

ORIGINAL RESEARCH PAPER

Effects of N Doping on Structure and Improvement Photocatalytic Properties of Anatase TiO₂ Nanoparticles

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ABSTRACT

In order to improve UV and visible lights photocatalytic activities of the pure anatase TiO₂, a novel and efficient N-doped TiO₂ photocatalyst was prepared by sol-gel method. N-doped titania is prepared using triethylamine (with difference molar ratios) as the nitrogen source. The crystalline structure, morphology, particle size, absorbance and band-gap and chemical structure of N-doped TiO₂ was characterized by X-ray diffraction, diffuse reflectance spectra, scanning electron microscopy, energy dispersive spectrometry and Fourier transform infrared techniques, respectively. Results indicate that the doping of N, cause absorption edge shifts to the visible light region compare to the pure TiO₂, reduces average size of the TiO₂ crystallites, enhances desired lattice distortion of Ti, promotes separation of photo-induced electron and hole pair, and thus improves pollutant decomposition under UV and visible lights irradiation. The photocatalytic activities of N-doped TiO₂ nanoparticles were evaluated using the photodegradation of methyl orange (MO) as probe reaction under the irradiation of UV and visible light and it was observed that the N-TiO₂ photocatalyst shows higher visible photocatalytic activity than the pure TiO₂. The optimal N/TiO₂ concentration to obtain the highest photocatalytic activity was 2:1 of triethylamine

INTRODUCTION

As one of the most promising photocatalysts for the degradation of organic pollutants, TiO₂ has attracted significant attention and it has biologically and chemically inert, mechanically robust, nontoxic, cheap, environmental freindliness and therefore a perfect candidate for wide scale application with high efficiency [1-4]. However, TiO₂ nanoparticles due to the band-gap of 3.0 and 3.2 eV for rutile and anatase which requires near ultraviolet irradiation ($\lambda < 388$ nm) which is about 3 % of the solar spectrum are excited by photons to produce electron-hole pairs for photocatalytic activation [1, 4-6]. It is commonly

believed that anatase TiO₂ has higher photocatalytic activity than rutile TiO₂. To improve the photocatalyst efficiency of TiO₂, it is necessary to reduce the band-gap by doping with a nonmetal atom has been introduced [4, 6]. Recently, many efforts have been made to modify titanium dioxide with nonmetals, such as nitrogen [7-9], carbon [10, 11], boron [12], sulfur [13], phosphorus [14, 15], fluorine [16], chlorine and bromine [17], iodine [18] to achieve enhanced visible light photocatalytic activities. Doping TiO₂ photocatalyst with a nonmetal element becomes a hot research topic and opens up new possibilities for development of photocatalytic materials with high photoinduced activity [1]. Nitrogen can be incorporated into the crystal lattice and more attractive

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among all of these anionic elements due to its comparable atomic size with oxygen, small ionization energy, metastable center formation, and stability [4, 19]. At present, N-doped TiO₂ has been prepared by various methods such as sputtering [7, 20], ion implantation [21], mechanochemical [22], plasma process [23, 24], chemical vapor deposition [23], sol-gel method [2, 25-27], oxidation of titanium nitride [28], sintering process [29], spray pyrolysis [30], electro-spinning [31], infiltrating organic materials [32], precipitation method [33], wet chemical impregnation [34], hydrothermal and solvothermal methods [35] and sonochemistry [36-38]. Some organic compounds were used as nitrogen sources such as triethylamine [2], urea and ammonium [39-41], thiourea and hydrazine hydrate [2], N,N,N',N'-tetramethylethane-1,2-diamine [4], ethylenediamine [19], nitric acid and ammonium nitrate [42].

In this work, nitrogen-doped nanocrystalline anatase TiO₂ was successfully synthesized by sol-gel method. The photocatalytic performance of TiO₂ nanoparticles was greatly enhanced due to the narrowed TiO₂ band-gap by N doping. Organic compound was used as nitrogen source is triethylamine. At the same time, the catalytic activity of the N doped TiO₂ catalyst is compared with that of pure anatase TiO₂. Then, photocatalytic activity of the N-doped catalyst was tested in removal of methyl orange dye under UV and visible light irradiation. Therefore, various factors affecting the photocatalytic degradation of the dyes were also discussed.

MATERIALS AND METHODS

The tetraisopropylorthotitanate (TTIP), acetic acid, ethanol and polyvinylpyrrolidone (PVP) were purchased from Merck and were used without any further purification. Deionized water was prepared by an ultra pure water system (Smart-2-Pure, TKA Co., Germany). Methyl orange (MO, M.W. = 695.58 g mol⁻¹) dye was provided by Alvan Co., Iran.

