

RESEARCH PAPER

Visible Light Activity of Nitrogen-Doped TiO₂ by Sol-Gel Method Using Various Nitrogen Sources

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ABSTRACT

In order to improve photocatalytic activities of the pure anatase TiO₂ under UV and visible light irradiations, a novel and efficient N-doped TiO₂ 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 TiO₂, reducing average size of the TiO₂ 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 TiO₂ 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-TiO₂ is better than the pure TiO₂. By comparing the photocatalytic activities of the N-TiO₂ with different nitrogen sources, triethylamine with 2 molar ratio was chosen as the optimum.

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INTRODUCTION

One of the most promising photocatalysts for the degradation of organic pollutants is TiO₂ 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, TiO₂ nanoparticles can be excited by photons to produce electron-hole pairs for photocatalytic activation, if the photons energy provides enough energy for the TiO₂ band gap (3.0 for rutile and 3.2 eV for anatase). The anatase TiO₂ has higher photocatalytic activity than rutile

TiO₂ [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 TiO₂, 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],

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chlorine, bromine [17] and iodine [18]. Nitrogen can be incorporated into TiO₂'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 TiO₂ (N/TiO₂) 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 TiO₂ was successfully synthesized through the sol-gel method. The photocatalytic activity of TiO₂ nanoparticles were greatly enhanced by decreasing the N/TiO₂ 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/TiO₂ catalyst is compared with the pure anatase TiO₂. The effects of various nitrogen sources on the photocatalytic properties of products were investigated. Then, the photocatalytic activity of the N/TiO₂ 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/TiO₂ 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 TiO₂ nanoparticles

Part 1. The pure anatase phase of TiO₂ and the N-doped TiO₂ 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 TiO₂ source and acetic acid was applied as catalyst. The preparation process was as follow: TTIP, ethanol and acetic acid with mole ratio 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 TiO₂ in this step. After that, the nitrogen source, deionized water and PVP with molar ratio of 2:10:1 were mixed together and added slowly to the first mixed solution. The resultant solution was kept under continuous stirring for a further 2 h for perform hydrolysis reaction, then dispersed under irradiation with a high intensity ultrasonic of 20 kHz in a sonication cell for 15 min, outcome is the formation of a transparent solution of TiO₂ sol. The prepared light-yellow solution was kept for 24 h in the dark for nucleation process. 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.

Part 2. As in Part 1, but here for the nitrogen source, various certain amount of triethylamine (the molar ratio of N:TiO₂ 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 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 un-doped and N/TiO₂ 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 TiO₂ and N/TiO₂ powders obtained from various nitrogen sources. The FT-IR spectra of the N/TiO₂ 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/TiO₂ resulted from Ti–O–Ti bending vibrations, being red-shifted compared with the peak for TiO₂ 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 TiO₂ and N/TiO₂ nanoparticles obtained from various nitrogen sources, 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. Characteristic peaks of anatase (2θ = 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 TiO₂ and undoped TiO₂ are in anatase phase (JCPDS no. 36-1451). It could also be seen from the XRD patterns that N/TiO₂ has the broader peaks compared to pure TiO₂. This means smaller crystallite size, according to Scherrer equation, and thus increase the photocatalytic activity of N/TiO₂ [5]. Generally, crystallite growth

