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Enhanced photocatalytic activity for degrading Rhodamine B solution of commercial Degussa P25 TiO_2 and its mechanisms

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ABSTRACT

In this paper, the Degussa P25 TiO_2 (P-TiO_2) is modified by the post-treatment with the phosphorous acid, and the resulting samples are also characterized by X-ray Powder Diffraction (XRD), Raman spectra (Raman), Brunauer–Emmett–Teller (BET) surface area analyzer, Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectra (FT-IR), X-ray Photoelectron Spectroscopy (XPS), Ultraviolet–Visible Diffuse Reflectance Spectra (UV–vis DRS) and Surface Photovoltage Spectroscopy (SPS). The effects of surface-modification on the thermal stability and photocatalytic activity of the P-TiO_2 are investigated in detail. The results show that the surface-modification enhances the thermal stability of P-TiO_2, even still with a main anatase phase after thermal treatment at 900 °C, which is close related to the inhibition effects of the PO_4^{3-} groups on the surface mass diffusion as well as the directing connections of P-TiO_2 nanoparticles. Interestingly, the modified P-TiO_2 by thermal treatment at 700 and 800 °C can exhibit much higher photocatalytic activity than un-modified ones. The reasons for the activity enhancement are involved with the enhanced anatase thermal stability, consequently improving photoinduced charge separation rate, and still keeping large surface area and a certain amount of surface hydroxyl groups.

1. Introduction

Heterogeneous photocatalysis, a new water and air purification technique, has attracted great attention in the past decade [1,2]. Among many kinds of photocatalysts used up to now, TiO_2 is believed to be a promising photocatalyst for degradation of organic pollutants present in wastewater because of its high activity, low cost, chemical inertness, and photostability [3–5]. However, its photocatalytic activity is still not high enough for practical application. Thus, it is desired to improve photocatalytic activity.

The photocatalytic activity of TiO_2 system mainly depends on its intrinsic properties, such as crystal phase, specific surface area and crystallinity [1,3]. Generally, large surface area is favorable to improve photocatalytic activity. For example, Yu et al. and Alvaro et al. reported mesoporous TiO_2 with large surface area exhibits high photocatalytic activity [6,7]. The large surface area often results from small particle size or porous structure, which usually corresponds to the low anatase crystallinity. The low anatase crystallinity means too many anatase defects, further promoting the recombination of photogenerated electrons and holes [8,9]. Thus, it is expected that increasing anatase crystallinity and retaining large surface area may further improve photocatalytic activity. Recently, our group successfully synthesized high active nanocrystalline TiO_2 photocatalysts by co-modifying with ammonia and cetyltrimethylammonium bromide or by modifying with mesoporous SiO_2, and the enhanced activity was ascribed to high anatase crystallinity and large surface area simultaneously [8,10].

The most popular commercial TiO_2 named by Degussa P25 TiO_2 (P-TiO_2), containing around 85% anatase and 15% rutile, usually exhibits high photocatalytic activity [2,4]. To further improve its photocatalytic activity, several modification attempts have been successfully made. Janus and Morawski reported that the modification of P-TiO_2 was completed under elevated pressure in organic solvent atmosphere, as a result, the carbon modified P-TiO_2 exhibits higher performance for azo dyes decomposition than un-modified one [11]. Yu et al. found that the photocatalytic activity of P-TiO_2 increased after hydrothermal treatment [12]. Yu et al. demonstrated an increase of photocatalytic activity after thermal treatment of P-TiO_2 at 400 °C in air [13]. However, these attempts are all based on increasing hydroxyl groups at the surface of TiO_2. Very recently, many papers reported that phosphate could delay the formation of the anatase phase and inhibit the crystallite growth and the anatase–rutile phase transformation of TiO_2 [14–17]. Our group demonstrated that the phosphorous acid

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modified TiO_2 exhibited higher photocatalytic activity than the unmodified P-TiO_2 [17]. However, few papers about P-TiO_2 modified with phosphorous acid have been reported until now.

In this work, P-TiO_2 has been modified by cheap phosphorous acid for the first time. The phosphorous acid modified Degussa P25 TiO_2 (PP-TiO_2) by thermal treatment at high temperature exhibits higher photocatalytic activity than P-TiO_2. It can be demonstrated that the PO_4^{3-} groups should play important roles in enhancing anatase thermal stability and retaining large surface area, which are responsible for the high photocatalytic activity. This paper would provide a simple strategy to further improve the anatase thermal stability and photocatalytic activity of TiO_2. Expectedly, the enhanced thermal stability of the P-TiO_2 with high activity will expand the application areas of TiO_2, like as coating materials of ceramic tiles with self-cleaning function.

2. Experimental

All used chemicals are of the analytical grade and are used as received without further purification, and doubly deionized water is employed throughout. TiO_2 is Degussa P25 TiO_2.

2.1. Modification of materials

P-TiO_2 is modified by phosphorous acid as the following procedures. Firstly, 1.0 g P-TiO_2 powder is added to a weighing bottle (4 cm × 7 cm) containing 5 mL water under stirring, then continuously stirring for 1 h. Subsequently, 1 mL of phosphorous acid solution (2% mass percentage ratio to TiO_2) is slowly added to the bottle. After ultrasonicating for 2 min and stirring for 1 h vigorously, that bottle is kept at 80 °C in the water bath to vaporize the liquid under stirring, then dried at 100 °C for 12 h. Finally, the modified TiO_2 samples are gained by calcining corresponding dried precursors at certain temperature for 2 h, and they are referred to as PP-TiO_2-*X*, in which *X* represents the thermal treatment temperature, PP represents the phosphorous acid modified P25 TiO_2. According to the similar procedure mentioned above, the un-modified P25 TiO_2 samples, referred to as P-TiO_2-*X*, are also obtained.

2.2. Characterization of P-TiO_2

The samples are characterized by X-ray Powder Diffraction (XRD) with a Rigaku D/MAX-rA powder diffractometer (Japan), using Cu Kα radiation ($\lambda = 0.15418$ nm), and an accelerating voltage of 30 kV and emission current of 20 mA are employed. The Raman spectra of the samples are recorded with JOBIN YVON HR800 Raman spectrophotometer (France), and the used excitation wavelength is 457.9 nm with an Ar ion laser beam. The specific surface areas of the samples are measured by Brunauer–Emmett–Teller (BET) instrument (Micromeritics automatic surface area analyzer Gemini 2360, Shimadzu), with nitrogen adsorption at 77 K. Transmission Electron Microscopy (TEM) observations are carried out on a JEOL 1200EX operated at an accelerating voltage of 100 kV. The Fourier Transform Infrared Spectra (FT-IR) of the samples are collected with a Bruker Equinox 55 Spectrometer, using KBr as diluents. The surface composition and elemental chemical state of the samples are examined by X-ray Photoelectron Spectroscopy (XPS) using a Model VG ESCALAB apparatus with Mg Kα X-ray source, and the binding energies are calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV). The Ultraviolet–Visible Diffuse Reflectance Spectra (UV–vis DRS) of the samples are recorded with a Model Shimadzu UV2550 spectrophotometer. The Surface Photovoltage Spectroscopy (SPS) measurements of the samples are carried out with a home-built apparatus that had been described in detail elsewhere [18–20], the powder samples are sandwiched between two ITO glass electrodes, and the change of surface potential barrier between in the presence of light and in the dark is SPS signal. The raw SPS data are normalized with a Model Zolix UOM-1S illuminometer made in China.

2.3. Evaluation of photocatalytic activity of materials

Rhodamine B (RhB) is one of the common chemicals used widely in the industrial production, which often causes environmental pollution [5]. Therefore, it is chosen as representative organic substance to evaluate the photocatalytic activity of the synthesized TiO_2 samples, and the high photocatalytic degradation rate corresponds to the high photocatalytic activity. The photocatalytic experiments are carried out in a 100 mL of photochemical glass reactor, and the light is provided from a side of the reactor by a 150 W GYZ220 high-pressure Xenon lamp made in China without any filter, which is placed at about 13 cm from the reactor. To examine the photocatalytic degradation rate of RhB, 0.1 g of the TiO_2 sample and 40 mL of 10 mg/L RhB solution are mixed by magnetic stirrer for 30 min in the dark firstly, in order to make the reactive system uniform and the adsorption–desorption equilibrium, then begin to illuminate. After photocatalytic reaction for 1 h, the RhB concentration is analyzed by the optical characteristic absorption at the wavelength of 553 nm of RhB solution after centrifugation with a Model Shimadzu UV2550 spectrophotometer [5]. To obtain the evolution curves of photocatalytic degradation of RhB, 0.2 g of the TiO_2 sample and 80 mL of 20 mg/L RhB solution are employed and the RhB concentrations after photocatalytic reaction for different time are measured.

3. Results and discussion

3.1. Measurements of XRD and Raman

The XRD peaks at $2\theta = 25.28^\circ$ and $2\theta = 27.40^\circ$ are often taken as the characteristic peaks of anatase (1 0 1) and rutile (1 1 0) crystal phase, respectively [20,21]. The mass percentage of anatase phase in the TiO_2 samples can be estimated from the respective integrated characteristic XRD peak intensities using the quality factor ratio of anatase to rutile (1.265), and the crystallite size can also be determined from the broadening of corresponding X-ray spectral peak by Scherrer formula [21]. It can be confirmed from Fig. 1A that the P-TiO_2 has a mixed phase with 85% anatase and 15% rutile, and its anatase crystallite size is about 20 nm. As the thermal treatment temperature rises, the rutile content gradually increases. When the temperature increases to 800 °C, the rutile phase content is nearly 50%. After the thermal treatment at 900 °C, there is only rutile phase. Compared with the P-TiO_2, PP-TiO_2 exhibits high anatase thermal stability since the phase transformation begins to occur at about 800 °C (Fig. 1B), even still with a main anatase phase (75%) after the thermal treatment at 900 °C, demonstrating that the modification with phosphorous acid can effectively inhibit the phase change so as to enhance anatase thermal stability. This is in good agreement with the literature [14–16].

In the Raman spectrum of TiO_2, the peaks, centering at 143, 199, 396, 514 and 636 cm^{-1}, are attributed to the anatase phase, while other peaks, located at 235, 443, 608 and 826 cm^{-1}, are characteristic of the rutile phase [22,23]. It can be confirmed from Fig. 2A that P-TiO_2 contains only anatase phase, which is due to too low amount of rutile phase. However, a small amount of rutile appears in the P-TiO_2-800, and there is only rutile phase in the P-TiO_2-900. Compared with P-TiO_2, PP-TiO_2 has high thermal stability of anatase phase, since the characteristic rutile Raman peaks with rather low intensity can be seen only after the thermal treatment at 900 °C (Fig. 2B).