Deposition of SnO₂ on the Anatase TiO₂ {105} Facets with High Photocatalytic Performance

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Anatase TiO₂ as a promising photocatalyst has been widely employed in the decontamination treatment of polluted water, air purification and water splitting. Coupling TiO₂ with other semiconductor materials could further enhance the photocatalytic activity. Here, we successfully synthesized the SnO₂/TiO₂ catalyst by depositing SnO₂ particles on the anatase TiO₂ {105} facets through a gas phase oxidation process. The SnO₂/TiO₂ catalyst shows higher photocatalytic activity for decomposition of MB than that of the pure TiO₂ catalyst. The enhanced photocatalytic activity can be attributed to the efficient charge separation since TiO₂ and SnO₂ catalyst have staggered energy level.

Keywords: High-index facets; SnO₂/TiO₂; Composite; Photocatalyst.

Introduction

Since the discovery of the photoelectrolysis of water on TiO₂ photoelectrode by Fujishima and Honda, anatase TiO₂ particles as photocatalyst have been widely employed in the decontamination treatment of polluted water, air purification and H₂ generation by splitting water [1-10]. Recently, theoretical calculations and experiment evidences have suggested that construction of anatase TiO₂ bounded by high activity facets is a significant approach to improve the photocatalytic activity of the TiO₂ catalyst. As a results, anatase TiO₂ particles dominated by {001}, {100}, {201} and {105} facets were intensively studied by experiments and theoretical calculations [12-18]. Particularly, single crystal anatase TiO₂ exposing high index {105} facets has unique surface structures with a high density of atomic steps, dangling bonds and kinks, which can act as active sites to facilitate photocatalytic water splitting or organic pollutant decontamination reaction. In our previous work, a high-temperature gas-phase oxidation route was introduced to prepare anatase TiO₂ crystals exposed by high-index {105} facets and the photocatalytic splitting water performance under UV light was studied experimentally and theoretically [16]. However, in practical terms, anatase TiO₂ bounded by {105} facets still shows lower photocatalytic efficiency due to its intrinsic feature of massive recombination of photo-induced electrons/holes. Therefore, many efforts have been focused on the

promotion of overall photocatalytic efficiency for anatase TiO₂. Among them, fabrication, design and tailoring of the semiconductor-semiconductor composite as an efficient solution for achieving better separation in a light energy conversion system has received significant attention [19-21]. Typically, coupling TiO₂ with a wide band gap semiconductor SnO₂ has been intensively explored to enhance the charge separation and thus the photocatalytic activity [22-29]. However, forming the composite on the anatase TiO₂ bounded by high-active facets as well as their photocatalytic activities have not been reported.

Figure 1 Schematic structure of composite SnO₂/TiO₂ (depositing SnO₂ on the anatase TiO₂ high-index {105} facets) and the mechanism of the interfacial charge transfer progress for the composite SnO₂/TiO₂ under the UV light irradiation

Herein, for the first time, we reported that the composite $\text{SnO}_2/\text{TiO}_2$ particles by depositing SnO_2 on the anatase TiO_2 high-index $\{105\}$ facets were synthesized through gas-phase oxidation method, as illustrated in Fig. 1. The results of photocatalytic decomposition of methylene blue (MB) suggest that the $\text{SnO}_2/\text{TiO}_2$ catalyst display higher photocatalytic activity compared with the pure TiO_2 catalyst.

Experimental

Preparation of catalyst particles

A schematic reaction apparatus is shown in Fig. S1, where a straight static furnace quartz pipe was used as the reactor. A thin spiral stainless steel tube with outer diameter of 3 mm (inner diameter of 2 mm) and a straight ceramic tube with outer diameter of 3 mm (inner diameter of 2 mm) were used as reactant feeder for TiCl_4 and SnCl_4 , respectively. Oxygen was used as reactant and carrier gas for TiCl_4 and nitrogen was acted as carrier gas for SnCl_4 . In the typical experiment, oxygen (0.2 L/min) bubbled TiCl_4 liquid heated to 98 °C by oil bath and then passed through the spiral tube with TiCl_4 vapor. The SnCl_4 vapor was introduced into the straight tube by bubbling nitrogen (0.02 L/min) into SnCl_4 liquid at 25 °C. The temperature of furnace was monitored by thermocouple and kept at a constant value of 1000 °C. The final products were collected at the downstream by a bag filter and washed with deionized water for 3 times to remove the adsorbed chlorine containing species on the surface. As reference, the mixture of $\text{SnO}_2/\text{TiO}_2$ catalyst was obtained by mixing the pure TiO_2 particles dominated with $\{105\}$ facets and pure SnO_2 crystal particles with the Sn/Ti atomic ratio of 0.06.

