Research Article

Sonochemical Synthesis, Characterization, and Photocatalytic Activity of N-Doped TiO₂ Nanocrystals with Mesoporous Structure

Tiekun Jia,¹ Fang Fu,¹ Junwei Zhao,¹ Jian Chen,¹ Xiaofeng Wang,¹ Zhenghua Fan,¹ Lijun Cui,¹ and Fancheng Meng²

¹ Department of Materials Science and Engineering, Luoyang Institute of Science and Technology, Luoyang 471023, China

² School of Materials Science and Engineering, Chongqing University of Technology, Chongqing 400050, China

Correspondence should be addressed to Tiekun Jia; tiekunjia@126.com

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N-Doped TiO₂ nanocrystals were synthesized via a simple sonochemical route, using titanium tetrachloride, aqueous ammonia, and urea as starting materials. The as-synthesized samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) equipped with an energy dispersion X-ray spectrometer (EDS), transmission electron microscopy (TEM), UV-vis diffuse reflection spectroscopy, Raman spectroscopy, and nitrogen adsorption-desorption isotherms. The results of TEM and nitrogen adsorption-desorption showed that the average size and specific surface area of the as-synthesized nanocrystals are 10 nm and 107.2 m²/g, respectively. Raman spectral characterization combined with the results of XRD and EDS revealed that N dopant ions were successfully doped into TiO₂. Compared with pure TiO₂, the adsorption band edge of N-doped TiO₂ samples exhibited an obvious red shift to visible region. The photocatalytic activities were evaluated by the degradation of Rhodamine B (RhB) under visible light, and the results showed that the N-doped TiO₂ sample synthesized by an optimal amount of urea exhibited excellent photocatalytic activity due to its special mesoporous structure and the incorporation of nitrogen dopant ions.

1. Introduction

Titanium dioxide (TiO₂) has attracted increasing attention for its unique physicochemical properties and wide applications in photocatalysts [1–3], lithium batteries [4], gas sensors [5], and solar cells [6, 7]. Among these applications, TiO₂ has been known as the most efficient photocatalysts due to its strong oxidizing power, cost effectiveness, and long-time stability against photocorrosion and chemical photocorrosion. Up to now, it has found potential application in self-cleaning coating, air purification, water purification, and water sterilization. However, pure TiO₂ has a wide band gap (3.2 eV) and only exhibits photocatalytic properties in the ultraviolet (UV) range (<385 nm). Furthermore, only 5% of the total irradiated natural sunlight is utilized to generate photosensitization [8]. Therefore, it is urgent to modify TiO₂ to gain the visible-light driven photocatalysts for utilizing solar energy efficiently.

Numerous efforts have been directed towards the modification of TiO₂ by the incorporation of metal and nonmetal dopant ions in order to improve the photocatalytic activity under visible illumination [9–14]. Compared with metal ions doping, nonmetal ions doping is environmentally friendly, which has less negative effect on the environment and ecosystem. Consulting the previous literatures [10–14], doping TiO₂ with nitrogen is one of the most effective means of narrowing the band gap and thus expands the light response range to visible light region. Surmacki et al. prepared nitrogen doped TiO₂ powders by an electron beam irradiation method [10]. Chen et al. synthesized nitrogen doped TiO₂ through a heat treatment in ammonia atmosphere route [11]. Zhou et al. proposed a hydrothermal route assisted by ultrasonic irradiation to synthesize nitrogen doped TiO₂ nanocrystals, using ethylenediamine, ethylene oxide/propylene oxide block copolymer (F127), and TiCl₄ as raw materials [12]. Qian et al.

proposed a sol-gel route for the synthesis of nitrogen doped TiO_2 nanoparticles, using tetrabutyl titanate (TBT) and urea as starting materials [13]. All the above-mentioned approaches have been proven to be impressive and effective; however, there exist some disadvantages and challenges in the synthetic process as follows. The first is that the conventional approaches need some special instruments, harsh conditions, and/or relatively toxic starting materials hazardous to environment. The second challenge is the phase purity and the yields of nitrogen-doped TiO_2 nanocrystals. The third is high specific surface area which is critical for the enhancement of photocatalytic activity of nitrogen-doped TiO_2 nanocrystals. Therefore, a simple and environment friendly approach is strongly desirable for the synthesis of nitrogen-doped TiO_2 nanocrystals with large scale.

