Preparation of transparent nanostructured N-doped TiO₂ thin films by combination of sonochemical and CVD methods with visible light photocatalytic activity

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Abstract: Pollution of water resources with pesticide compounds has raised serious environmental problems, and for photocatalytic degradation of these pollutants, thin film photocatalysts are preferred to colloidal ones due to the separation problem of colloidal nanoparticles. In this work, nanostructured TiO₂ and N-doped TiO₂ thin films with high transparency were deposited on glass and quartz substrates through sonochemical–chemical vapor deposition (CVD) method. The films prepared on glass and quartz substrates had nanocubic and nanospherical morphology, respectively. The presence of N atoms in the structure of TiO₂ resulted in a decrease in the band gap energy of TiO₂ and also in the reduction of photogenerated electron–hole recombination rate. Furthermore, the presence of N atoms induced the formation of Ti³⁺ species which can act as hole trapping centers. The prepared thin films were also used for the visible light photocatalytic degradation of paraoxon pesticide. According to these results among the prepared thin films, the N-doped TiO₂ thin films have higher photocatalytic activity than pure TiO₂ thin films. Moreover, in comparison with the thin films deposited on quartz substrate, the films on glass substrate have higher photocatalytic performance, which can be related to the special nanocubic morphology of these samples.

Keywords: N-doped; TiO₂ film; transparent; photocatalyst; chemical vapor deposition (CVD); ultrasonic

1 Introduction

Semiconductor-based photoactive films are deposited on various substrates of metals, ceramics, silicon wafer, and glass in widespread applications such as solar cells, self-cleaning surfaces, air purification, hydrogen

production, and photocatalysis [1]. Among these substrates, glass is the best one because of its low cost, high transmittance, and excellent chemical stability. Films used on vehicle's and building's windows must have high transparency, thus photoactive transparent films have attracted growing interests in recent years [2,3].

Among various semiconductors like ZnO [4], WO₃ [5], and BiVO₄ [6], TiO₂ is the most important one because of its good photochemical and chemical

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stability, non-toxicity, highest light conversion efficiency, facile preparation, strong oxidizing power, and cheap availability [7]. However, because of the wide band gap energy of TiO_2 (3.2 eV for the anatase phase and 3.0 eV for the rutile phase [8]), pure TiO_2 -based photocatalysts have low photocatalytic activity under visible light irradiation. Recent methods used for improving the visible light photocatalytic performance of TiO_2 are substitutional metal/non-metal ion doping [9,10], codoping with foreign ions [11], compositing with carbon nanomaterials such as graphene [12], and sensitizing with semiconductor quantum dots [13].

Compared to other non-metal dopants such as S, F, C, and B, nitrogen is more beneficial for the doping of TiO_2 because of its high stability, small ionization energy, and metastable center formation [7]. Furthermore, because of its comparable atomic size with oxygen, nitrogen can be easily incorporated into the TiO_2 structure [14]. Introduction of nitrogen into the TiO_2 lattice, in the forms of substitution or interstitial, alters both the electronic and surface properties of TiO_2 , and in this way, the band gap energy of TiO_2 and charge carrier recombination rate on its surface decrease [15].

Moreover, the photocatalytic activity of semiconductor photocatalysts can be improved by tailoring the shape and surface structure of these compounds [16]. Recent studies have demonstrated that the shape of nanomaterial has a significant effect on its photocatalytic activity [17–19]. Based on the literature, the photocatalytic activity of TiO_2 , especially in nanometer length scale, is strongly dependent on the surface atomic structure which differs by changing the crystal facets [20,21]. Li *et al.* [22] compared the photocatalytic activity of N-doped TiO_2 nanocrystals with various shapes of nanocube and nanosphere, and they found that N-doped TiO_2 nanocube has higher photocatalytic activity due to the increased exposure of high-energy (001) facets in this structure. In a similar work by Zhao *et al.* [23], the anatase nanocuboid TiO_2 showed high photocatalytic activity owing to the increased exposure of active (100) and (001) facets. There are some other similar reports in the literature about the high photocatalytic performance of TiO_2 and N-doped TiO_2 nanocubes because of the increased exposure of active (100) and (001) facets on their surface [24–26]. Despite the many studies about TiO_2 and N-doped TiO_2 nanoparticles, to the best of our knowledge, there

is no report about the preparation and photocatalytic activity of the transparent TiO_2 and N-doped TiO_2 thin films with nanocube morphology.