Characterizations of catalyst particles

The morphology and structure of the samples were characterized by field emission scanning electron microscopy (FESEM, HITACHI S4800). Crystall-ographic information of high-index anatase TiO_2 single crystals was obtained with X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer, $\text{Cu K}\alpha$ radiation, 40 kV). Chemical compositions as well as the bonding states of anatase TiO_2 single crystals were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250, $\text{Al K}\alpha$ exciting radiation). XPS spectra of Sn 3d, Ti 2p and O 1s were measured with constant analyzer-pass energy of 20.0 eV. All binding energies were referenced to the C 1s peak (284.8 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). Prior to peak deconvolution, X-ray satellites and inelastic background (Shirley-type) were subtracted for all spectra. The optical absorption spectra of the samples were recorded in a UV/Vis spectrophotometer (CARY 500).

Photoactivity assessment of the as-obtained catalyst particles

The photocatalytic activities of the samples were assessed by the degradation of methylene blue (MB) under UV light irradiation (300 W and main wavelength of 365 nm) at room temperature. 50 mg catalyst was dispersed in 100 ml MB solution with the original concentration of 0.1 mM and irradiated under a UV light at a distance of 15 cm. Before the photoreaction, the solution was magnetically stirred in dark for 30 minutes to reach adsorption /desorption equilibrium and then illuminated with stirring. The concentration change of the methylene blue was determined by the absorbance of the solution at 665 nm.

Results and discussion

Characterization of pure TiO_2 and composite $\text{SnO}_2/\text{TiO}_2$

Figure 2 FESEM images and EDS results of as-obtained composite $\text{SnO}_2/\text{TiO}_2$ dominated with $\{105\}$ facets.

The field emission scanning electron microscopy (FESEM) images of the composite are shown in Fig. 2a-c. Most of the as-synthesized crystals display bipyramidal morphology with an average length of 1~10 μm . In our previous report, we have already confirmed that the exposed surfaces in the bipyramidal crystals are the high-index $\{105\}$ surfaces of anatase TiO_2 [16]. Compared with pristine anatase TiO_2 bounded by $\{105\}$ facets, the shapes of TiO_2 single crystals show no

obvious change (see Fig. S2). Interestingly, for the composite $\text{SnO}_2/\text{TiO}_2$ sample, it is very clear that a lot of little particles are attached on the anatase TiO_2 high-index {105} facets, but the high-index {105} facets of the pure TiO_2 exhibit clean and smooth features. X-ray energy dispersive spectroscopy (EDS) was used to explore the content of the little particles anchoring on the high-index {105} facets of anatase TiO_2 (shown in Fig. 2d, e). From the EDS results, we can see that the little particles attached on the high-index {105} facets are SnO_2 crystal particles. It is noted that these SnO_2 crystal particles aggregated rather than uniformly dispersed on the {105} facets.

Figure 3 The X-ray diffraction (XRD) patterns of the as-synthesized composite $\text{SnO}_2/\text{TiO}_2$ particles and pure TiO_2 exposed by high-index {105} facets.