In this paper, we reported the preparation of N-doped TiO_2 nanocrystals with mesoporous structure via a fast sonochemical route followed by calcination, using titanium tetrachloride, aqueous ammonia, and urea as starting materials. A series of measurements, including XRD, SEM, TEM, BET, and Raman spectrum, were performed to characterize the prepared N-doped TiO_2 samples. The photocatalytic activities of the as-obtained samples were evaluated by the degradation of RhB under visible-light irradiation.

2. Experimental Details

2.1. Preparation of N-Doped TiO_2 . All the reagents were used as received without purification. In a typical procedure, 7.5 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ (28 wt%) was added into 60 mL deionized water; then a certain amount of urea was added into the above solution under magnetic stirring to obtain homogeneous solution (labeled as solution A). 10 mL TiCl_4 was mixed with 10 mL glycol and 40 mL deionized water under magnetic stirring to obtain homogenous solution (labeled as solution B). Solution A was dropped into solution B under constant magnetic stirring. The pH value of the obtained solution was adjusted to be 4.3 by the addition of diluted H_2SO_4 (1 M). After stirring for 30 min, the above solution was irradiated by the 40 kHz ultrasonic wave at the power of 100% (240 W) for 30 min. The final suspended solution was aged at the room temperature for 6 h. The products were centrifuged and washed with distilled water and ethanol for several times, followed by drying in a vacuum oven at 80°C for 10 h. The dried products were crushed to obtain fine powders and further calcined at 500°C for 2 h to obtain the catalysts with a heat rate of $2^\circ\text{C}/\text{min}$. For the comparison, undoped TiO_2 was prepared according to the similar procedure, using $\text{NH}_3 \cdot \text{H}_2\text{O}$ as precipitation agent in the absence of urea.

2.2. Characterization. XRD pattern patterns were obtained on a Bruker D8 Advance X-ray diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV and 40 mA in a scanning range of $10^\circ - 70^\circ$. FESEM images were observed by a Hitachi S-4800 field emission scanning electron microscope equipped with an energy dispersion X-ray spectrometer (EDS). TEM images were recorded on a Philips Tecnai G20 microscope, operated at an acceleration voltage of 200 kV.

FIGURE 1: XRD patterns of the as-obtained samples synthesized under different conditions: (a) pure TiO_2 ; (b) NT1; (c) NT3; (d) NT2.

UV-vis diffuse reflectance spectra were recorded by a UV-vis spectrophotometer (TU 1901, Puxi) with BaSO_4 as reference. Raman spectra were recorded by using Renishaw inVia spectrometer at the room temperature, and the 514 nm line of an Ar^+ laser was used as the excitation source. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Quantachrome NOVA 2000e absorption analyzer after samples were vacuum-dried at 473 K overnight.

2.3. Photocatalytic Experiments. The photocatalytic activity was evaluated by the decolorization of RhB aqueous solution under visible light irradiation. As reported in our previous work [15, 16], 30 mL RhB aqueous solution with a concentration of $1.0 \times 10^{-5} \text{ M}$ was added into the dish with 0.1 g prepared catalyst. A 150 W halogen lamp was used as light source to trigger the photocatalytic reaction. A glass attenuation slice (70%) and a 420 nm cut-off quartz optical filter were placed in the front of the lamp. The distance between the lamp and the dish coated by the catalysts was 15 cm. Prior to irradiation, an adsorption-desorption equilibrium was demanded to reach among the catalyst, RhB, and water in the dark. After irradiating for a certain time, the reacted solution was filtrated to measure the concentration variation of RhB by recording the variation of the intensity of absorption peak centered at 554 nm using an UV-visible spectrophotometer (TU1901, Puxi, China). Consulting the literatures [17, 18], the photodegradation of efficiency of RhB was evaluated by C/C_0 , where C is concentration of the RhB solution at reaction time t and C_0 is the adsorption-desorption equilibrium concentration of RhB solution (at reaction time 0).