Inspired by the above mentioned papers, it was decided to prepare the TiO_2 and N-doped TiO_2 thin films with nanocube morphology for the first time, by a novel combination of sonochemical and chemical vapor deposition (CVD) methods. There are various methods for preparation of N-doped TiO_2 thin films like sol–gel [27], sputtering [28], spray pyrolysis [29], pulsed laser deposition [30], hydrothermal and solvothermal synthesis [31] methods. However, because of some disadvantages of these techniques, such as high temperature, expensive instruments, and toxic precursors, in the current work, a new design of sonochemical–CVD method was proposed for preparation of the TiO_2 and N-doped TiO_2 samples. In this method, the sol solution of each sample is sprayed as small mist particles by application of ultrasonic waves, and these mist particles are thermally decomposed in the subsequent CVD chamber to produce the desired thin films. The main advantages of the new design of sonochemical–CVD technique are as follow: simple controlling of the deposition rate and thin film thickness, preparation of thin films with various morphologies, easy doping of the films with different elements, and high uniformity and monodispersity of the prepared thin films which result in the low light scattering and high transparency.

Organophosphorus compounds are the most widely used pesticides, and about 38% of the total used pesticides belong to this group of chemicals [32]. However, overuse of these pesticides has raised significant environmental problems by contamination of soils and groundwater [33]. Therefore, in the current work, the photocatalytic activity of the prepared thin films in degradation of paraoxon (as model of organophosphorus compounds) was studied.

2 Materials and methods

2.1 Materials

The following chemicals were used in this work without further purification: titanium (IV) butoxide ($\geq 97.0\%$ from Sigma-Aldrich), urea ($> 99\%$ from Merck), concentrated hydrochloric acid (37 wt% from Merck), and absolute ethanol (99.5% v/v from Merck).

2.2 Preparation of TiO₂ thin films

Similar to the work by Rasoulnezhad *et al.* [34], in the current study, TiO₂ and N-doped TiO₂ thin films were prepared by sonochemical–CVD method with some modifications in deposition step and reaction conditions. The main modifications are increasing of deposition temperature from 320 to 400 °C, increasing of N₂ gas flow rate from 60 to 200 mL/min, changing the outlet gas position, and decreasing the substrate and mist inlet distance from 20 to 5 cm; all of these modifications decrease the deposition time from 3 h to 45 min. Briefly, 30 mL ethanolic solution of HCl (0.01 M) was added dropwise into 20 mL ethanolic solution of titanium (IV) butoxide with concentration of 0.71 M for formation of TiO₂ colloidal suspension (sol). The pH of the final solution was adjusted to about 2.1 by addition of desired amount of concentrated hydrochloric acid. After 2 h stirring at this condition, the obtained solution was poured into the flask 1 in the thin film deposition setup (Fig. 1). By applying ultrasonic waves (produced by Sonicator 3000; Bandeline, MS 72, Germany) as nebulizing agent, the TiO₂ sol solution was sprayed and carried by N₂ gas (with flow rate of 200 mL/min) into the flask 2. In addition to nebulizing action of ultrasonic waves [35], they could accelerate the hydrolysis of titanium (IV) butoxide precursor and facilitate the formation of the TiO₂ sol solution [36]. Flask 2 was devised in this part as the deposition setup for improving of the monodispersity of the obtained thin films, by settling down of the large mist particles. In the flask 3 (as a CVD chamber), the migrated mist particles were thermally decomposed at 400 °C to form TiO₂ thin films on glass or quartz substrates after 45 min deposition time. The procedure for the preparation of N-doped TiO₂ thin films was the same as that of the TiO₂ thin films except that 50 mg urea precursor as a source of nitrogen was added into the titanium (IV) butoxide solution and the pH of the final TiO₂ sol solution was adjusted to about 2.1 by addition of concentrated hydrochloric acid. The TiO₂ thin films prepared on glass and quartz substrates were labeled as TiO₂-G and TiO₂-Q, respectively, and the N-doped TiO₂ thin films deposited on glass and quartz substrates were labeled as NTiO₂-G and NTiO₂-Q, respectively. According to the SEM images from the cross sections of the prepared samples, all of the samples have nearly the same thickness of 700 nm.