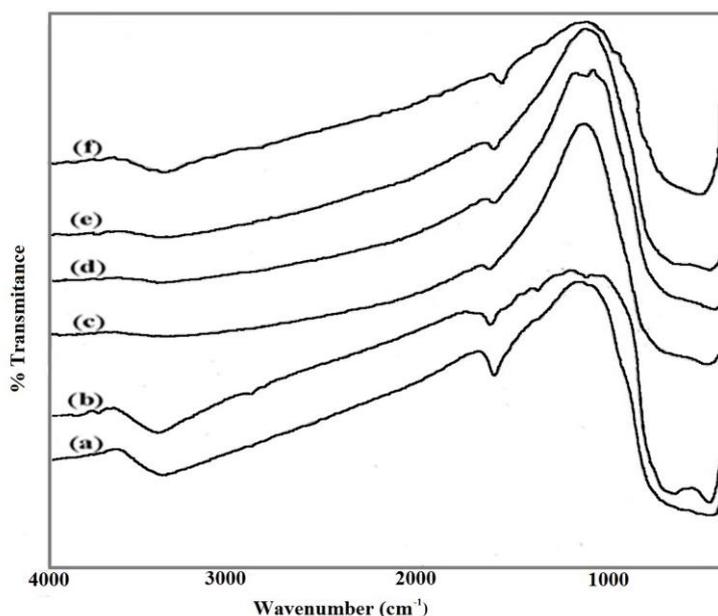


Fig. 1. FT-IR spectra of N/TiO₂ nanoparticles with the molar ratio of 2:1 nitrogen from various sources: (a) triethylamine, (b) 1,2-phenylenediamine, (c) propylenediamine, (d) ethyldiamine, (e) N,N,N',N'-tetramethylethane-1,2-diamine and (f) propanolamine.

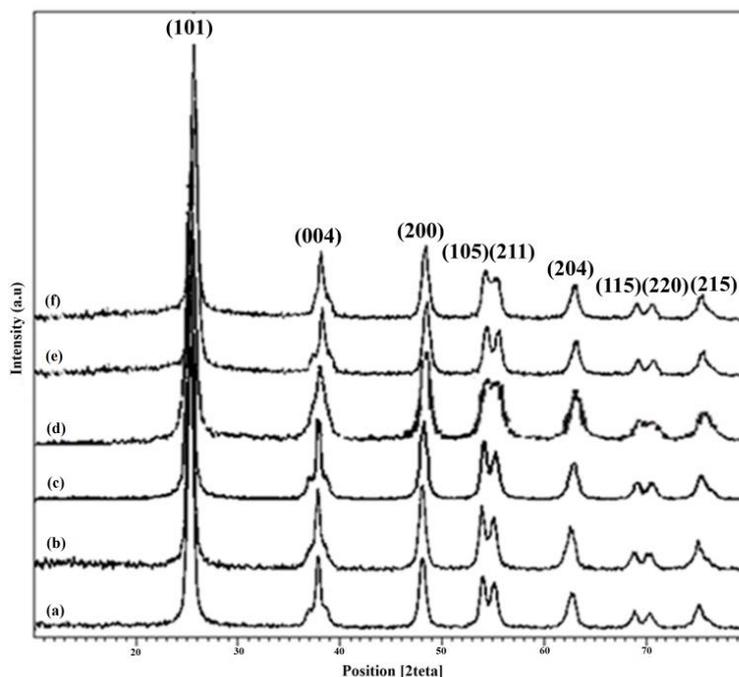


Fig. 2. XRD patterns of N/TiO₂ nanoparticles with the molar ratio of 2:1 nitrogen from various sources: (a) triethylamine, (b) 1,2-phenylenediamine, (c) propylenediamine, (d) ethyldiamine, (e) N,N,N',N'-tetramethylethane-1,2-diamine and (f) propanolamine.

in TiO₂ is considerably affected by the dopant [46].

The photocatalytic degradation of MO under UV and visible lights were measured for pure and N/TiO₂ samples. Fig. 3 clearly shows photodegradation of MO by N/TiO₂ 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/TiO₂ in the degradation of MO dye. All N/TiO₂ samples show better catalytic activity compared to pure TiO₂, except one that was used from 1,2-phenylenediamine as nitrogen source (sample 2). The degradation percent for N/TiO₂ 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 TiO₂ 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 TiO₂ and N/TiO₂ powders from different mole ratio of trimethylamine, respectively. The average crystallite size of pure TiO₂ and N/TiO₂ were calculated using the Scherrer equation. Pure TiO₂ had a particle size

of 16.3 nm; doped TiO₂, about 13.2 nm. N/TiO₂ powders showed smaller size than pure TiO₂ prepared at the same calcinations temperature. In general, crystallite growth in TiO₂ is considerably affected by the dopant. This smaller crystallite size enhanced the photocatalytic activity of N/TiO₂.

The surface morphology of the N-doped TiO₂ nanoparticles have been investigated by SEM, respectively, shown in Fig. 6. It is observed that the N/TiO₂:2.0 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/TiO₂:2.0 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 TiO₂ and N/TiO₂ samples. The pure TiO₂ shows absorption only in the UV region. The optical absorption of the N/TiO₂ samples was extended

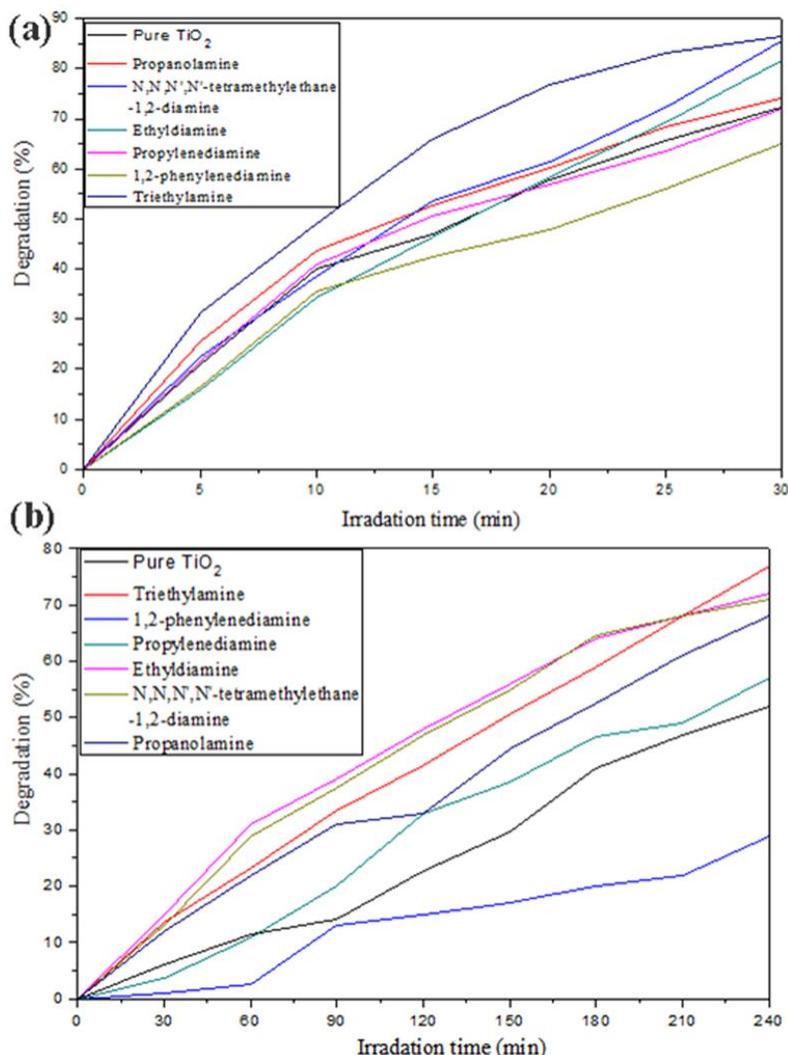


Fig. 3. Photodegradation of MO by N-TiO₂ with the molar ratio of 2:1 nitrogen from various nitrogen sources under UV (a) and visible (b) irradiation.

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]

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

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/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].

