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Pt-TiO_2 microspheres with exposed {001} facets for degradation of formaldehyde in air: Formation mechanism and enhanced visible light photocatalytic activity

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ABSTRACT

In this study, TiO_2 microspheres with exposed {001} facets were successfully synthesized by a low-temperature hydrothermal method without using any organic solvents as morphology controlling agent. Furthermore, an active Pt-TiO_2 catalyst was prepared by impregnation and deposition-precipitation methods with reduction processes. The photocatalytic activity of the samples was evaluated by degradation of formaldehyde in air under visible light irradiation at room temperature. After modification with Pt, the optical absorption property of the Pt-TiO_2 microspheres was extended to visible light range. More importantly, the Pt-TiO_2 microspheres exhibited excellent photocatalytic performance for formaldehyde degradation under visible light irradiation, being superior to pure TiO_2 microspheres and even Pt-P25. The formation mechanism of the TiO_2 microspheres with exposed {001} facets was studied. Moreover, the proper photocatalytic mechanism was also proposed. This work provided new insight into the improvement of photocatalytic activity by special high-energy facet exposing and noble metal depositing.

1. Introduction

Photocatalysis has attracted much more attentions because of its easy operation, no secondary pollution and energy saving, etc. Although TiO_2 is widely used as a semiconductor photocatalyst [1], its photocatalytic activity is low and it only absorbs UV light in solar irradiation, which limits its practical application. To improve the photocatalytic activity of TiO_2, many methods such as metal or nonmetal doping, constructing heterojunction and so on have been studied. Usually, the structure and exposed surface of photo-catalysts are two major factors driving the separation of photoexcited carriers and affecting its photocatalytic activity [2–6]. In order to obtain high efficient photocatalyst, controllable synthesis of TiO_2 with exposed active facets has been a fashionable subject in photocatalysis field [7].

Yang et al. [8] synthesized a series of TiO_2 single crystals with reactive facets, and put forward that the {001} facets has high photo-catalytic activity. Chen et al. [9] prepared the anatase TiO_2 with {001} facets fraction nearly 100%. Han et al. [10] synthesized nanosheet-like TiO_2 with up to 89% of {001} facets exposure and superior photocatalytic performance. TiO_2 single crystals with different facet exposed rate have been studied [11]. According to studies by Ohno [12,13], the {001} facets of TiO_2 anatase could promote the oxidation reaction, as opposed to the {101} facets. It could be ascribed to that the different energy levels of energy band structure between two kinds of facets caused the separation of photoelectrons from vacancies gathered different crystal facets [14].

Meanwhile, noble metal (such as Au, Ag, and Pt) deposition has been used to improve the visible light photocatalytic activity of semiconductor photocatalysts because of their high electron affinity behavior and unique electronic structure, which is also an effective method to promote the visible light photocatalytic performance of TiO_2 [15–19]. As mentioned above, combination of special high-energy facets exposing and noble metal modification may probably provide a new promising strategy to further improve the photocatalytic activity of catalyst.

Herein, TiO_2 microspheres with exposed {001} high energy facets were successfully synthesized by a facile hydrothermal route without using any organic solvents as morphology controlling agent. The effects of hydrothermal reaction temperature and time on the morphology of TiO_2 microspheres were investigated. Then,

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Pt/TiO_2 catalysts were prepared by impregnation and deposition-precipitation method. The photocatalytic activities of samples were evaluated by degradation of formaldehyde with the irradiation of visible light at the room temperature.

2. Experimental

2.1. Preparation of TiO_2 microspheres

All used materials are of analytic purity. Deionized water was used for all the experiments. The hydrothermal reaction was carried out at 110–150 °C for 3, 6, 9, 12, 15, 18, 21, 24 h, respectively. In a typical experiment, 1 mL $TiCl_4$ were dissolved into 60 mL of hydrochloric acid (1 mol/L) with ice-water bath, and then continuously stirred for 30 min after adding 0.15 g of $NaBF_4$ to $TiCl_4$ solution in a 100 mL Teflon-lined stainless steel autoclave. The autoclave was kept at certain temperatures for given time in an electric oven. After reaction, the products were separated by centrifugation, washed with deionized water for 4–5 times and then dried in vacuum at 60 °C. The as obtained sample was washed by NaOH solution (0.1 mol/L) before further treatment.

2.2. Synthesis of Pt-TiO_2

Pt-TiO_2 catalysts were prepared by impregnation and deposition-precipitation method. In a typical synthesis, 2.65 mL chloroplatinic acid solution (10 mg/mL) and 1 g TiO_2 were firstly added into 100 mL ethyl alcohol, and the suspension was kept at the room temperature under mild stirring for 1 h. After stirring, 5 mL of the ascorbic acid solution (10 mg/mL) were slowly added into the suspension under vigorously stirring for 2 h at 80 °C. After reduction, the suspension was washed with deionized water 5 times. Finally, the product was dried in vacuum at 60 °C for 12 h.