Fig. 1 Schematic illustration of the thin film deposition setup.

2.3 Characterization

X-ray diffraction (XRD) patterns of the prepared thin films were recorded using Philips-X'Pert Pro MPD (Netherlands) X-ray diffractometer with Cu K α irradiation ($\lambda = 1.54018$ Å). Furthermore, the crystallite sizes of the samples were calculated from the XRD peak broadening using Scherrer's formula [37]. Field emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDS) elemental analysis of the prepared samples were acquired by MIRA3 TESCAN field emission scanning electron microscope (Czech Republic). X-ray photoelectron spectroscopy (XPS) spectra of the samples were obtained under ultrahigh vacuum by using a Gamma-data-scienta ESCA 200 hemispherical analyzer equipped with an Al K α X-ray source (1486.6 eV). All binding energy values were corrected by calibrating the C 1s peak at 284.6 eV. Photoluminescence (PL) emission spectra of the prepared samples were recorded using Cary Eclipse fluorescence spectrophotometer (Varian, Inc., USA) at room temperature, with an excitation wavelength of 320 nm. The UV–visible absorption spectra of the prepared thin films were obtained using Cary 100 Bio spectrophotometer (Varian, Inc., USA) in the wavelength range of 200–800 nm. For TiO₂-based semiconductors (as an indirect-band-gap semiconductor), the values of the band gap energy (E_g) of samples can be estimated from the absorption spectra by using Tauc's equation [38,39]:

$$\alpha h\nu = A(h\nu - E_g)^2 \quad (1)$$

where α , h , ν , A , and E_g refer to the absorption coefficient, Planck's constant, incident light frequency, constant value, and band gap energy, respectively.

2.4 Evaluation of the visible light photocatalytic activity of the thin films

For evaluating the visible light photocatalytic activity

of the prepared thin film samples in the photocatalytic degradation of paraoxon pesticide (with chemical formula of $C_{10}H_{14}NO_6P$), 4 mL of pesticide solution with an initial concentration of 60 mg/L was added to a cuvette containing thin film sample with an active surface area of 2 cm². Then the cuvette was sealed with glass to prevent the solution evaporation. Before irradiation, the reaction solution was stirred in the dark condition for 24 h with a magnetic stirrer to achieve an adsorption–desorption equilibrium between pesticide and thin film surface. Afterward, a 570 W xenon lamp (OSRAM Co.) as a visible light irradiation source was placed above the reaction solution, and the solution was irradiated at room temperature. L41 UV cut-off filter (Kenko Co.) with a cut-off wavelength of 400 nm was used for elimination of any UV light from the radiation source. For determination of the remaining concentration of paraoxon in the solution, the samples were withdrawn from the solution at given time intervals, and the paraoxon concentration was analyzed using a Cary 100 Bio spectrophotometer (Varian). Furthermore, a blank test without any photocatalyst was done in the same conditions. The mineralization of paraoxon under visible light irradiation over the prepared thin films was followed by total organic carbon (TOC) measurements using a total organic carbon analyzer (Shimadzu TOC-VCSH, Japan).