Fig.3 shows the X-ray diffraction (XRD) patterns of the as-synthesized composite $\text{SnO}_2/\text{TiO}_2$ and pure TiO_2 exposed by high-index {105} facets. The main diffraction peaks of pure TiO_2 exposed by high-index {105} facets can be indexed into anatase crystal phase (space group: $I4_1/amd$, JCPDS No. 21-1272) which are marked with letter A and only very small numbers of rutile impurities can be detected, which are marked with letter R. With respect to the composite $\text{SnO}_2/\text{TiO}_2$ crystal particles, there is an additional peak (positioned at 26.5°) corresponding to cassiterite SnO_2 (space group: $P4_2/mnm$, JCPDS No. 46-1088). Moreover, for these two samples, the relative intensity of the {105} is much stronger than that of the standard TiO_2 XRD pattern, which also implies that more {105} facets have been exposed, and this result is consistent with the FESEM observations. In agreement with the EDX results, no shift of the XRD peaks of composite $\text{SnO}_2/\text{TiO}_2$ compared to pure TiO_2 (Fig.3) indicates that Sn atoms do not enter into the TiO_2 lattices to substitute Ti atoms, which is mainly ascribed to the nucleation and growth process of the $\text{SnO}_2/\text{TiO}_2$ composite. In our experiment, at the beginning part of the reactor, TiCl_4 first reacted with O_2 , and then nucleated and quickly grew into well-defined crystal particles. However, SnCl_4 did not

take part in the oxidation reaction at this stage since the SnCl_4 vapor was limited inside the straight pipe and prevented from contacting with O_2 . After flowing out the straight pipe, SnCl_4 vapor started to react with O_2 at the middle part of the reactor, while oxidation reaction of TiCl_4 is almost finished at this region. Therefore, SnO_2 crystal particles deposited on the anatase TiO_2 particle bounded by high-index {105} facets rather than forming Sn doped TiO_2 .

The Sn/Ti atomic ratio of the composite $\text{SnO}_2/\text{TiO}_2$ particles was detected to be 0.059 by X-ray photoelectron spectroscopy (XPS) (see Fig. 4). The characteristic peaks at around 495.2 and 486.8 eV are assigned to the Sn 3d electrons (Fig. 4 upper left inset). The O 1s spectrum of composite $\text{SnO}_2/\text{TiO}_2$ (Fig. 4 upper right inset) can be deconvoluted into four peaks. The peak located at 529.8 eV is attributed to lattice oxygen of anatase TiO_2 crystals, whereas the peak located at 530.8 eV is attributed to lattice oxygen of SnO_2 crystals [30]. This result further illustrates that Sn atoms are favorable to form pure SnO_2 phase rather than enter the lattice of anatase TiO_2 by substituting Ti atoms. The other two peaks located at 513.3 and 532.6 eV could be assigned to Ti-OH and surface adsorbed species containing oxygen only.

As shown in Fig. S3, composite $\text{SnO}_2/\text{TiO}_2$ particles and pure TiO_2 particles show the similar UV-vis absorption properties with a threshold of 395 nm. It is well-known that high-index {105} facets show unique geometrical and electronic structures such as high densities of atom steps, kinks, dangling bonds, and ledges. As a result, there are a lot of oxygen vacancies on the high-index {105} facets, and oxygen vacancies can give rise to surface states which are located between the valance band and conduction band. Therefore, the optical absorption between 400 and 700 nm is attributed to the surface states [31].

Figure 4 XPS spectra of composite $\text{SnO}_2/\text{TiO}_2$ dominated with {105} facets. The insets are high resolution XPS spectra for Sn 3d electrons (upper left), O 1s electrons (upper right) and Ti 2p electrons (lower left).

Photoactivity assessment of the as-obtained catalyst particles

The results of the MB degradation under UV light irradiation are shown in Fig. 5a. It can be noted that almost no change in the concentration of MB was observed in the absence of any photocatalysts. However, obvious photocatalytic decomposition of MB could be observed when the catalysts were added into the solution. After irradiation for 6 hours, the photocatalytic decomposition of MB in the presence of composite $\text{SnO}_2/\text{TiO}_2$ catalyst was nearly 91%; meanwhile, only 58% of MB could be decomposed by pure TiO_2 under the same condition. In addition, only 56% of MB could be decomposed in the mixture of $\text{SnO}_2/\text{TiO}_2$ system, whose photocatalytic activity was comparable with that of pure TiO_2 particles. Therefore, we can conclude that the composite of $\text{SnO}_2/\text{TiO}_2$ particles displays higher photocatalytic activity than the pure TiO_2 and the mixture $\text{SnO}_2/\text{TiO}_2$ catalyst. Among these catalysts, P25 powder displayed the highest photocatalytic activity (about 94% of MB decomposed in 3 hours) under the same experimental condition, mainly because whose specific area was as high as $53 \text{ m}^2/\text{g}$, whereas the specific area of composite $\text{SnO}_2/\text{TiO}_2$ photocatalyst was only $2.2 \text{ m}^2/\text{g}$. Considering surface area effect of the heterogeneous reaction, the composite $\text{SnO}_2/\text{TiO}_2$ material indeed exhibits superior photocatalytic activity for MB degradation. The stability of highly efficient composite $\text{SnO}_2/\text{TiO}_2$ photocatalyst was further evaluated by the recycle experiments in degradation of MB. The as-prepared composite $\text{SnO}_2/\text{TiO}_2$ catalyst remained similar degradation rate after five cycles (as shown in Fig. 5b), suggesting that the composite $\text{SnO}_2/\text{TiO}_2$ exhibits high photocatalytic activity and stability during the degradation of MB.