3. Results and Discussion

3.1. Phase and Morphology. XRD patterns of the as-obtained samples synthesized under different conditions are shown in Figure 1. Herein, the N-doped TiO_2 samples synthesized with different molar ratios of urea to TiCl_4 of 1, 3, and 5 are labeled as NT1, NT2, and NT3, respectively. From Figure 1, it can be found that the XRD patterns of the pure and N-doped TiO_2 samples exhibit the same diffraction peaks at 2θ of 25.3° , 37.0° , 37.8° , 38.3° , 48.1° , 53.5° , 55.1° , 62.5° , and 68.9° . All the characteristic diffraction peaks are assigned to the anatase TiO_2 with lattice parameters comparable to the standard values (JCPDS, number 84-1285). Furthermore, it is noteworthy to be mentioned that the diffraction peaks of N-doped TiO_2 samples have no change with the increase of the dosage of urea. However, compared with those of pure TiO_2 samples, the diffraction peaks of N-doped TiO_2 samples tended to become slightly broader and the relative intensity decreased, revealing that the crystal size of N-doped TiO_2 samples decreased due to the incorporation of nitrogen ions.

Figure 2 shows the FESEM image and its EDS mapping of the NT2 sample. As seen in the typical FESEM image (Figure 2(a)), the as-prepared NT2 sample is composed of a large scale of nanoparticles. O-mapping, N-mapping, and Ti-mapping are shown in Figures 2(b), 2(c), and 2(d), respectively, revealing that as-prepared NT2 sample consists of O, N, and Ti elements. The microstructure of as-prepared NT2 sample was investigated with transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). Figure 3(a) is the TEM image with its SAED pattern inset. Figure 3(b) is the HRTEM image of the as-prepared NT2 sample. It is clearly observed from Figure 3(a) that the average size of the nanocrystal is about 10 nm. Additionally, the Debye rings shown in the inset of Figure 3(a) suggest a sequence of diffraction rings consistent with what is expected for anatase N-doped TiO_2 as the nanocrystal of the mesoporous sample. As shown in Figure 3(b), the average space between adjacent lattices is 0.35 nm, which is assigned to be the (101) planes of anatase TiO_2 .

3.2. BET Surface Area and Pore Volume. Nitrogen adsorption and desorption were used to determine the specific surface area, pore volume, and pore size of the sample. Figure 4 shows the nitrogen adsorption-desorption isotherm and its pore size distribution of the obtained NT2 sample. From Figure 4, it can be concluded that the Barrett-Joyner-Halenda (BJH) pore size distribution and nitrogen adsorption-desorption isotherm correspond to type IV isotherm. As shown in Figure 4(a), the sharp decline in the desorption curve occurred, suggesting that the NT2 sample was mesoporous in nature. The specific surface area estimated by Brunauer-Emmett-Teller method is $107.2 \text{ m}^2/\text{g}$. Furthermore, some macropores were also observed in the BJH pore size distribution curve, which perhaps resulted from the ultrasound-induced aggregation effect [19]. Additionally, the nitrogen adsorption-desorption isotherms and pore size distribution curves of NT2 sample were similar to those of NT1 and NT3 samples and no obvious differences were observed. Therefore,

the other two curves of the NT1 and NT3 samples were not presented in this paper.

3.3. Raman Spectra and UV-Vis Spectra. Raman spectra were employed to further investigate the phase structure of pure TiO_2 and N-doped TiO_2 samples. Figure 5 shows Raman spectra of pure TiO_2 and NT2 samples. It can be observed from Figure 5 that peaks centering at 145 cm^{-1} (E_g , very strong), 197 cm^{-1} (E_g , weak), 401 cm^{-1} (B_{1g} , medium), 519 cm^{-1} ($A_{1g} + B_{1g}$, medium), and 637 cm^{-1} (E_g , medium) are present, corresponding to the vibrations of the anatase lattice [20], which is consistent with the result of XRD patterns. Additionally, compared with those of the pure TiO_2 sample, the intensity of the peaks of NT2 sample was enhanced in this study, which was in agreement with the previous literature [10, 20].

Figure 6 shows the UV-vis absorbance spectra of pure TiO_2 , NT1, NT2, and NT3 samples. Compared with pure TiO_2 , the adsorption band edge of N-doped TiO_2 samples extends to the visible region. Additionally, it can also be seen that, with the amounts of urea increasing, the adsorption edge of the N doped TiO_2 samples shifts to high wavelength region firstly when the urea : Ti^{4+} molar ratio reaches 3 : 1 and then shifts to low wavelength region when the urea : Ti^{4+} molar ratio reaches 5 : 1 conversely, revealing that the band gap of NT2 sample is smaller than those of NT1 and NT3 samples.

