Visible Light Activity of Nitrogen-Doped TiO$_2$ by Sol-Gel Method Using Various Nitrogen Sources

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ABSTRACT
In order to improve photocatalytic activities of the pure anatase TiO$_2$ under UV and visible light irradiations, a novel and efficient N-doped TiO$_2$ photocatalyst was prepared by sol-gel method. N-doped titania is prepared using the various nitrogen sources such as: triethylamine, N,N,N',N'-tetramethylethane-1,2-diamine, ethyldiamine, 1,2-phenylenediamine, propanolamine, and propylenediamine and then the effect of these source on properties of products was investigated. The as-prepared products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflectance spectra (DRS), energy dispersive spectrometry (EDS) and Fourier transform infrared (FT-IR) techniques. Results indicate that the shifting of absorption edge to visible region compare to the pure TiO$_2$, reducing average size of the TiO$_2$ crystallites, enhancing of lattice distortion of Ti, effective separation of photo-induced electron and hole pair, and improvement of pollutant decomposition under UV and visible light irradiations are due to doping of N in titania. The photocatalytic activities of N-doped TiO$_2$ nanoparticles were evaluated using the photodegradation of methyl orange (MO) under the irradiation of UV and visible light and it confirmed that the photocatalytic activity of N-TiO$_2$ is better than the pure TiO$_2$. By comparing the photocatalytic activities of the N-TiO$_2$ with different nitrogen sources, triethylamine with 2 molar ratio was chosen as the optimum.

INTRODUCTION
One of the most promising photocatalysts for the degradation of organic pollutants is TiO$_2$ that has attracted significant attention. This material is biologically and chemically inert, mechanically robust, nontoxic, cheap, environmentally friendly and therefore a perfect candidate for wide scale applications with high efficiency [1-4]. Furthermore, TiO$_2$ nanoparticles can be excited by photons to produce electron-hole pairs for photocatalytic activation, if the photons energy provides enough energy for the TiO$_2$ band gap (3.0 for rutile and 3.2 eV for anatase). The anatase TiO$_2$ has higher photocatalytic activity than rutile TiO$_2$ [4-6]. They require near ultraviolet irradiation ($\lambda$<388 nm), which is about 3% of the solar spectrum [1, 4-6]. To improve the photocatalyst efficiency of TiO$_2$, it is necessary in order to reduce the band gap. For this end, one of the introduced approaches is doping a nonmetal atom. This process has become a rather major research topic and has opened new windows for improving the common photocatalytic cells [1]. To achieve enhanced visible light photocatalytic activities, many efforts have been recently 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, bromine [17] and iodine [18]. Nitrogen can be incorporated into TiO$_2$‘s crystal lattice and is more attractive than all of these anionic elements due to its closer atomic size with oxygen, small ionization energy, metastable center formation, and stability [4, 19]. Up to now, N-doped TiO$_2$ (N/TiO$_2$) has been prepared by various methods such as sputtering [7, 20], ion implantation [21], mechanochemical synthesis [22], plasma processing [23, 24], chemical vapor deposition [23], sol-gel method [2, 25-27], titanium nitride oxidation [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 TiO$_2$ was successfully synthesized through the sol-gel method. The photocatalytic activity of TiO$_2$ nanoparticles were greatly enhanced by decreasing the N/TiO$_2$ band gap. Organic compounds were used as nitrogen sources such as triethylamine, N,N,N’,N’-tetramethylethane-1,2-diamine, ethyldiamine, 1,2-phenylenediamine, propanolamine and propylenediamine. At the same time, the catalytic activity of the N/TiO$_2$ catalyst is compared with the pure anatase TiO$_2$. The effects of various nitrogen sources on the photocatalytic properties of products were investigated. Then, the photocatalytic activity of the N/TiO$_2$ catalyst was tested for the removal of methyl orange dye under UV and visible light irradiation. Through the comparison of the photocatalytic activities of the N/TiO$_2$ with different nitrogen sources, the best source was optimized.