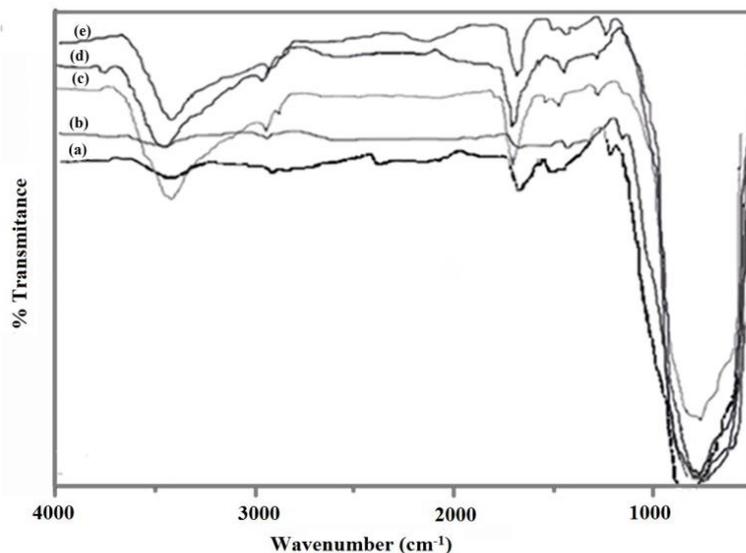


Fig. 4. FT-IR spectra of TiO_2 nanoparticles from different ratio of triethylamine: (a) pure TiO_2 , (b) N/TiO_2 :0.5, (c) N/TiO_2 :1.0, (d) N/TiO_2 :1.5 and (e) N/TiO_2 :2.0.

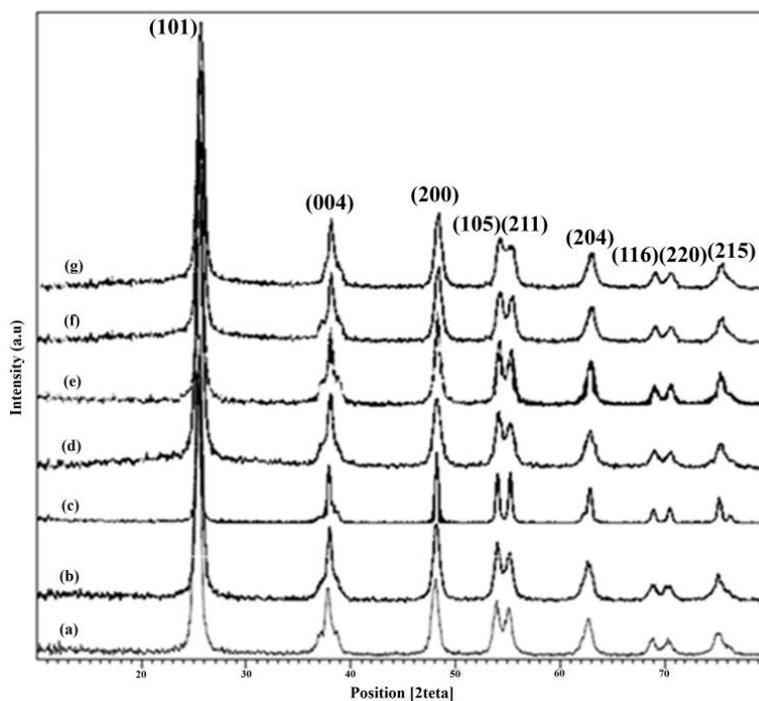


Fig. 5. XRD patterns of TiO_2 nanoparticles from different ratio of triethylamine: (a) pure TiO_2 , (b) N/TiO_2 :0.1, (c) N/TiO_2 :0.5, (d) N/TiO_2 :1.0, (e) N/TiO_2 :1.5 and (f) N/TiO_2 :2.0, and (g) N/TiO_2 :2.5.

Accordingly, it can be presumed that the N/TiO_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_2 samples (triethylamine as source of nitrogen). The results in Fig. 9 clearly show that, under the irradiation of UV and visible,

