

Research Article

The Photocatalytic Property of Nitrogen-Doped TiO₂ Nanoball Film

Haiying Wang and Yanchun Hu

College of Physics and Electronic Engineering, Henan Normal University, Xinxiang, Henan 453007, China

Correspondence should be addressed to Haiying Wang; why@htu.cn

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TiO₂ nanoball films of nitrogen doping and no doping were prepared by anodic oxidation method. The nitrogen-doped samples exhibited significant enhanced absorption in visible light range, narrowing band gap from 3.2 eV to 2.8 eV and the smaller nanoball diameter size. The concentrations of methyl blue reduce to nearly 44% after 4-hour photodecomposition test by nitrogen-doped sample. It is indicated that there may be two main reasons for the enhanced photocatalytic activity: the increase of O vacancy and photocatalytic reactivity surface area in nitrogen-doped samples.

1. Introduction

Due to the strong photocatalytic activity, antiphotocorrosion ability, biologic compatibility, and chemical stability of TiO₂, TiO₂ has become the most promising photocatalyst [1–4]. However, the wideband gap of TiO₂ (3.2 eV for the anatase phase and 3.0 eV for the rutile phase) needs ultraviolet (UV) light for electron-hole separation, which is only 5% of the natural solar light [5]. It is of great significance to enlarge the TiO₂ absorption band border to visible light range and to improve the photocatalytic efficiency of the TiO₂ that can be used in visible light irradiation.

Recently, it was recognized that compared with metal doping (Ca²⁺, Sr²⁺, and Ba²⁺) [6], transition metal ions (Fe³⁺, Cr⁶⁺, Co³⁺, and Mo⁵⁺ [7–10]), rare earth cations (La³⁺, Ce³⁺, Er³⁺, Pr³⁺, Gd³⁺, Nd³⁺, and Sm³⁺) [11], and some nonmetal doping (C [12], S [13], and F [14, 15]), nitrogen-doped TiO₂ exhibited a valid process for narrowing the band gap and demonstrated a more appropriate solution for extending the photocatalytic activity of TiO₂ into the visible region [16–22]. Macak et al., and Shankar et al., and Allam and El-Sayed pointed out that the morphology, crystallinity, composition, and illumination geometry of nanotube arrays were critical factors in their performance as photoelectrodes [23–25]. TiO₂ nanostructure materials displayed high performance for their potential in improving photocatalytic activity because of their high surface area.

In this work, the N-doped nanoball films were prepared and their photocatalytic activities were evaluated by the degradation of methyl blue under visible light irradiation.

2. Experimental

The titanium foils (0.6 mm thick, 99.5% purity, and cut in 1 cm × 2 cm) were used as the substrates for the growth of the TiO₂ nanowire arrays. The titanium sheets were cleaned by sonicating in 1 : 1 acetone and ethanol solution, followed by being rinsed with deionized water and dried in airstream. The anodization was carried out in a two-electrode electrochemical cell with a graphite sheet as the cathode at a constant potential 60 V. A DC power supply (WYK-6010, 0–60 V, and 0–10 A) was used to control the experimental current and voltage for 1.2 h. The electrolyte contained 0.5 wt% NH₄F, 5 mL H₂O, and 195 mL ethylene glycol. After anodization, the specimens were cleaned in 10% HCl by ultrasonic immediately for 20 minutes and dried in airstream. Postannealing in air at 700°C was employed to transform the amorphous titania to nanocrystalline TiO₂ and remove most of the organic and inorganic species encapsulated in the arrays. Nitrogen doping was carried out by annealing the samples in ammonia atmosphere at 520°C. The reagents—acetone (CH₃COCH₃), ethanol (C₂H₅OH), ammonium fluoride (NH₄F), and ethylene glycol (C₂H₆O₂)

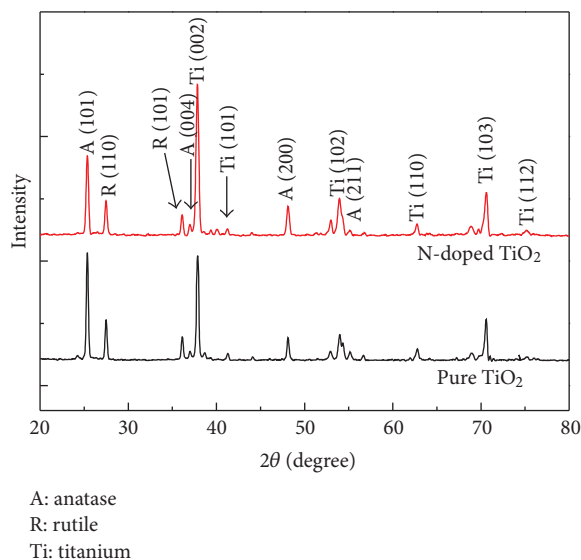


FIGURE 1: XRD patterns of nitrogen-doped and undoped TiO_2 nanoball films.

were of analytical grade without further purification. The water used in all the experiments was deionized water.

The crystal structures of samples were characterized by X-ray diffraction (XRD, Bruker AXS D8 Advance diffractions) using $\text{Cu K}\alpha$ radiation. The surface morphologies and thickness of the nanoball films were observed by scanning electron microscopy (SEM, S-4800). The X-ray photoelectron spectroscopy (XPS) experiments were performed on a VG MultiLab 2000 spectrometer to obtain the information on chemical binding energy of the TiO_2 nanoballs which was calibrated with the reference to the C 1s peak at 284.6 eV. The UV-visible absorption spectra were measured using a Cary 5000 UV-Vis-NIR spectrophotometer; BaSO_4 was used as a reflectance standard in a UV-visible diffuse reflectance experiment. The photocatalytic activities under visible light irradiation were evaluated by the degradation of methyl blue irradiated by a 450 W xenon lamp. In the process, a TiO_2 nanoball film with dimensions of $0.5 \text{ cm} \times 0.5 \text{ cm}$ was immersed into a quartz colorimetric cuvette filled with 3 mL 10 mg/L methylene blue (MB) solution and placed below xenon lamp. The distance between the film and the lamp is 10 cm distance. And the intensity of the light incident on the samples is measured about 900 mW/cm^2 . The solution in the photoreactor was placed in dark for 30 minutes to reach the absorption-desorption equilibrium of the dye molecules on the sample surface. After 30-minute visible-light irradiation and 5-minute waiting, the content of methyl blue was measured by Cary 5000 UV-Vis-NIR spectrophotometer and the deionized water was used as a reflectance standard. Then the process was repeated for 8 times to get degradation data.

3. Results and Discussion

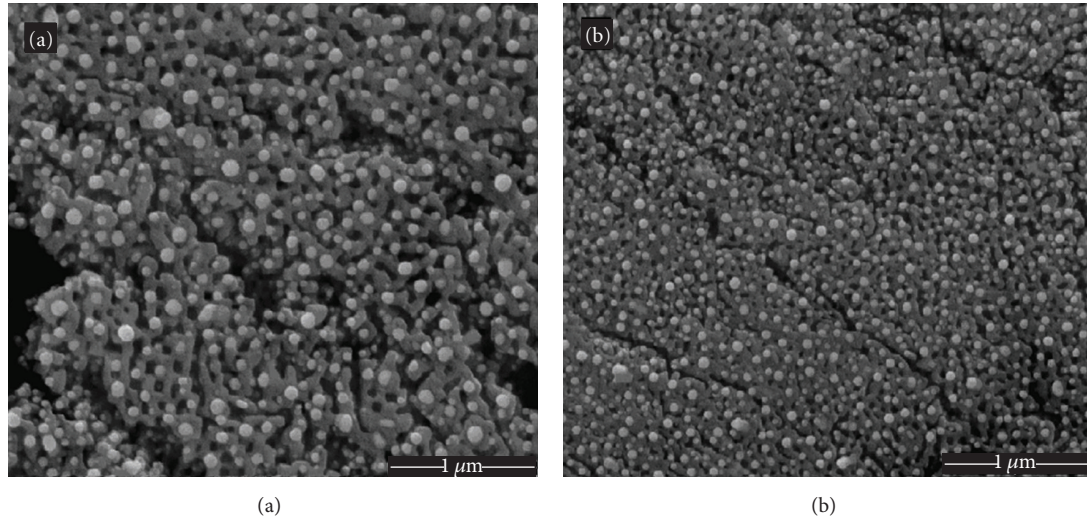
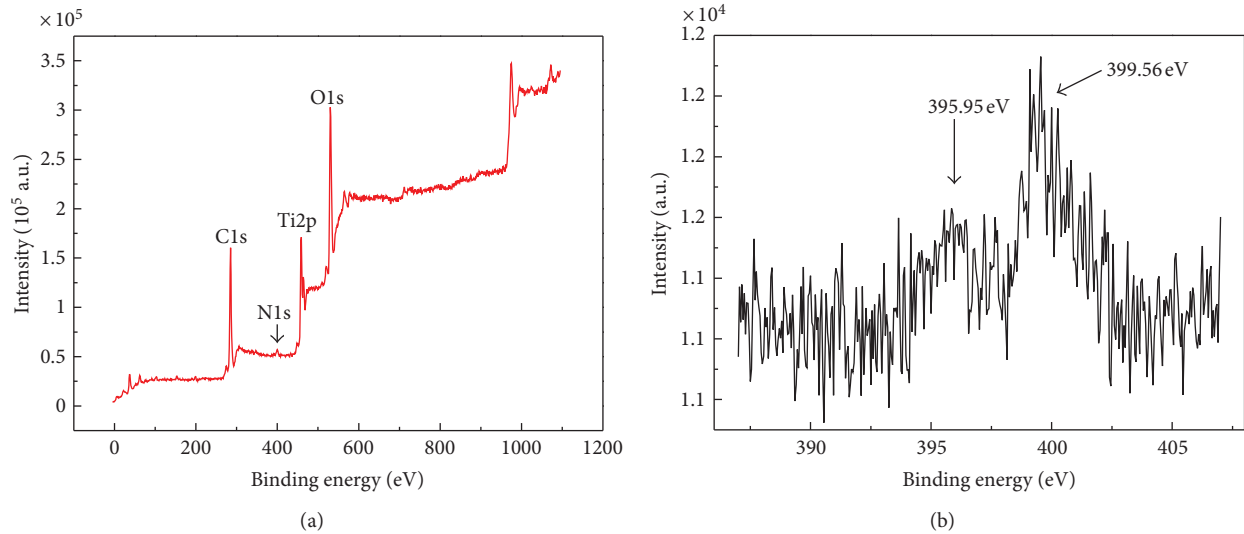
Figure 1 shows the XRD patterns of nitrogen-doped and undoped TiO_2 nanoball films. For the pure sample annealed