MATERIALS AND METHODS

The tetraisopropyl orthotitanate (TTIP), triethylamine, N,N,N’,N’-tetramethylethane-1,2-diamine, ethyldiamine, 1,2-phenylenediamine, propanolamine, propylenediamine, acetic acid, ethanol and polyvinylpyrrolidone (PVP) were purchased from Merck and used without any further purification. Deionized water was prepared by a 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 TiO$_2$ nanoparticles

Part 1. The pure anatase phase of TiO$_2$ and the N-doped TiO$_2$ were prepared by sol-gel method. The products were synthesized using one of the following compounds as N source: triethylamine, N,N,N’,N’-tetramethylethane-1,2-diamine, ethyldiamine, 1,2-phenylenediamine, propanolamine or propylenediamine. Also, TTIP was used as TiO$_2$ source and acetic acid was applied as catalyst. The preparation process was as follow: TTIP, ethanol and acetic acid with mole ration of 1:2:2 were mixed together and the mixed solution was stirred for 3 h. The pH of the mixture was adjusted to about 3.0 using acetic acid to prevent the formation of TiO$_2$, 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 TiO$_2$ powders were obtained after adequate rubbing.

Part 2. As in Part 1, but here for the nitrogen source, various certain amount of triethylamine (the molar ratio of N:TiO$_2$ is 0.1, 0.5, 1.0, 1.5, 2.0 and 2.5) were used.

Characterization of photocatalysts

X-ray diffraction (XRD) patterns were recorded by a Philips-X’PertPro, X-ray diffractometer using Ni-filtered Cu Kα radiation at scan range of 10°<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,
Photocatalytic decomposition of methyl orange

Photocatalytic activity of un-doped and N/TiO$_2$ nanoparticles was 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 methyl orange aqueous solution (pH =2-3) with 11 mg/L concentration. The decomposition of MO was performed in a glass vessel with a diameter of 10 cm. A Xenon lamp (500 W) was hanged perpendicularly to the glass vessel as light source. A quartz filter was placed between lamp and vessel that allow to pass the wavelength <420 nm, causes to get the visible and UV light by vessel’s solution. The distance between the lamp and solution was around 25 cm for visible and 40 cm for UV light. The solution was magnetically stirred before and 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 TiO$_2$ and N/TiO$_2$ powders obtained from various nitrogen sources. The FT-IR spectra of the N/TiO$_2$ catalyst show a strong peak at 3000–3700 cm$^{-1}$ and narrow band at 1628 cm$^{-1}$ that assign to the O-H stretching and H-O-H bending vibrations of adsorbed water molecules. 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/TiO$_2$ resulted from Ti–O–Ti bending vibrations, being red-shifted compared with the peak for TiO$_2$ at 539 cm$^{-1}$ and the peak at 653–550 cm$^{-1}$ is ascribed to the Ti–O stretching vibration [36, 45].

XRD patterns for pure TiO$_2$ and N/TiO$_2$ nanoparticles obtained from various nitrogen sources, are shown in Fig. 2. In all the XRD patterns, TiO$_2$ anatase diffraction lines could be seen and no other crystal phase could be detected. Characteristic peaks of anatase ($2\theta$ = 25.2, 37.76, 48.02, 54.05, 55.03, 62.80, 68.85, 70.19, and 75.07) can be associated with (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes respectively, were observed. This indicates that the produced doped TiO$_2$ and undoped TiO$_2$ are in anatase phase (JCPDS no. 36-1451). It could also be seen from the XRD patterns that N/TiO$_2$ has the broader peaks compared to pure TiO$_2$. This means smaller crystallite size, according to Scherrer equation, and thus increase the photocatalytic activity of N/TiO$_2$ [5]. Generally, crystallite growth

![Fig. 1. FT-IR spectra of N/TiO$_2$ nanoparticles with the molar ratio of 2:1 nitrogen from various sources: (a) triethylamine, (b) 1,2-phenylenediamine, (c) propylenediamine, (d) ethyldiamine, (e) N,N,N',N'-tetramethylethane-1,2-diamine and (f) propylamine.](image-url)
in TiO$_2$ is considerably affected by the dopant [46].