3 Results and discussion

3.1 Surface morphology and roughness

Figure 2 shows the surface morphology images and EDS elemental analysis results of the prepared thin film samples. As this figure reveals, both of the TiO₂ and N-doped TiO₂ thin films on a glass substrate (TiO₂-G and NTiO₂-G samples) have nanocubic morphology. However, the films deposited on a quartz substrate (TiO₂-Q and NTiO₂-Q samples) contain irregular spherical nanoparticles in their structures. Furthermore, in comparison with the films prepared on a glass substrate, the agglomerated particles clearly can be observed in the structure of the films prepared on a quartz substrate. Therefore by changing of the substrate, it is possible to tailor the surface morphology of the prepared thin film on its surface. The high monodispersity of the prepared samples clearly can be seen in this figure. The average particle sizes of TiO₂-Q, TiO₂-G, and NTiO₂-Q samples are about 42,

55, and 50 nm, respectively, and the particle size of NTiO₂-G is in the range of 60–100 nm.

In comparison with the EDS spectra of TiO₂-G and TiO₂-Q samples, the co-presence of N, Ti, and O elements, along with the substrate elements, in the EDS spectra of the NTiO₂-G and NTiO₂-Q samples, indicates successful doping of N atoms in the structure of these thin films.

3.2 XRD

Figure 3 depicts the XRD patterns of the prepared thin film samples. As shown in this figure, in XRD patterns of these samples, the diffraction from the (101), (004), (200), (105), (211), (204), (116), (220), and (115) planes of TiO₂ are appeared at $2\theta = 25.3^\circ, 37.7^\circ, 47.9^\circ, 54.1^\circ, 55.1^\circ, 62.8^\circ, 68.9^\circ, 70.6^\circ,$ and 75.3° , respectively, which well match with the standard peaks of the anatase TiO₂ phase (JCPDS No. 01-083-2243). The XRD patterns of these samples elucidate that the crystalline structure of TiO₂ in the NTiO₂-G and NTiO₂-Q samples is not affected by N doping. The sharpness of the diffraction peaks indicates good crystallinity of the thin films. The broadness of diffraction peaks can be related to the nanostructure nature of the thin films, and the crystallite sizes calculated by the Scherrer equation of the TiO₂-Q, TiO₂-G, NTiO₂-Q, and NTiO₂-G samples are 40, 52, 47, and 56 nm, respectively. Except NTiO₂-G sample, these sizes are nearly equal to the sizes observed in the SEM images; therefore, NTiO₂-G is polycrystalline sample. In both of the TiO₂ and N-doped TiO₂ thin films on a glass substrate, the relative intensity of the (004) and (200) diffraction planes is reversed which could be related to the special nanocube morphology of these samples (Figs. 2(b) and 2(d)). Because of the texture effect [40], in nanostructures with the non-spherical morphology such as nanorods or nanocubes, the relative intensities of the XRD peaks from the different lattice planes are different from the reported standard XRD patterns.

There are some reports about the effects of crystallinity, chemical nature, and conductivity of substrate on the crystal structure and shape of nanostructures. Tao *et al.* [41] and Dong *et al.* [42] in their work studied the effect of fluorine-doped tin oxide (FTO) and glass substrates on the morphology of TiO₂, and Panda *et al.* [43] reported the different morphologies of ZnO nanostructures on Si (100) and glass substrates. According to the results of these works and our XRD

Fig. 2 FESEM images and EDS analysis results of (a) NTiO₂-Q, (b) NTiO₂-G, (c) TiO₂-Q, and (d) TiO₂-G thin film samples.

and SEM results, it can be concluded that with changing of substrate, and due to the change of matching or mismatching of the different crystal planes of TiO₂ with respect to different orientation of substrates' molecules, the energies of crystal planes change. In such condition, because of the variation of the growth rate of the different crystal planes, nanostructures with different morphologies are formed on different substrates.