at 700°C , an anatase characteristic diffraction peak appears at 25.38° and a rutile diffraction peak appears at 27.48° , which are in well accordance with the (101) diffraction peak position of anatase TiO_2 (JCPDS 21-1272) and the (110) diffraction peak position of rutile TiO_2 (JCPDS 21-1276). The contents of rutile phase and anatase phase are calculated by the XRD results, using the method described by Zhu et al. [26]. The calculation results indicate that both films contain major anatase phase with minor rutile (about 20% content) and the titanium substrate peaks showing up without other phases. The smaller full width at half maximum (FWHM) ($\Delta\theta = 0.134^\circ$) of (101) peak of pure TiO_2 samples indicates a larger crystallite size of undoped nanoballs compared with nitrogen-doped samples ($\Delta\theta = 0.161^\circ$).

SEM images of pure and nitrogen-doped TiO_2 nanoball films are shown in Figure 2. It is found that for both films with the pure nanoball particles and nitrogen-doped nanoball particles, the shape of the nanoballs does not show any obvious change after the treatment in NH_3 flow at 520°C . But it can be seen that the size of nitrogen-doped nanoball (the ball diameter is about 50 nm and the film thickness is about 500 nm) is obviously smaller than undoped TiO_2 nanoballs (the ball diameter is about 100 nm), in accordance with the XRD results. The doping of N element may retard the growth of nanoballs, which is similar with the report in papers [27, 28].

In order to get the composition and the chemical states information, XPS measurements were performed. Figure 3(a) shows the XPS survey spectrum of the nitrogen-doped sample, where the peaks at 458.86 eV, 530.01 eV, 399.69 eV, and 284.7 eV correspond to the binding energy of $\text{Ti}2\text{p}_{3/2}$, O 1s, N 1s, and C 1s, respectively. The C 1s peak is a signal of adventitious elemental carbon as reported in other works [17, 29, 30]. The existence of N element and the entering of N ion into the structure of anatase TiO_2 within the limits of instrumental error were confirmed.