The photocatalytic degradation of MO under UV and visible lights were measured for pure and N/TiO$_2$ samples. Fig. 3 clearly shows photodegradation of MO by N/TiO$_2$ versus time under UV and visible irradiation. According to Fig. 3, the results show that the type of used nitrogen source is effective in photocatalytic activity of synthesized N/TiO$_2$ in the degradation of MO dye. All N/TiO$_2$ samples show better catalytic activity compared to pure TiO$_2$, except one that was used from 1,2-phenylenediamine as nitrogen source (sample 2). The degradation percent for N/TiO$_2$ samples (except sample 2) against 240 minutes visible irradiation or 30 minutes UV light irradiation were 57 to 76 and 72 to 87 percent. The photocatalytic activity of N doped TiO$_2$ samples was best when used triethylamine as source of nitrogen. In the next stage, the results of different ratio of triethylamine were studied.

Fig. 4 and Fig. 5 show the FT-IR spectra and XRD patterns of pure TiO$_2$ and N/TiO$_2$ powders from different mole ratio of trimethylamine, respectively. The average crystallite size of pure TiO$_2$ and N/TiO$_2$ were calculated using the Scherrer equation. Pure TiO$_2$ had a particle size of 16.3 nm; doped TiO$_2$ about 13.2 nm. N/TiO$_2$ powders showed smaller size than pure TiO$_2$ prepared at the same calcinations temperature. In general, crystallite growth in TiO$_2$ is considerably affected by the dopant. This smaller crystallite size enhanced the photocatalytic activity of N/TiO$_2$.

The surface morphology of the N-doped TiO$_2$ nanoparticles have been investigated by SEM, respectively, shown in Fig. 6. It is observed that the N/TiO$_2$:2.0 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. As it can be seen in Fig. 6, the larger particles are obtained by the aggregation of smaller particles.

The EDS data of N/TiO$_2$:2.0 sample (Fig. 7) 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. 8(a) shows the DRS spectra of the pure TiO$_2$ and N/TiO$_2$ samples. The pure TiO$_2$ shows absorption only in the UV region. The optical absorption of the N/TiO$_2$ samples 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/TiO₂.

The main absorption edges of the N/TiO₂ change significantly compared to that of the un-doped 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) [48]

\[ \alpha h\nu = A(h\nu - E_g)^\gamma \]  

(1)

where \( A \) is a constant, \( h\nu \) is the photon energy, \( E_g \) is the optical energy gap of the material and \( \gamma \) 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/TiO₂ has changed from 3.38 eV (pure TiO₂) to 3.26 eV for N/TiO₂:2.0 sample is shown in Fig. 8(b). 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].

Fig. 3. Photodegradation of MO by N-TiO₂ with the molar ratio of 2:1 nitrogen from various nitrogen sources under UV (a) and visible (b) irradiation.
Accordingly, it can be presumed that the N/TiO\textsubscript{2} sample may exhibit high photocatalytic activity under visible irradiation. The photocatalytic degradation of MO under UV and visible lights were measured for pure and N doped TiO\textsubscript{2} samples (triethylamine as source of nitrogen). The results in Fig. 9 clearly show that, under the irradiation of UV and visible,
the photocatalytic performance of anatase TiO$_2$ is greatly improved with the doping of N. The photocatalytic activity of N doped TiO$_2$ sample that triethylamine was source of nitrogen shows comparable activity to that of pure TiO$_2$ and the samples under UV light with increase the nitrogen concentration in the degradation of MO dye was more, resulting in a degradation of N/TiO$_2$:2.0 sample was 87% and selected as the optimum sample. Also, the samples under visible light with increase the nitrogen concentration in the degradation of MO dye was more, finally in a degradation of N/TiO$_2$:2.0 sample was 76.4% and was selected as the optimum sample.

CONCLUSION

In summary, in this work N/titania photocatalyst with a spherical shape was prepared using sources of nitrogen such as N,N,N',N'-tetramethylethane-1,2-diamine, ethyldiamine, 1,2-phenylenediamine, propanolamine, propylenediamine (the molar ratio of 2:1). After that, using triethylamine (with difference molar
ratios) as the optimize 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 TiO$_2$ was greatly improved by the N-doping. The nitrogen doping had predominant effects on the improvement of the photocatalytic activity: On the other hand, it could limit the band gap of titania and extends its absorption to the visible light region, furthermore, it could increase the separation efficiency of the photoinduced electron and hole. The prepared N/TiO$_2$:2.0 shows a great potential as a catalyst for photocatalytic applications.

CONFLICT OF INTEREST
The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES