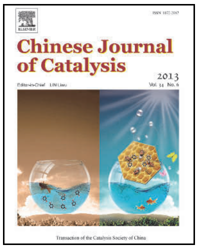
Chinese Journal of Catalysis 34 (2013) 1216–1223

available at www.sciencedirect.com

ScienceDirect

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



Article

A novel approach for the preparation of phase-tunable TiO_2 nanocomposite crystals with superior visible-light-driven photocatalytic activity

YU Fuhai [a,b], WANG Junhu [a,*], ZHAO Kunfeng [a,b], YIN Jie [a,b], JIN Changzi [a], LIU Xin [a]

[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

ARTICLE INFO

Article history:
Received 8 January 2013
Accepted 15 March 2013
Published 20 June 2013

Keywords:
Chemical solution process
Titanium oxide
Nanocomposite crystal
Phase modulation
Visible light
Photocatalysis
Adsorption capacity

ABSTRACT

A series of novel TiO_2 nanocomposite crystals with superior visible-light-driven photocatalytic activity were successfully prepared using a soft chemical solution process involving direct reaction of aqueous H_2O_2 with a 2-ethoxyethanol solution of tetraisopropyl titanate before calcination of the resulting peroxo-titanium complexes at 500 °C for 4 h. The synthesized TiO_2 samples are composed of anatase and rutile phases, and the ratio of rutile could be continuously tuned from 0 to 96% by altering the 2-ethoxyethanol volume. There are clear red-shifts in the UV-Vis absorption spectra and apparent band gap narrowing for the synthesized TiO_2 in comparison with Evonik P-25. The synthesized TiO_2 samples are found to be much more efficient for methylene blue degradation under visible-light irradiation. The optimized sample (2-ethoxyethanol: 5 ml; rutile in bulk: 46%) exhibits 5-fold higher adsorption capacity and 3-fold higher photocatalytic activity than those of Evonik P-25 ($\lambda \geq 400$ nm). Characterizations including X-ray diffraction and Raman spectroscopy reveal that the surface of the optimized TiO_2 sample only contains a small quantity of rutile. It is concluded that the surface phase composition and distribution of the TiO_2 nanocomposite crystals are essential to their greatly enhanced photocatalytic activities and strong adsorption capacities. In addition, the concentration of defects existing in the synthesized TiO_2 is also regarded to account for these enhanced properties.

1. Introduction

Since the discovery of hydrogen production via water splitting over TiO_2 by Fujishima and Honda [1] almost 40 years ago, the photocatalytic properties of TiO_2 [2–6] and many other kinds of semiconductor oxides [7–9] have been widely studied. In addition to water splitting, great potential has been found for self-cleaning materials [10–12] and trace contaminant degradation and mineralization [13–15] in the environment. However, there are two main shortcomings that considerably restrict the wider application of TiO_2 photocatalysts. First, the band gap of TiO_2 is about 3.0 eV for rutile and 3.2 eV for anatase. As a consequence, TiO_2 can only absorb ultraviolet light, which only makes up a small part (namely 3%–5%) of the energy of solar light. Different approaches have been pursued to narrow the band gap and thereby increase visible-light absorption. The most common approach is to dope TiO_2 with other ions. Different kinds of transition metal cations such as Fe^{3+},

---

* Corresponding author. Tel: +86-411-84379159; Fax: +86-411-84685940; E-mail: wangjh@dicp.ac.cn

This work was supported by the Chinese Academy of Sciences for “100 Talents” Project, the National Natural Science Foundation of China (11079036), and the Natural Science Foundation of Liaoning Province (20092173).

DOI: 10.1016/S1872-2067(12)60574-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 6, June 2013

Sn^{4+}, and Ti^{3+} [16–19] are reported to be effective in increasing visible-light absorption. Doping of anions C, N, and S into TiO_2 [20–24] is also reported to be effective for band gap narrowing. Although doped TiO_2 can exhibit great increases in light absorption, there is no remarkable corresponding increase in photocatalytic activity because the doping ions can also act as recombination centers for the photo-induced electron-hole pairs [25].

