Materials Science in Semiconductor Processing 74 (2018) 109–115

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Remarkably enhanced sunlight-driven photocatalytic performance of TiO_2 by facilely modulating the surface property

Xingwen Zheng, Huanhuan Liu, Junbo Zhong*, Shengtian Huang*, Jianzhang Li, Dongmei Ma

Key Laboratory of Green Catalysis of Higher Education Institutes of Sichuan, College of Chemistry and Environmental Engineering, Sichuan University of Science and Engineering, Zigong 643000, PR China

ARTICLE INFO

Keywords:
Semiconductors
Interfaces
Chemical synthesis
Catalytic properties

ABSTRACT

The photocatalytic performance of TiO_2 is critically dependent on its surface properties; therefore it is feasible to boost the photocatalytic performance of TiO_2 by modulating the surface properties of TiO_2. In this paper, a series of TiO_2 photocatalysts with remarkably enhanced photocatalytic performance were facilely prepared by a Sol-Gel method with the assistance of $(NH_4)_3PO_4$ and studied by the Brunauer-Emmet Teller (BET) method, X-ray diffraction patterns (XRD), UV–Vis diffuse reflectance spectra (DRS), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), Fourier-transform infrared (FT-IR), surface photovoltage (SPV) spectroscopy and X-ray photoelectron spectroscopy (XPS). The corresponding photocatalytic activities of the samples for Rhodamine B (RhB) decay were also examined. The obtained results substantially revealed that a much higher specific surface area, separation rate of the photo-induced charge pairs and amount of hydroxyl radicals were produced in $(NH_4)_3PO_4$-TiO_2 photocatalytic system, therefore the TiO_2 photocatalysts prepared with the assistance of $(NH_4)_3PO_4$ display a much higher photocatalytic performance than the pure TiO_2, and when the molar ratio of $(NH_4)_3PO_4/Ti(OC_4H_9)_4$ = 1.0%, the sample displays the highest photocatalytic activity among all these $(NH_4)_3PO_4$ modified TiO_2 photocatalysts.

1. Introduction

As an n-type semiconductor, TiO_2 has emerged as the most famous and prospective photocatalyst for environment purification because of its fascinating properties [1–8]. However, photocatalytic efficiency of the pure TiO_2 is still significantly inhibited by its intrinsic drawbacks [9–17], especially high recombination rate of the photo-induced electron-hole pairs, resulting in a low photocatalytic performance. Therefore, it is a key issue to enhance the photocatalytic performance of TiO_2. To achieve this goal, various strategies have been exploited to improve the photocatalytic activity of TiO_2, such as doping, surface plasmon resonance (*e.g.*, Ag, Au) and construction of heterojunctions [18–29]. All these results have well revealed that photocatalytic performance of TiO_2 can be significantly promoted by boosting the separation of the photo-induced electron-hole pairs.

According to the principle of photocatalysis, photocatalytic reaction happens on the surface of the photocatalysts. The catalytic performance of a photocatalyst is critically dependent on its surface properties [30,31], thus it is feasible to enhance the photocatalytic performance of TiO_2 by tuning the surface state properties of TiO_2.

Our previous work revealed that the surface state of TiO_2 can be altered by NH_4Cl modification [31], and the TiO_2 photocatalysts prepared with the assistance of NH_4Cl displayed excellent photocatalytic activities. Due to the similar property of NH_4Cl and $(NH_4)_3PO_4$, during the preparation process of the photocatalysts, $(NH_4)_3PO_4$ will be thermal decomposed to NH_3 and H_3PO_4, and the gaseous NH_3 and residual phosphate anions incline to alter the surface state of TiO_2 catalyst, affecting the separation rate of photo-induced charge pairs and the corresponding photocatalytic activity. Thus it is theoretically feasible to modulate the surface state properties of TiO_2 with the assistance of $(NH_4)_3PO_4$.

Herein, we describe a facile and effective way to promote the photocatalytic activity by modulating the surface state properties of TiO_2 with the assistance of $(NH_4)_3PO_4$ through a Sol-Gel route. Our experimental results manifest that adding $(NH_4)_3PO_4$ into the synthetic system dramatically enhance the specific surface area and pore volume, the separation rate of photo-generated charge pairs, the formation of active free radicals and the hydroxyl content on the surface, all these advantageous factors result in remarkably improved photocatalytic performance of TiO_2.