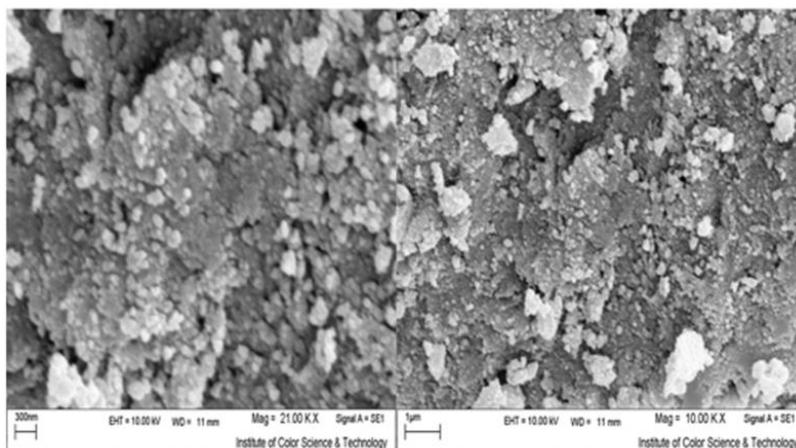


Fig. 6. SEM images of N-doped TiO₂ nanoparticles with the molar ratio of 2:1 nitrogen from triethylamine (N/TiO₂:2.0 sample) with two magnification, left: 300 nm and right:1 μm.

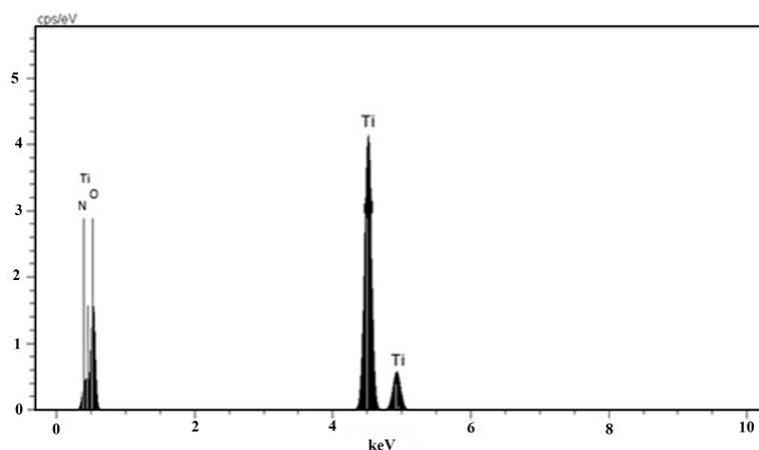


Fig. 7. EDS spectrum of N-doped TiO₂ nanoparticles with the molar ratio of 2:1 nitrogen from triethylamine (N/TiO₂:2.0 sample).

the photocatalytic performance of anatase TiO₂ is greatly improved with the doping of N. The photocatalytic activity of N doped TiO₂ sample that triethylamine was source of nitrogen shows comparable activity to that of pure TiO₂ 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/TiO₂:2.0 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/TiO₂:2.0 sample was 76.4% and was selected as the optimum sample.

The higher photocatalytic activity of N/TiO₂

than pure 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].

CONCLUSION

In summary, in this work N/titania nano-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