The synthesis of nanocomposites is another important approach for improving the photocatalytic performance of TiO_2 [26,27] because the resulting so-called hetero-junctions will promote the separation of photo-induced electron-hole pairs. Exposure of high energy facets can also enhance the photocatalytic activity of TiO_2 [28,29]. Furthermore, great progress has recently been achieved in the synthesis of pure TiO_2 with greatly increased visible-light absorption ability and enhanced visible-light-driven photocatalytic activity. For example, Chen et al. [30] reported a new kind of black TiO_2 that exhibited relatively efficient water-splitting activity under visible-light irradiation. Tao et al. [31] reported a two-dimensional phase of TiO_2 with a remarkably narrowed band gap of 2.1 eV. Etacheri et al. [32] reported a visible-light-active, high-temperature stable, and dopant-free TiO_2 anatase photocatalyst that was formed by the modification of amorphous TiO_2 with H_2O_2. Despite progress in narrowing the band gap of TiO_2, low adsorption capacity is still a barrier to be solved. As is known, TiO_2 can only photocatalytically degrade contaminants that come into contact with or are only tens of nanometers away from its surface. Therefore, the improvement of its adsorption capacity is of great significance for its wider application. In most cases, TiO_2 is combined with other sorbing materials (such as hydroxyapatite, activated carbon, and graphene) [33–36] to form a nanocomposite. Although it seems that TiO_2 based nanocomposites reported so far can exhibit increased adsorption capacity, their photocatalytic activities need to be further improved. Reports of the synthesis of pure TiO_2 with both increased adsorption capacity and superior photocatalytic activity under visible-light irradiation are rare.

Herein, we report the preparation, structural characterization, and superior visible-light-driven photocatalytic performance of a series of novel TiO_2 nanocomposite crystals that were successfully synthesized through a soft chemical solution process, in which an aqueous H_2O_2 solution and a 2-ethoxyethanol solution of tetraisopropyl titanate were mixed together to form a gel-like peroxo-titanium complex. The obtained peroxo-titanium complexes were then calcined at 500 °C for 4 h. The prepared TiO_2 samples were composed of anatase and rutile, and the phase compositions could be continuously tuned in a wide range by adjusting the volume of 2-ethoxyethanol. The surface crystal phase composition and distribution of the TiO_2 nanocomposites, and their defect concentration, were considered to be essential to their greatly enhanced photocatalytic activities and adsorption capacities. This is the first report of the synthesis of pure TiO_2 with both greatly enhanced adsorption capacity and superior visible-light-driven photocatalytic activity.

2. Experimental

2.1. Preparation of the TiO_2 samples

The soft chemical solution process used in the current study to prepare the TiO_2 nanocomposite crystals is a modified method previously reported by our group for the preparation of fine antimonic acid nanoparticles [37,38]. In this modified method, a peroxo-titanium complex was produced as a precursor by adding an aqueous H_2O_2 solution to a 2-ethoxyethanol solution of tetraisopropyl titanate [39]. All reagents were used without further purification. A typical synthesis procedure for the optimized TiO_2 sample (2-ethoxyethanol: 5 ml; rutile in bulk: 46%) is described as follows. Tetraisopropyl titanate (Aladdin, 98%, 2ml) was dissolved in 5 ml 2-ethoxyethanol ($C_2H_5OCH_2CH_2OH$, Alfa Aesar, 99%) under magnetic stirring. Then, 30 ml aqueous H_2O_2 solution (Kemiou, 30 wt%) was added to the tetraisopropyl titanate solution to form a peroxo-titanium complex. The obtained colloid solution was heated in a water bath at 50 °C for 30 min to produce an orange gel. After drying the orange gel in an oven at 120 °C overnight, the xerogel thus obtained was calcined at 500 °C for 4 h in a muffle furnace. A series of different TiO_2 nanocomposite crystals were synthesized by tuning the volume of 2-ethoxyethanol. A control sample of TiO_2 was also prepared without the introduction of 2-ethoxyethanol. The TiO_2 samples prepared are hereafter marked as n-TiO_2, in which n denotes the volume of 2-ethoxyethanol. The P-25 sample used as a standard was purchased from Evonik.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected on a PW3040/60 X'Pert PRO (PANalytical) diffractometer equipped with a Cu K_α radiation source (λ = 0.1542 nm). A continuous mode was used for collecting data in the 2θ range from 10° to 80° operating at 40 kV and 40 mA. The amount of rutile phase present in each sample was calculated using the Spurr equation [40], $F_R = 1/[1 + 0.8\ I_A(101)/I_R(110)]$, where F_R is the amount of rutile in the anatase-rutile composite, and I_A (101) and I_R (110) are the anatase and rutile main peak intensity, respectively. In addition, the crystallite size of the different samples was calculated using the Scherrer Equation $\Phi = K\lambda/\beta\cos\theta$, where Φ is the crystallite size, λ is the X-ray wavelength used, K is the shape factor, β is the full line width at the half-maximum height of the main intensity peak, and θ is the diffraction angle of the peak.

Nitrogen adsorption-desorption measurements were performed at –196 °C with a Micromeritics ASAP 2010 instrument. Prior to the measurements, the samples were degassed at 110 °C for 1 h and at 250 °C for 4 h. The specific surface areas (A_{BET}) were calculated using the BET equation. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2000EX microscope operating at 120 kV. Samples for TEM were prepared by dispersing the sample powder in methanol followed by sonication for 30 min. UV Raman spectra (325 nm laser) and visible-light Raman spectra (532 nm laser) were