---

* Corresponding authors.
E-mail addresses: zxwasd@126.com (X. Zheng), 1214011263@qq.com (H. Liu), junbozhong@163.com (J. Zhong), sth499@163.com (S. Huang), lyl63@sina.com (J. Li), madongmei1127@163.com (D. Ma).

http://dx.doi.org/10.1016/j.mssp.2017.10.013
Received 15 August 2017; Received in revised form 10 October 2017; Accepted 11 October 2017

2. Experimental section

2.1. Preparation of samples

All the chemicals used in this work were analytic grade and obtained from Chengdu Kelong chemical reagent factory. TiO_2 was prepared following the procedures described in the Ref [32]. with some modification. Tetrabutylorthotitanate (17 mL) and diethanolamine (5 mL) were dissolved in ethanol (67 mL). After stirring intensively for 2 h at room temperature, a mixture of $(NH_4)_3PO_4$ aqueous solution (3 mL) and ethanol (7 mL) was added dropwise to the above solution under vigorous stirring, and then kept standing at room temperature for 2 h to form TiO_2 sol. The molar ratio of $(NH_4)_3PO_4$ /$Ti(OC_4H_9)_4$ was 0%, 0.5%, 1.0%, 1.5% and 2.0%, respectively. The dried TiO_2 gel was baked at 823 K for 2 h to obtain TiO_2 powder. The corresponding powder samples were named as 0% (TiO_2), 0.5%, 1.0%, 1.5% and 2.0%, respectively.

2.2. Characterization of the samples

Specific surface area parameters of the samples were measured on a SSA-4200 automatic surface analyzer. The crystal structures of samples were detected on a DX-2600 X-ray diffractometer using Cu/Kα radiation, 40 kV, 20 mA. The UV–Vis diffuse reflectance spectra (DRS) were measured on a TU-1907 spectrometer. The morphologies were observed on a JSM-5900 LV scanning electron microscopy (SEM), EDS analysis of the samples was performed on a JSM-7500 F SEM with an accelerating voltage of 15 kV. X-ray photoelectron spectroscopy (XPS) measurements were taken on an XSAM 800 using Mg Kα at 12 kV and 12 mA. SPV experiments were carried out on a home-built apparatus as described in the Ref [33]. Fourier-transform infrared (FT-IR) characterization was performed using an FT-IR spectrophotometer (NICOLET 6700, America) in KBr pellets. The measurement of •O_2^- was followed the methods given in the Ref [34]. using nitrotetrazolium blue chloride (NBT) method. To detect the level of •OH radicals, 10 mg of photocatalyst was added in 50 mL of aqueous solution containing 20 mM NaOH and 6 mM terephthalic acid (TA). The solution was stirred in the dark for 40 min before exposure to UV light. After irradiation with 500 W Xe lamp for 20 min, the suspension was centrifuged, and the supernatant was sampled for analysis by recording the fluorescence signal of the generated 2-hydroxyterephthalic acid (TAOH) on a fluorescence spectrometer (Cary Eclipse, Agilent, USA). The wavelength of the excitation light was 312 nm, and the scanning speed was 600 nm min^{-1}. The widths of the excitation slit and the emission slit were both 5 nm [35,36]. Photocatalytic properties of the samples were studied by measuring the decay of RhB. A 500 W Xe lamp was employed as light source. 50 mg photocatalyst was dispersed into a 50 mL of 10 mg L^{-1} RhB aqueous solution, the initial pH of RhB solution was 6.0.

3. Results and discussion

Surface area can influence the adsorption, separation and transfer ability of photo-induced charge pairs, affecting the photocatalytic performance. Therefore, it is necessary to investigate the specific surface area. As demonstrated in Table 1, the S_{BET} of the samples dramatically increases as the amount of $(NH_4)_3PO_4$ elevating. However, considering the measurements error (± 10 m^2/g), the specific surface area of the 1.0%, 1.5% and 2.0% samples exhibits no obvious difference, suggesting that $(NH_4)_3PO_4$ cannot effectively alter the S_{BET} of the samples within the amount investigated. Once heating, $(NH_4)_3PO_4$ will produce NH_3 and H_3PO_4, notably increasing the intrinsic pore volume and surface area. High surface area can provide more active sites, which is beneficial to the photocatalytic property.