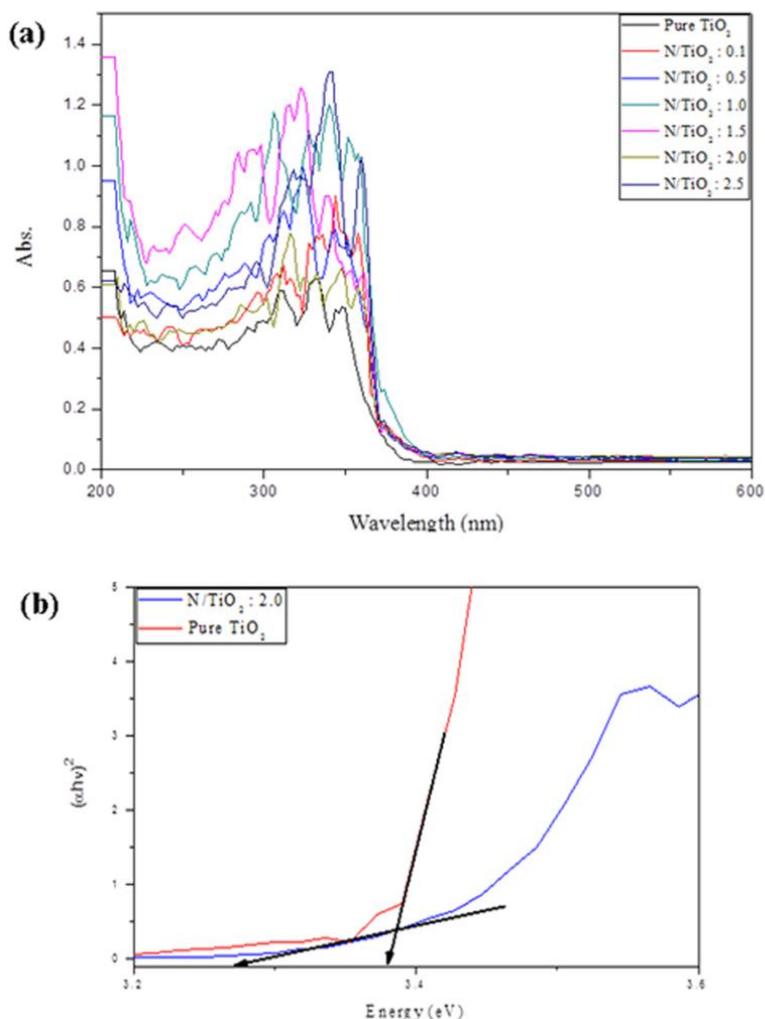


Fig. 8. (a) Diffuse reflectance spectrum and (b) The band gap of pure TiO₂ and N-TiO₂ with the molar ratio of 2:1 nitrogen from triethylamine (N/TiO₂:2.0).

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 TiO₂ 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/TiO₂:2.0 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.

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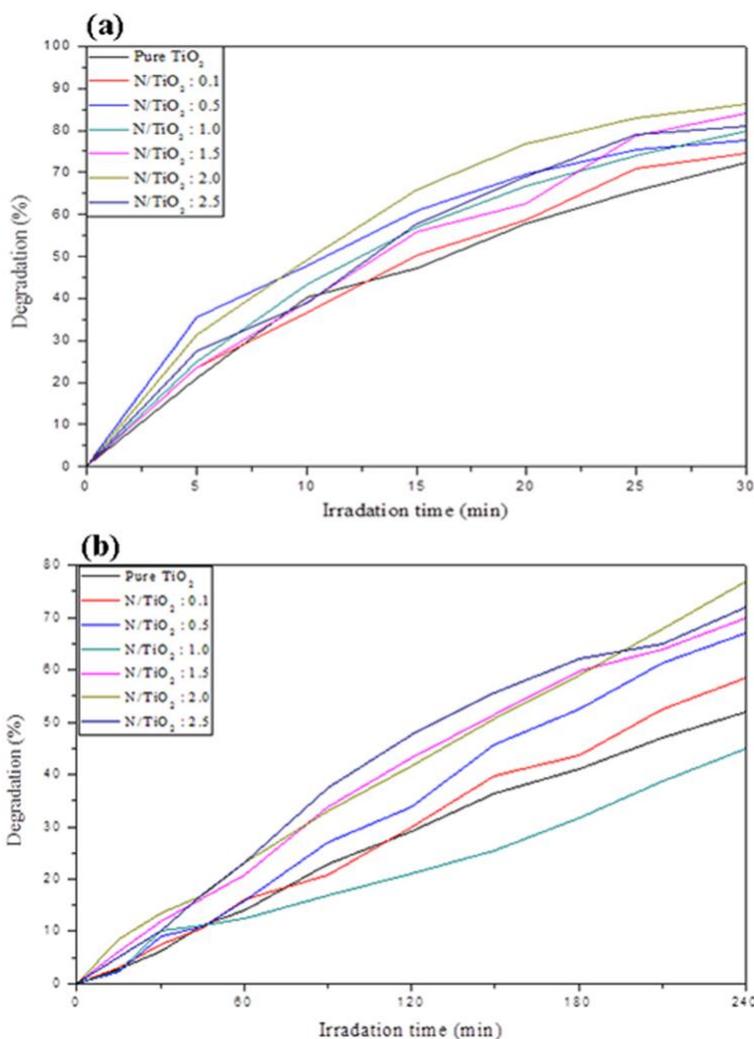


Fig. 9. Photodegradation of MO by pure TiO₂ and N-TiO₂ using triethylamine as the nitrogen source with various N doping concentrations under UV (a) and visible (b) irradiation

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