2.3. Characterization

Phase identification of TiO_2 was finished on a Rigaku D/Max-2400 X-ray diffractometer with Cu Kα radiation. The morphology and microstructure of TiO_2 and Pt-TiO_2 were investigated by field emission scanning electron microscopy (FESEM, Hitachi, S-4800) and trans-mission electron microscopy (TEM, FEI Tecnai F30, operated at 300 Kv), respectively. X-ray photoelectron spectroscopy (XPS) measurements were conducted on VG Multilab 2000 with Al Kα source. Ultraviolet−visible (UV–vis) diffuse reflectance absorption spectra analysis of the samples was conducted with a UV–vis spectrophotometer (UV-2550, Shimadzu Co., Japan).

2.4. Photocatalytic activity test

The photocatalytic activity of Pt-TiO_2 catalyst was evaluated by the degradation of formaldehyde under visible light irradiation at ambient environment. In a typical experiment, 0.1 g of photocatalysts was dispersed on the surface of petri dish. HCHO with 400 ppm was generated by the volatilization of HCHO solution in an sealed pot at 20 °C. The concentration of HCHO was analyzed by a Photoacoustic Field Gas-Monitor-INNOVA 1412. The photocatalytic activities of Pt-TiO_2, Pt-P25, TiO_2 and P25 were determined under the same conditions.

3. Results and discussion

3.1. Morphology and structure of TiO_2 microspheres

On the basis of the previous reports, the synthesis of TiO_2 using $TiCl_4$ as precursor can be explained as follows [20–22]:

(1-1) $TiCl_4 + H_2O = TiOH^{3+} + H^+ + 4Cl^-$

(1-2) $TiOH^{3+} = TiO^{2+} + H^+$

(1-3) $TiO^{2+} + H_2O = TiO_2 + 2H^+$

However, it is difficult to synthesize the TiO_2 exposed {001} facets without any morphology controlling agent [23,24]. Thus, it was of great significance for investigating the growth mechanism of anatase TiO_2 with {001} exposed facets [25–29].

Fig. 1 shows XRD patterns of the TiO_2 microspheres synthesized for 12 h under different reaction temperatures. The crystal phase of the TiO_2 microspheres matches well with anatase TiO_2 (JCPDS PDF No.21-1272), and no other redundant peaks are observed. The increased intensity of the (004) peak of the sample synthesized at 140 °C indicates that more {001} facets have been exposed [30]. Fig. 2a–e show SEM images of the TiO_2 microspheres synthesized under different reaction temperatures. From Fig. 2, it can be observed that the diameters of these microspheres are ranged in 1–2um and the reaction temperature has important influence on the morphology of microspheres. The surface of these particles became rough from smooth sphere with increasing the reaction temperature, which is ascribed to the covering of the curved sheets with exposed {001} facet. The Fig. 2c shows that the spheres obtained at 140 °C were from agglomeration of some smaller sheet-like crystals due to the surface effect, and their surfaces are rougher than the samples synthesized at lower temperature (as shown in Fig. 2a–b). Interestingly, with further increasing the reaction temperature, some hollows appeared on the middle site of sheets on the surfaces; the vacant areas expanded rapidly when the reaction temperature was higher than 150 °C. The sheet like curved surfaces at truncated ends should be {001} facets [31–33]. Fig. 2f represents the selected area electron diffraction (SAED) pattern of the TiO_2 microspheres, in which diffraction spots and rings are corresponded to (004), (200) and (204) planes of anatase, confirming that the TiO_2 microsphere is composed of single crystals and polycrystals [9]. Obviously, the hollow sheets with exposed {001} facet may be due to the stable effect by F^- on {001} facets [31,32].

To further investigate this phenomenon, Fig. 3 shows the SEM images of TiO_2 microspheres synthesized at 140 °C for different reaction time. It can be seen that the morphology of the sample

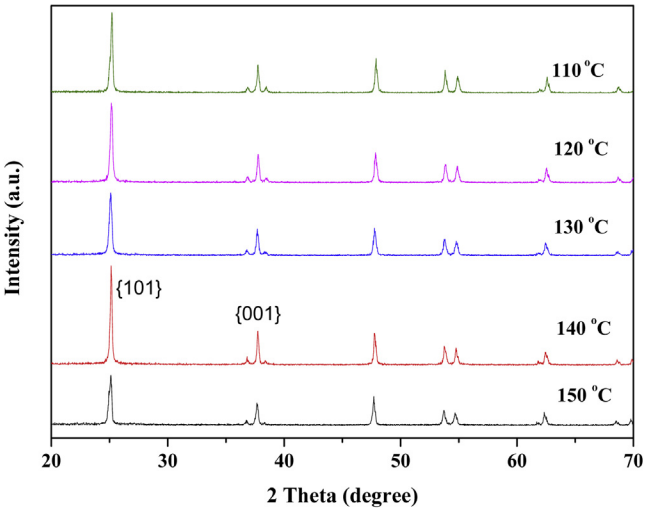

Fig. 1. XRD patterns of the TiO_2 samples synthesized at different reaction temperatures for 12 h.

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