Hydrothermal synthesis of well-dispersed ultrafine N-doped TiO$_2$ nanoparticles with enhanced photocatalytic activity under visible light

Shaozheng Hu [a], Anjie Wang [a,b,*], Xiang Li [a,b], Holger Löwe [c]

[a] State Key Laboratory of Fine Chemicals, Department of Catalysis, Dalian University of Technology, Dalian 116012, PR China
[b] Liaoning Key Laboratory of Petrochemical Technology and Equipments, Dalian University of Technology, Dalian 116012, PR China
[c] Institute of Organic Chemistry, Johannes Gutenberg University Mainz, Duisbergweg 10-14, 55128 Mainz, Germany

ARTICLE INFO

ABSTRACT

Ultrafine nitrogen-doped TiO$_2$ nanoparticles with narrow particle size distribution, good dispersion, and high surface area were synthesized in the presence of urea and PEG-4000 via a hydrothermal procedure. TEM observation, N$_2$ adsorption, XRD, UV–vis spectroscopy, the Raman spectroscopy and XPS analysis were conducted to characterize the synthesized TiO$_2$ particles. The synthesized TiO$_2$ particles were a mixture of 49.5% anatase and 50.5% rutile with a size of around 5 nm. The photocatalytic activities were tested in the degradation of an aqueous solution of a reactive Brilliant Blue KN-R under both UV and visible light. The synthesized TiO$_2$ particles showed much higher photocatalytic activity than a commercial P25 TiO$_2$ powder under both UV and visible light irradiations. The high performance is associated to N doping, the reduced particle size, good dispersion, high surface area, and a quantum size effect.

1. Introduction

As a photocatalyst, TiO$_2$ is widely used for the decomposition of various organic pollutants because of its low-cost, chemical stability, and non-toxicity [1]. However, due to its wide band gap (3.2 eV for anatase), TiO$_2$ can be excited only with UV light, which accounts for only a small fraction of solar light (3–5%). Therefore, it is highly desirable to develop TiO$_2$-based photocatalysts with enhanced activities under visible light.

The photocatalytic performance of TiO$_2$ particles are highly related with the particle size and dispersion. The quantum size effect becomes significant in the photocatalysis of TiO$_2$ particles when the particle size is smaller than 10 nm, leading to a widening of the band gap and thus to the enhancement of redox ability of photogenerated electron–hole pairs [2]. In addition, reduction in the particle size increases the number of surface active sites, thus improving the surface charge carrier transfer rate in photocatalysis [3]. High surface area favors the adsorption of hydroxyl groups, which is a prerequisite in photocatalytic reactions. Dispersion is another important factor affecting the photocatalytic performance of TiO$_2$ nanoparticles because high

dispersion facilitates the adsorption of reactants over the surface of TiO$_2$ particles.

Although the reduction in particle size can enhance the photoactivity, the adsorption band will be blue-shifted, making it more difficult to utilize solar energy. Recently, N doping into TiO$_2$ has been reported to be one of the most effective approaches to enhance the visible light activity. However, the mechanism of the enhancement by N-doping is still controversial. Asahi et al. [4] claimed that the doped N atoms narrowed the band gap of TiO$_2$ by mixing N 2p and O 2p states, thus explaining the activity for the decomposition of acetone and methylene blue. Irie et al. [5] argued that the isolated narrow band located above the valence band is responsible for the visible light response. Ihara et al. [6] suggested that the visible light activity is attributed to the oxygen vacancies caused by N doping.

Heating TiO$_2$ powders in N$_2$ and/or NH$_3$ at elevated temperatures is the conventional method to prepare N-doped TiO$_2$[4,5]. However, high temperature generally gives rise to particle agglomeration and collapse of pore structure, leading to remarkable surface area reduction. Therefore, new strategies for preparing N-doped TiO$_2$, such as sputtering [7], sol–gel preparation [8], ion implantation [9], pulsed laser deposition [10], plasma surface modification [11], solvothermal synthesis [12], and hydrothermal synthesis [13,14], have been proposed more recently.

In the hydrothermal approach, the nitrogen sources include urea, triethylamine, and triethanol amine. Peng et al. [13] found that the chemical environment of nitrogen was as Ti–N–Ti–O and

* Corresponding author at: School of Chemical Engineering, Dalian University of Technology, Dalian 116012, PR China. Tel./fax: +86 411 39893693.
E-mail address: ajwang@dlut.edu.cn (A. Wang).

Ti–O–N in the lattice. Kometani et al. [14] reported that the efficiency of nitrogen doping was strongly dependent on the kind of nitrogen compound, treatment method as well as treatment temperature.

In the present work, we report a facile hydrothermal method to synthesize ultrafine N-doped TiO_2 nano-particles. PEG-4000 was used to improve the dispersion of the synthesized TiO_2 particles. The synthesized TiO_2 particles were tested in the photocatalytic degradation of a reactive dyestuff in aqueous solution under UV light and visible light. The possible mechanism of N doping is also discussed.

2. Experimental

2.1. Preparation and characterization

0.8 ml $TiCl_4$ was added dropwise into 20 ml de-ionized water at 0 °C under stirring to obtain solution A. 0.015 g PEG-4000 and 0.2 g urea were dissolved in 10 ml de-ionized water at room temperature to form solution B. The above solutions were mixed and stirred for 10 min. The resulting mixture was transferred into a 30 ml stainless steel autoclave, and heated at 105 °C for 6 h. The obtained white precipitate was washed with deionized water, separated by centrifugation and dried at room temperature overnight under vacuum. The obtained TiO_2 powder is denoted as AR50. For comparison, three other TiO_2 samples were prepared in the presence of urea (U-TiO_2), in the presence of PEG-4000 (P-TiO_2), and in the absence of urea and PEG-4000 (H-TiO_2) in a similar way. To investigate the effect of particle size, AR50 was calcined at 500 °C for 10 h to obtain C-TiO_2.