Synthesis of N-doped TiO₂ nanoparticles

The pure anatase TiO₂ and the N-doped TiO₂ used as photocatalyst were prepared by sol-gel method followed by annealing. TTIP was used as TiO₂ source and triethylamine was used as N dopant, respectively, water as solvent and the acetic acid as catalyst were selected for preparation. The preparation process was as follows: TTIP, water and acetic acid with ration of

1:25:2 were mixed together and the mixed solution was stirred for 3.0 h. The pH of the mixture was adjusted to about 3.0 using acetic acid to prevent the formation of TiO₂ precipitates. After that, requisite amount of triethylamine (the molar ratio of N/TiO₂ is 0.1, 0.5, 1.0, 1.5, 2.0 and 2.5), deionized water, PVP and ethanol with ration of 10:1:1.5 were mixed together then added slowly to the mixed solution. The resultant solution was kept under continuous stirring to perform hydrolysis reaction for a further 2.0 h and under irradiation with a high intensity ultrasonic of 20 kHz in a sonication cell for 15 min, resulting in the formation of a transparent solution of TiO₂ sol. The prepared light-yellow solution was kept in the dark for nucleation process for 24.0 h. After this period, the gel was dried at 100 °C, and subsequently the catalyst was crushed into fine powder and calcined in a muffle furnace at 500 °C for 2.0 h. The nanosized N-doped TiO₂ powders were obtained after adequate rubbing.

Characterization of photocatalysts

X-ray diffraction (XRD) patterns were recorded by a Philips-X'Pert Pro, X-ray diffractometer using Ni-filtered Cu K α radiation at scan range of 10<2 θ <80. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope. The diffused reflectance UV-visible spectrum (DRS) of the sample was recorded by an Ava Spec-2048TEC spectrometer. Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were recorded on a Nicolet Magna IR 550 spectrometer, USA.

Photocatalytic decomposition of methyl orange

Photocatalytic activity of undoped and N-doped TiO₂ nanoparticles were evaluated by the decomposition of MO solution in water under UV and visible light irradiation. In each experiment, the recyclable photocatalyst (0.1 g) was added into 100 mL of 11 mg/L methyl orange aqueous solution (pH 2-3). The decomposition of MO was performed in a glass vessel with a diameter of 10 cm. A Xe lamp (500 W) was used as light source and hang perpendicularly above the vessel. A filtration glass that only allowed the wavelength >420 nm to pass through was placed above the vessel to get the visible light. The distance between the lamp and solution was around 30 cm. The solution was magnetically stirred before and during illumination

and oxygen was bubbled into the suspension during illumination and oxygen was bubbled into the suspension during the photoreaction. The MO oxidation experiments were carried out in a Teflon cell equipped with a quartz window.

RESULTS AND DISCUSSION

Fig. 1 shows the FT-IR spectra of pure TiO₂ and N-doped TiO₂ powders calcined at 500 °C. The FT-IR spectrum of the N-doped TiO₂ catalyst showed a strong peak at 3000–3700 cm⁻¹ and narrow band at 1628 cm⁻¹ was assigned to the O-H stretching and H-O-H bending vibrations. The peaks observed in 1384, 1163 and 1019 cm⁻¹ are typical of N-O stretching and O-N-O bending vibrations, respectively [43, 44]. Additionally, the peak at 514 cm⁻¹ for N-doped TiO₂ resulted from Ti-O-Ti bending vibrations, being red-shifted compared with the peak for TiO₂ at 539 cm⁻¹ and 653–550 cm⁻¹ is ascribed to the Ti-O stretching vibration [36, 45].

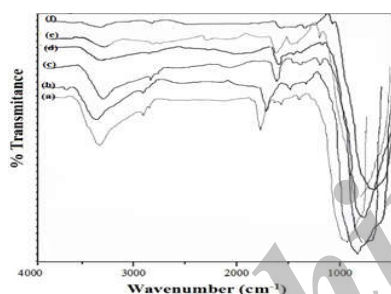


Fig. 1. FT-IR spectra of TiO₂ nanoparticles: (a) pure TiO₂, (b) N/TiO₂ : 0.1, (c) N/TiO₂ : 0.5, (d) N/TiO₂ : 1.0, (e) N/TiO₂ : 1.5 and (f) N/TiO₂ : 2.0.

XRD patterns for pure TiO₂ and N-doped TiO₂ nanoparticles are shown in Fig. 2. In all the XRD patterns, TiO₂ anatase diffraction lines could be seen and no other crystal phase could be detected. It could also be seen from the XRD patterns that N-doped TiO₂ showed peak broadening compared with pure TiO₂. Characteristic peaks of anatase ($2\theta = 25.2, 37.76, 48.02, 54.05, 55.03, 62.80, 68.85, 70.19, \text{ and } 75.07$), were observed. This indicates that the supplied doped TiO₂ and undoped TiO₂ were anatase structure (JCPDS no. 36-1451). The average crystallite size of pure TiO₂ and N-doped TiO₂ were calculated using the Scherrer equation. Pure TiO₂ had a particle size of 10.3 nm; doped TiO₂, about 7.6 nm. N-doped TiO₂ powders showed

smaller size than pure TiO₂ prepared at the same calcination temperature. In general, crystallite growth in TiO₂ is considerably affected by the dopant [46]. This smaller crystallite size enhanced the photocatalytic activity of N-doped TiO₂ [5].