3.4. Photocatalytic Activity. Figure 7 presents the variations of absorbance spectra of aqueous RhB in the presence of pure TiO_2 , NT1, NT2, and NT3 samples at different periods of time under visible light irradiation. It is clearly observed from Figure 7(a) that the intensity of the characteristic adsorption peak of RhB at about 554 nm decreased with the irradiation time in the degradation process. Meanwhile, the color of the suspension faded away gradually with the irradiation time prolonging in the experiment. The percentage degradation of RhB aqueous solution induced by NT2 sample was about 94% when the irradiation time reached 60 min. The photocatalytic performance of different photocatalysts with otherwise identical conditions under visible light irradiation is shown in Figure 7(b). Blank test (RhB without any catalyst) exhibited little photolysis. Meanwhile, the variation of the concentration of RhB with the catalysts in the dark was unobvious, revealing that the adsorption of RhB on the as-prepared photocatalysts was negligible after the adsorption-desorption equilibrium was reached. Furthermore, it was also observable that pure TiO_2 and N-doped TiO_2 samples had different photocatalytic activity rates, and the order was as follows: NT2 > NT3 > NT1 > pure TiO_2 . Accordingly, it comes to a conclusion that the NT2 sample had high photocatalytic efficiency. The reason could be explained as follows. It is well known that the crystallite phase, crystallite size, surface area, and porosity have a significant effect on the photocatalytic activity of TiO_2 -based photocatalysts. In this paper, the most important cause for the enhancement of the photocatalytic activity is the adsorption shift to the visible light region due to the incorporation of nitrogen ions, which leads to the improvement of interfacial charge transfer and the

FIGURE 2: FESEM image and EDS mapping of the NT2 sample: (a) the panoramic FESEM image; (b) O-mapping; (c) N-mapping; (d) Ti-mapping.

FIGURE 3: (a) TEM image with its SAED pattern inset and (b) HRTEM image of the NT2 sample.

inhibition of charge recombination when the amount of urea is relatively low. Excessive nitrogen ions in doped TiO_2 samples may act as a recombination center, leading to the deterioration of the photocatalytic activity, when the urea: Ti^{4+} molar ratio reaches 5:1. Based on the above

analysis, the optimal ratio of N/Ti^{4+} is crucial for the improvement of the photocatalytic activity. Additionally, the NT2 sample has high specific surface area and produces numerous surface reaction sites due to its mesoporous structure. Furthermore, the small grain size results in a shorter

FIGURE 4: (a) The nitrogen adsorption-desorption isotherm and (b) the corresponding pore size distribution of the NT2 sample.

FIGURE 5: Raman spectra of the pure TiO_2 and NT2 sample.

FIGURE 6: UV-vis absorbance spectra of pure TiO_2 , NT1, NT2, and NT3 samples.

distance for photoinduced electrons and holes to transfer to reaction sites, which is beneficial for the improvement for photocatalytic activity. That is why the NT2 sample excels the NT1, NT3, and pure TiO_2 samples in the degradation of RhB aqueous solution.

4. Conclusions

In summary, N-doped TiO_2 nanocrystals were successfully prepared via a simple sonochemical route. The N-doped TiO_2 sample with the size of about 10 nm has higher specific surface area with mesoporous structure. The investigation of the photocatalytic activity revealed that N-doped TiO_2 nanocrystals have excellent photocatalytic activity, which was attributed to the dopant ions induced elevated visible light

absorption and its special mesoporous structure. Moreover, our route for synthesizing N-doped TiO_2 nanocrystals is environmentally friendly with the advantages of low cost, simple processing, and easy large-scale production. This synthetic route may be scaled up for industries application.

Conflict of Interests

The authors declared that they do not have a direct financial relation with the commercial identities mentioned in this

FIGURE 7: (a) The variations of absorbance spectra of aqueous RhB in the presence of the NT2 sample at different periods of time under visible light irradiation; (b) the comparisons of photocatalytic degradation activity of different photocatalysts, including pure TiO_2 , NT1, NT2, and NT3 samples.

paper that might lead to any conflict of interests for any of the authors.

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