Table 1
Specific surface parameters of the samples.

Sample	S_{BET} (m^2/g)	Pore volumes (cc/g)
0%	29.4	0.0140
0.5%	59.5	0.0296
1%	128.5	0.0621
1.5%	130.9	0.0644
2%	115.2	0.0571

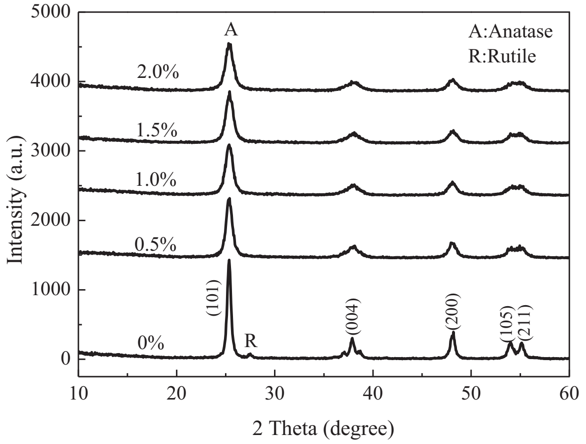

Fig. 1. XRD patterns of the samples.

The XRD profiles of the samples were displayed in Fig. 1. For the 0% sample, anatase and rutile phase were simultaneously detected. While for others, all the strong peaks situated at 2θ = 25.35°, 37.93°, 48.08°, 53.93° and 55.07° can be readily allocated to the (101), (004), (200), (105) and (211) crystal facet of the pure anatase-type TiO_2 (JCPDS No. 89-4921), substantially confirming that $(NH_4)_3PO_4$ retards the transformation of TiO_2 from anatase to rutile. As bidenate ligands, the residual phosphate anions in the samples can link firmly with the surfaces of the as-prepared TiO_2, forming $>$ Ti-O-PO_3^{2-} [37], which can effectively hinder the phase transformation. Moreover, the full width at half maximum (FWHM) of the sample gradually widens, implying the crystal sizes of the samples become small, relative small crystal size can greatly increase the S_{BET}, which accords well with the result of BET surface area. Moreover, relative small crystal size can promote the separation of photo-induced charge pairs. Compared to big crystal size, photo-induced charge pairs on the sample with small crystal size can be more easily transferred to the surface before recombination, resulting in high photocatalytic activity.

The morphologies of the samples were demonstrated in Fig. 2A-D. It is evident that all the samples possess lump-like shapes, indicating that the morphology of TiO_2 cannot be effectively altered by NH_3 and H_3PO_4. Thus, the difference in photocatalytic performance is not induced by the shape of the samples. In addition, the EDS images of the 2% sample were exhibited in Fig. 2E, it is apparent that C, Ti, P and O elements were observed, no other elements were detected, indicating that NH_3 was escaped during the heating process.

The FT-IR spectra of as-obtained samples were exhibited in Fig. 3. For the pure TiO_2, the absorption peaks at 3414 cm^{-1} and 1626 cm^{-1} are attributed to the hydroxyl group from water and Ti-OH, respectively, while the peak situated at 500 cm^{-1} could be assigned to the characteristic frequency of Ti-O-Ti. As for the PO_4^{3-}-TiO_2 samples, there are no significant differences were observed, indicating that the introduction of $(NH_4)_3PO_4$ into TiO_2 synthetic system cannot alter the structure of TiO_2, which accords well with the XRD results.

The bandgap will greatly determine the light response ability, influencing the solar-driven photocatalytic properties. Therefore, it is absolutely necessary to investigate the UV–Vis DRS of the samples. Owing to the partial overlap of the DRS of the samples prepared with the assistance of $(NH_4)_3PO_4$, thus only the UV–Vis DRS of the 0% and