To further investigate the N 1s core level states, the XPS spectrum of N 1s core level electron for N-doped sample is measured and is shown in Figure 3(b). Although, the N doping in TiO_2 has been reported by many papers, the XPS peak of N 1s has still been under debate. Typically, there are two forms of N doping. One is the substitutional doping (O-Ti-N) in which the N atom is bound to Ti atoms directly and replaces the lattice oxygen atoms with a binding energy of N about 396 eV; the other one is the interstitial doping (Ti-O-N) in which the N atoms are bound to lattice oxygen atoms and locate in the TiO_2 lattice interstice with a binding energy of N of about 400 eV [31–36]. In this work, the N 1s XPS spectrum has a major peak at 399.56 eV which can be assigned to the substitutional nitrogen atoms in the anatase lattice of TiO_2 , and a minor peak at 395.95 eV which can be ascribed to the contributions of the nitrogen atoms in the interstitial sites forming the Ti-O-N oxynitrides. The doping content of N is 1.98%, calculating from the N 1s peaks spectrum. In this work, the doped N atoms are inclined to be in the substitutional sites forming the N-Ti-O oxynitrides, and after the N atoms in the substitutional sites forming the N-Ti-O oxynitrides become saturated (the content is close to 1.53%), the excessive N atoms were then present in the

FIGURE 2: SEM images of pure (a) and nitrogen-doped (b) TiO_2 nanoball films.FIGURE 3: XPS spectra of nitrogen-doped TiO_2 nanoball film. (a) Survey; (b) N 1s peaks.

substitutional sites forming the N–Ti–N structure, as it was reported in paper [37].

Figure 4(a) illustrates the UV-Vis absorption spectroscopy of undoped and N-doped TiO_2 with the wavelength in the range of 200–800 nm. The undoped TiO_2 samples exhibit the characteristic spectrum of TiO_2 with its fundamental absorption sharp edge around 380 nm. However, the nitrogen-doped samples exhibit the absorption edge around 440 nm. This absorption edge shifted toward visible light range indicates that a significant enhancement of absorption visible light range is observed. According to the equation $\lambda = 1240/E_g$, the band gaps of the pure and N-doped TiO_2 are 3.23 eV and 2.82 eV, respectively. These band gaps are determined by fitting the absorption spectra data according to the equation $(\alpha h\nu)^2 = B(h\nu - E_g)$ (α is the absorption coefficient; $h\nu$ is the photo energy; B is a constant number;

E_g is the absorption band gap energy). Figure 4(b) illustrates the $(\alpha h\nu)^{1/2}$ versus $h\nu$ curves. As it can be seen, the band gaps of the pure and N-doped TiO_2 are 3.2 eV and 2.8 eV individually, which are in accordance with the results in Figure 4(a) and similar to those reported in [38]. The band gap energy of the nitrogen-doped samples has been narrowed compared with undoped sample. The reason for this change has been discussed elsewhere [39]. For the presence of nitrogen atoms in the lattice, the results of density functional theory (DFT) calculations [37] have shown a large decrease in the formation energy for oxygen vacancies. It has been reported that oxygen vacancy induced by N doping or self-doping plays an important role in the photocatalytic activity of TiO_2 catalyst by trapping the photoinduced electron and acting as a reactive center for the photocatalytic process. And it is known that N has a lower valence state than O so that the