Figure 5 (a) Concentration variation of methylene blue as a function of irradiation time under UV light for pure TiO_2 , mixture of $\text{SnO}_2/\text{TiO}_2$ (Mix- $\text{SnO}_2/\text{TiO}_2$), composite $\text{SnO}_2/\text{TiO}_2$ (Com- $\text{SnO}_2/\text{TiO}_2$) and Degussa TiO_2 (P25) and (b) photodegradation recycle of composite $\text{SnO}_2/\text{TiO}_2$

Based on the above observation, the enhanced photocatalytic activity of the composite $\text{SnO}_2/\text{TiO}_2$ catalyst can be attributed to the fact that the SnO_2 particles which are attached on the anatase TiO_2 {105} facets can efficiently suppress the recombination of photogenerated holes and electrons and this mechanism is illustrated in Fig. 1. It is widely known that both TiO_2

and SnO_2 are n-type semiconductors with band gap of 3.2 eV and 3.8 eV, respectively [32-34]. Upon illumination by the UV light, hole-electron pairs are generated in each semiconductor and then the photogenerated electrons prefer to flow to the SnO_2 particles which are tightly attached on the {105} facets of anatase TiO_2 , since the conduction band edge of TiO_2 (-0.34 V) is more negative than that of SnO_2 (0.07 V). On the contrary, the photogenerated holes favor to transfer oppositely to the TiO_2 particles because of the fact that the valance band edge of SnO_2 (+3.67 V) is much more positive than that of anatase TiO_2 (+2.87 V) (as shown in Fig. 1). The transfer of electrons from SnO_2 to TiO_2 is forbidden and shift of holes from TiO_2 to SnO_2 is forbidden as well. Consequently, more electrons can accumulate at the surfaces of SnO_2 particles to cause the reduction reaction while more holes can concentrate at the surfaces of TiO_2 and are consumed for oxidation reaction. Thus, the interfacial transfer of electrons from TiO_2 to SnO_2 rationalizes the lower activity for photocatalytic reduction and higher activity for photocatalytic oxidation of composite $\text{SnO}_2/\text{TiO}_2$ catalyst.

Conclusions

In summary, composite $\text{SnO}_2/\text{TiO}_2$ catalyst particles were synthesized by high temperature gas phase oxidation method. The results of photocatalytic decomposition of MB suggest that the composite $\text{SnO}_2/\text{TiO}_2$ displays higher photocatalytic activity compared with the pure TiO_2 catalyst. Both samples display the similar UV-vis adsorption properties, therefore the enhanced photocatalytic activity of the composite $\text{SnO}_2/\text{TiO}_2$ catalyst can be attributed to more efficient separation of photogenerated holes and electrons by depositing SnO_2 particles on the anatase TiO_2 {105} facets.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (91022023, 21076076), SRF for ROCS, SEM, Programme for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning, Major Basic Research Programme of Science and Technology Commission of Shanghai Municipality (10JC1403200), Australian Research Council's Future Fellowships (FT120100913) and Shanghai Municipal Natural Science Foundation (12ZR1407500).

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Depositing SnO₂ on {105} facets of TiO₂ crystal shows enhanced the photocatalytic activity that can be attributed to the efficient charge separation since TiO₂ and SnO₂ catalyst have staggered energy level.