XRD patterns of the prepared TiO_2 samples were recorded on a Rigaku D/max-2400 instrument using Cu-Kα radiation (λ=1.54 Å). TEM images were taken on a Philips Tecnai G220 model microscope. UV–vis spectroscopy measurement was carried out on a Jasco V-550 spectrophotometer, using $BaSO_4$ as the reference sample. Nitrogen adsorption was measured at −196 °C on a Micromeritics 2010 analyzer. BET Surface area was calculated according to the adsorption isotherm. Raman spectra were collected on a home-made DL-2 Raman spectrometer. The samples were excited with a 532 nm line of a SUNTECH DPGL-2200 laser. An acton triple monochromator was used as spectrometer for Raman scattering. The spectra were collected by a Prinston CCD detector. The power of the 532 nm laser line was below 5 mW at the sample. XPS measurements were conducted on a Thermo Escalab 250 XPS system with Al Kα radiation as the exciting source. The binding energies were calibrated by referencing the C 1 s peak (284.6 eV) to reduce the sample charge effect.

2.2. Photocatalytic reaction

KN-R, a type of anthraquinone dye, is more difficult to decolorize than azo dyes because of its conjugated structure [15]. Therefore, KN-R was selected as model compound to evaluate the photocatalytic performance of the prepared TiO_2 particles in an aqueous solution under visible light and UV irradiations. 40 mg of TiO_2 powder were dispersed in 100 ml KN-R solution (50 ppm) in an ultrasound generator for 10 min. The suspension was transferred into a 250 ml beaker and stirred for 30 min in the dark to achieve the adsorption equilibrium. For photoreaction under visible light irradiation, the suspension was exposed to a 110 W high-pressure sodium lamp with main emission in the range of 400–800 nm, and bubbled with air (130 ml/min). The UV light portion of the sodium lamp was filtered by a 0.5 M $NaNO_2$ solution [16]. In the investigation of

photodegradation by UV light, a 125 W high-pressure mercury lamp with a water-cooled cylindrical jacket was used. All runs were conducted at 25 °C and atmospheric pressure. The concentrations of KN-R before and after reaction were measured by means of a UV–vis spectrophotometer at a wavelength of 600 nm.

The percentage of degradation D% was determined as follows:

$$D\% = \frac{A_0 - A}{A_0} \times 100\% \tag{1}$$

where A_0 and A are the absorbances of the liquid sample before and after degradation, respectively.

The reaction rate constant k was obtained by assuming that the reaction followed first order kinetics [17]. In a batch reactor, the performance equation is as follows:

$$-\ln(C/C_0) = kt \tag{2}$$

where C_0 and C represent the concentrations of KN-R dye before and after photocatalytic degradation, respectively. If a linear relationship is established when $-\ln(C/C_0)$ is plotted against t, the rate constant k can be obtained from the slope of the line.

3. Results and discussion

Fig. 1 shows the XRD patterns of the synthesized TiO_2 particles and a commercial TiO_2 powder (P25). The patterns indicate that each sample was a mixture of anatase and rutile phases. The phase contents of the samples were estimated from their XRD patterns by the following equation [18]:

$$x_A = \frac{1}{1 + 1.26 \times \frac{I_R}{I_A}} \tag{3}$$

where x_A is the fraction of anatase phase, I_R and I_A are the intensities of the anatase (1 0 1) and rutile (1 1 0) diffraction peaks, respectively. The contents of anatase phase in AR50, P-TiO_2, U-TiO_2, H-TiO_2 and C-TiO_2 were estimated to be 49.5%, 49.3%, 49.7%, 49.3% and 49.7%, respectively, indicating that the addition of urea and/or PEG-4000 did not change the phase content of the synthesized samples. The synthesized TiO_2 particles have lower anatase contents than P25 (76%).
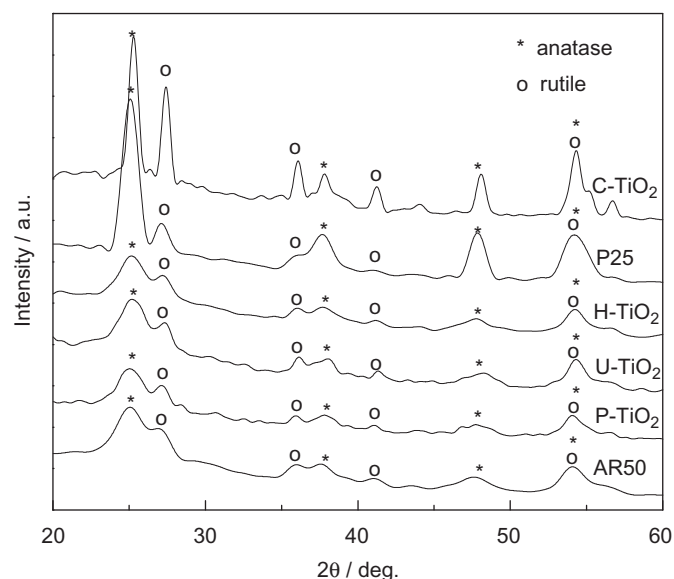

Fig. 1. XRD patterns of the synthesized and a commercial P25 TiO_2 particles.