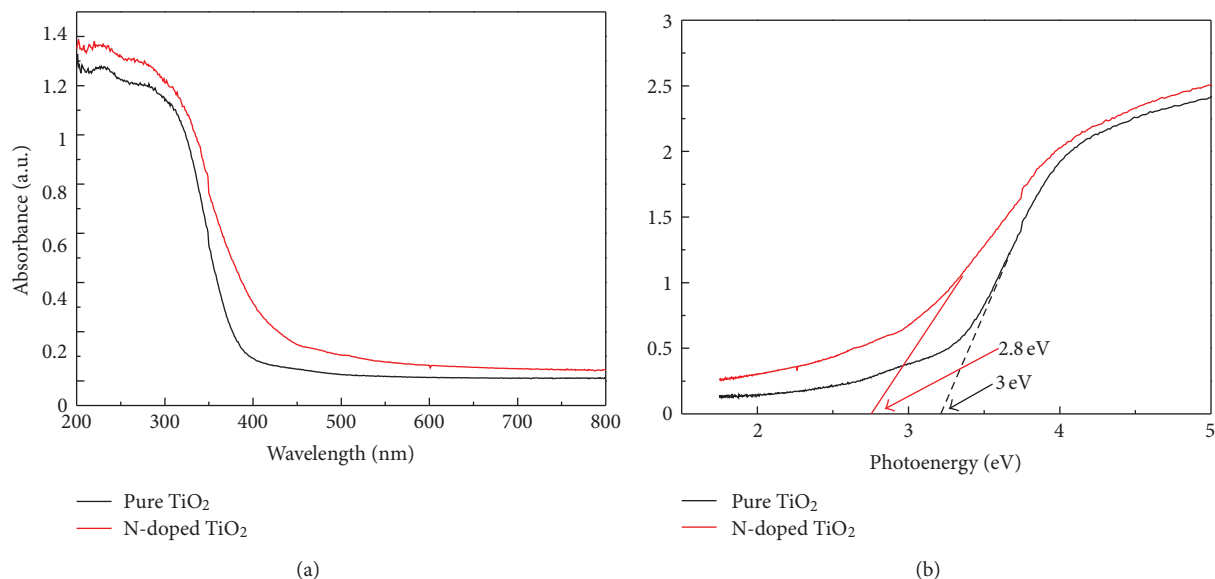


FIGURE 4: UV-vis absorption spectroscopy of undoped and N-doped TiO₂ with the wavelength in the range of (a) 200–800 nm and (b) $(\alpha h\nu)^{1/2}$ versus $h\nu$ curves.

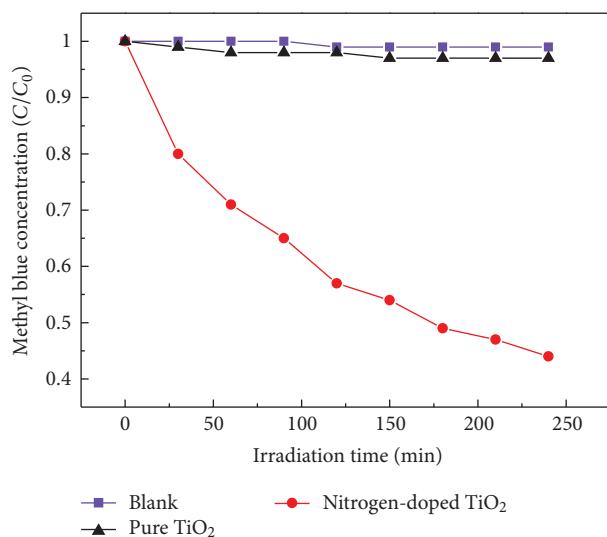


FIGURE 5: Concentrations of methyl blue photodegraded by the pure TiO₂ and nitrogen-doped TiO₂.

incorporation of N must promote the synchronous formation of oxygen vacancies for the charge equilibrium in TiO₂ [40]. That is to say, for nitrogen-doped TiO₂, the increase of visible light response for N-doped TiO₂ is attributed to both oxygen vacancies and the N 2p states.

Figure 5 shows the concentrations of methyl blue photodegraded in an aqueous solution under visible light irradiation by insert a filter ($\lambda \leq 400$ nm) between the Xe-lamp and the samples by the pure TiO₂ and nitrogen-doped TiO₂. The blank test without photocatalyst is carried and the result is shown in Figure 5 as a compared data. The concentration of

methyl blue decreases to nearly 44% in 4 hours for nitrogen-doped samples, while for the pure TiO₂ nanoball film, almost no photocatalytic activity has been observed. The methyl blue degradation rate constants of the nitrogen-doped sample ($3.657 \times 10^{-3} \text{ min}^{-1}$) is much higher than that of the pure sample ($0.128 \times 10^{-3} \text{ min}^{-1}$), calculated from Figure 5. For the nitrogen-doped sample, the size of nanoball diameter is about 50 nm which is only half of the size of undoped nanoball, the surface area to volume ratio associated with the nanosize of titania crystals increased, which assures the higher total amount of the surface active sites available for adsorption of reactant molecules and facilitates the mass transfer, hence enhancing the photocatalytic efficiency [41–45]. At the same time, after nitrogen doping, the visible light absorption band as evidenced in Figure 4 can be reasonably thought to arise from the localized states of N 2p above the valence band and also concomitant oxygen vacancy states below the conduction band [41]. Hence, as the results show that nitrogen-doped sample has a superior photocatalytic property than pure sample under visible light irradiation.

4. Conclusions

In conclusion, TiO₂ nanoball films were synthesized by an anodic oxidation method. The nitrogen doping could significantly enhance absorption in visible light range, narrowband gap from 3.2 eV to 2.8 eV and reduce nanoball diameter compared with that of the pure samples. The N-doped TiO₂ nanoball films possess a stronger photocatalytic activity for catalyzing the degradation of methyl blue. The concentration of methyl blue reduces to nearly 44% in 4 hours for nitrogen-doped sample. The increasement of O vacancies and surface area for photocatalytic reactivity may be the important two

reasons for the increase of photocatalytic activity in the nitrogen-doped TiO_2 nanoball films.

Acknowledgments

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