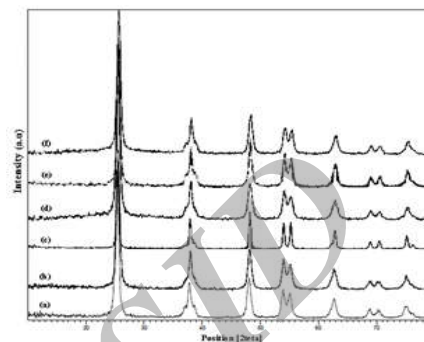


Fig. 2. XRD patterns of TiO₂ nanoparticles: (a) pure TiO₂, (b) N/TiO₂ : 0.5, (c) N/TiO₂ : 1.0, (d) N/TiO₂ : 1.5, (e) N/TiO₂ : 2.0, and (f) N/TiO₂ : 2.5.

The surface morphology of the N-doped TiO₂ nanoparticles have been investigated by SEM, respectively, shown in Figs. 3. It is observed that the N/TiO₂ : 2.0 sample is composed of large quantity of relatively uniform particles with diameter from 20 to 30 nm, which indicates sample could have good dispersion in solution. Further analysis also shows that these big particles are composed of small particles.

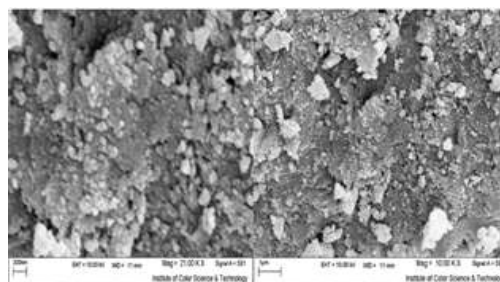


Fig. 3. SEM images of N/TiO₂ : 2.0 sample.

The EDS data of N/TiO₂ : 2.0 sample (Fig. 4) shows a peak around 0.4 and 0.5 keV and another intense peak appears at 4.5 and 4.9 keV for Ti [47]. The peaks due to nitrogen and oxygen are clearly distinct at 0.3 and 0.6 keV, respectively. These results confirm that Ti, O, N exist in the catalyst structure.

Fig. 5a shows the DRS spectra of the undoped TiO₂

and N-doped TiO₂ samples. The undoped TiO₂ is black in color and shows absorption only in the UV region. The N-doped TiO₂ samples are other color and their optical absorption was extended to the visible region. It is noted that the band-gap was expanded from 380 to 480 nm upon N doping. Noticeable shifts of the absorbance shoulder from a wavelength below 400 nm to the visible light region were observed for the N-doped TiO₂. The main absorption edges of the N-doped TiO₂ change significantly compared to that of the undoped sample. It is likely that nitrogen doping creates a new N 2p state slightly above the valence band top consists of O 2p state, and this pushes up the valence band top and leads to visible light response as a consequence [6].

In addition, the bandgap of the titania was determined from the Eq. (1)

$$\alpha h\nu = A(h\nu - E_g)^{\gamma} \quad (1)$$

where A is a constant, $h\nu$ is the photon energy, E_g is the optical energy gap of the material and γ is characteristic of the optical transition process, which is equal to 2.0 for an indirect allowed optical transition of an amorphous semiconductor. The bandgap of N-doped TiO₂ has changed from 3.38 eV (undoped TiO₂) to 3.26 eV for N/TiO₂ : 2.0 sample is shown in Fig. 5b. The first bandgap reflects the effect of N-doping on the main band edges of the oxide. The second gap, which is narrower than the original value, suggests that nitrogen doping contributed to the red shift of the bandgap [48]. Accordingly, it can be presumed that the N-doped TiO₂ sample may exhibit high photocatalytic activity under visible irradiation.

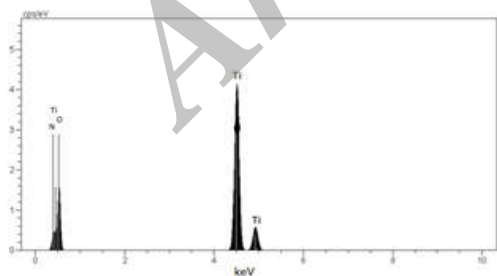


Fig. 4. EDS spectrum of N/TiO₂ : 2.0 sample.

