl_3$, Sb:Ti = 5%).
6) Synthesis of ATO/SOC heterostructures. P25/SOC heterostructures were fabricated via a further hydrothermal route. In this process, 100 mg ATO were mixed with relative $SbCl_3$ in 60 mL of deionized water in a 100 mL Teflon-lined autoclave. Then the mix solutions were heated at 100 °C for 12 h. Finally, the products were deal under the same route as ATO to purify and dry. Samples with various Sb:Ti mole ratios were labeled as ASC1 (2.1 mg $SbCl_3$, Sb:Ti = 0.75%), ASC2 (2.9 mg $SbCl_3$, Sb:Ti = 1%), ASC3 (7.1 mg $SbCl_3$, Sb:Ti = 2.5%) and ASC4 (14.3 mg $SbCl_3$, Sb:Ti = 5%).

2.2. Characterizations

X-ray diffraction (XRD) (Miniflex600, Rigaku, Japan) with Cu-Kα radiation at a scan rate of $0.02^\circ\ s^{-1}$ was employed to detect the crystal structures of the samples. The work voltage and current were set at 40 kV and 15 mA. To measure and calculate the Brunauer–Emmett–Teller (BET) specific surface area, a nitrogen adsorption process was analyzed by a nitrogen adsorption apparatus (ASAP, 2020, Micromeritics, USA). All the obtained samples were degassed at 180 °C before measurements. High-resolution transmission electron microscopy (HRTEM) (Tecnai F30 S-Twin, FEI, Hillsboro, USA) technology were employed to characterize the morphologies and microstructures. X-ray photoelectron spectroscopy (XPS) measurements were executed using ESCLAB250Xi (Thermo Fisher Scientific, USA) spectrometer with a charge neutralizer to gain information on the chemical binding energy of the photocatalysts. A C1s peak (284.8 eV) of the adventitious carbon was referenced to rectify the binding energies. UV–vis spectrophotometer (UV-3600, Shimadzu, Tokyo, Japan) with an integrating sphere (MPC-3100, Shimadzu, Tokyo, Japan) was used to tested the UV–vis diffuse reflectance spectroscopy (DRS) of the samples. Fluorescence spectrophotometer (RF-530TPC, Shimadzu, Japan) with a 300 nm line from a xenon lamp was employed to test the fluorescence emission spectra (FL) of the samples.

2.3. Photocatalytic test

The photocatalytic activity of the photocatalysts was measured by calculating the degradation rates of methylene blue (MB) under the illuminated of UV–vis light. The light source was a 250 W high-pressure mercury lamp placed 8 cm above the liquid surface in the experiment. 20 mg photocatalyst was put into 100 mL of 4×10^{-5} M MB aqueous solution. Before illumination, the mixed solution was put in a dark environment with persistently stirred for 60 min to achieve a saturated adsorption, and the remained concentration of MB was measured. In the photocatalytic degradation process, after every 10 min, 3 mL solutions were extracted to measure the remained concentrations of dye. MB concentration was calculated by comparing maximum absorbance intensities with pristine MB solution by UV–vis spectrometry (UV-3600, Shimadzu, Tokyo, Japan).

3. Results and discussion

3.1. Crystal structure and morphology

At first, the structure and photocatalytic performance of TO/SOC heterostructures were studied. The preparing progress of TO/SOC heterostructures has been demonstrated as Fig. 1. The XRD patterns of pristine TO, SOC and TO/SOC composites with different ratios are shown in Fig. 2. The XRD pattern of TO exhibits a typical anatase TiO_2 feature compared with standard XRD pattern (JCPDS data file No. 21-1272) which can confirm the pure anatase phase of TO. Through further