The photocatalytic degradation of MO under UV and visible lights were measured for pure and doped TiO₂ samples. The results in Fig. 6 and tabulated in

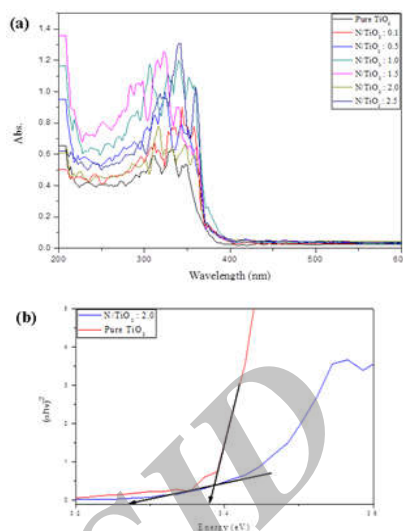


Fig. 5 (a) Diffuse reflectance spectrum of pure TiO₂ and N-doped TiO₂ nanoparticles with the different molar ratio of nitrogen source and (b) The band-gap for samples pure TiO₂ and N/TiO₂ : 2.0 sample.

Table 1 clearly show that under the irradiation of UV and visible, the photocatalytic performance of anatase TiO₂ is greatly improved with the doping of N. Fig. 6 shows that N/TiO₂ : 2.0 sample higher activity than other samples under UV and visible irradiation. The higher photocatalytic activity of N-doped TiO₂ than undoped TiO₂ under UV and visible irradiation may be due to the substitution of nitrogen for oxygen atoms in the crystal structure of TiO₂ that improves the visible light sensitivity by introducing a mid-gap (N 2p) level, which formed slightly above the top of the (O 2p) valence band [49].

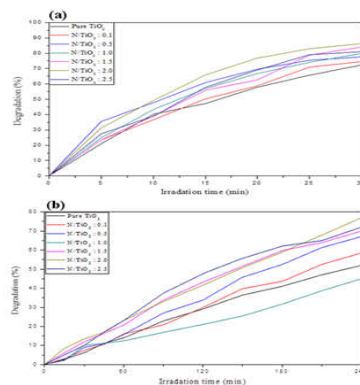


Fig. 6. Photodegradation of MO by pure TiO₂ and N-TiO₂ with various N doping concentrations under UV (a) and visible (b) irradiation.

Table 1. Photocatalytic degradation of MO using pure TiO₂ and N-TiO₂ nanoparticles under UV and visible light irradiation.

Photocatalyst type	UV irradiation time (min)							
	0	5	10	15	20	25	30	
Pure TiO ₂	0	21.1	40.2	47.3	57.8	65.7	71.2	
N/TiO ₂ : 0.1	0	23.5	36.5	50.4	58.7	70.8	74.6	
N/TiO ₂ : 0.5	0	35.4	47.7	61	69.4	75.4	77.7	
N/TiO ₂ : 1.0	0	25.1	43.3	57.0	66.8	74.0	80.1	
N/TiO ₂ : 1.5	0	23.5	39.3	55.8	62.5	78.6	84.0	
N/TiO ₂ : 2.0	0	31.2	49.1	65.8	76.7	83.1	87.2	
N/TiO ₂ : 2.5	0	27.5	38.8	57.8	69.1	79.0	81.1	
	visible irradiation time (min)							
	0	30	60	90	120	180	240	
Pure TiO ₂	0	6.2	14.1	22.8	29.3	41.2	52.4	
N/TiO ₂ : 0.1	0	7.5	16.1	20.7	29.9	43.8	58.6	
N/TiO ₂ : 0.5	0	9.2	15.8	27.2	33.7	52.6	67.3	
N/TiO ₂ : 1.0	0	10.1	12.6	17.0	21.1	32.2	45.6	
N/TiO ₂ : 1.5	0	12.0	20.7	33.9	43.2	59.8	70.0	
N/TiO ₂ : 2.0	0	13.5	23.8	32.2	42.9	60.1	76.4	
N/TiO ₂ : 2.5	0	10.0	22.3	36.4	45.6	62.2	72.0	

CONCLUSION

The studied report that N-doped titania nano-photocatalyst with a spherical shape was prepared using triethylamine as the nitrogen source by the sol-gel method. The doping mechanism was explained by XRD, FT-IR, EDS, SEM and UV-visible absorption analyses. The photocatalytic performance of pure TiO₂ was greatly improved by the N-doping. The nitrogen doping had predominant effects on the improvement of the photocatalytic activity: on one hand, it could narrow the band-gap of titania to extend its absorption to the visible light region; on the other hand, it could increase the separation efficiency of the photoinduced electron and hole. The as-prepared N/TiO₂ : 2.0 sample shows a great potential as a catalyst for photocatalytic applications.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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