3.3 XPS

XPS is a widely used chemical analysis technique for the characterization of surface elements and their chemical states. As shown in the XPS survey spectra of the prepared thin films (Fig. 4(a)), three elements of C, Ti, and O can be observed in the XPS survey spectra of undoped TiO₂ thin films, and in the XPS survey spectra of N-doped TiO₂ samples, there is an additional weak peak related to the N element. In the XPS survey

Fig. 3 XRD patterns of (a) $\text{TiO}_2\text{-G}$, (b) $\text{TiO}_2\text{-Q}$, (c) $\text{NTiO}_2\text{-G}$, and (d) $\text{NTiO}_2\text{-Q}$ samples.

spectra of all samples, there is a C 1s peak at about 284.5 eV which is assigned to the adventitious carbon and is related to the reference carbon. The co-presence of N, Ti, and O elements in the structure of N-doped TiO_2 samples demonstrates successful preparation of the N-doped TiO_2 thin films.

In the Ti 2p XPS core level spectra of the undoped TiO_2 thin films (Fig. 4(b)), there are two peaks located at 458.9 and 464.6 eV, corresponding to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ states, respectively, and indicating the presence of titanium in the form of Ti^{4+} [44]. In the case of the N-doped TiO_2 thin films, because of the substitution of some O atoms with N atoms with lower electronegativity, the positions of these two peaks are shifted to the lower binding energy. Moreover, In the Ti 2p XPS core level spectra of the N-doped TiO_2 samples, there are additional peaks related to the formation of Ti^{3+} [45]. Indeed, the presence of N atoms in the structure of TiO_2 induces the formation of Ti^{3+} species as reported in previous works. Compared to the N-doped TiO_2 films on a quartz substrate (i.e., $\text{NTiO}_2\text{-Q}$ sample), the N-doped TiO_2 film deposited on glass substrate (i.e., $\text{NTiO}_2\text{-G}$ sample) has more Ti^{3+} in its structure.

As the results of the high-resolution XPS spectra of the N 1s peak for the N-doped TiO_2 samples (Fig. 4(c)) indicate, the N 1s peaks in both of the $\text{NTiO}_2\text{-Q}$ and $\text{NTiO}_2\text{-G}$ thin films can be deconvoluted to two peaks located at 398.7 and 400.3 eV. The peak located at 398.7 eV is assigned to the formation of N–Ti–O linkage because of the substitution of O atoms by anionic N atoms and incorporation of N in the TiO_2 lattice, while the peak at 400.3 eV is related to the formation of oxidized N in the form of Ti–O–N bond

Fig. 4 (a) XPS survey spectra, (b) Ti 2p XPS core level spectra, and (c) N 1s XPS core level spectra of the prepared samples.

and resulted from the interstitial N doping in the TiO₂ structure [46,47]. In both of the samples, the relative intensity of the peak at 400.3 eV is higher than that of the peak at 398.7 eV. Therefore, the interstitial N doping is the dominant form of the N element in the N-doped TiO₂ thin films. Moreover, the absence of a peak at about 396 eV in these spectra confirms that TiN phase is not formed in these samples [48]. According to the calculation of area of the N 1s XPS core level, total amount of surface N in NTiO₂-G thin film is about 1.14 times of that of NTiO₂-Q thin film; therefore, compared to the quartz substrate, the glass substrate induces more amount of N doping in TiO₂. As can be seen in Figs. 4(b) and 4(c), the amount of Ti³⁺ in N-doped TiO₂ is directly related to the amount of N present in this sample, and with the amount of N doping in TiO₂ increasing, the amount of Ti³⁺ species increases. Therefore, because the more amount of N doping in the NTiO₂-G thin film, this film has more Ti³⁺ than the film deposited on quartz substrate. Different chemical composition and crystallinity of the glass may cause that the film deposited on this substrate has higher amount of N dopant and Ti³⁺ in its structure than the film deposited on quartz.

3.4 Optical properties

The optical properties of the prepared thin films were investigated by UV–visible absorption spectroscopy. The UV–visible absorption spectra of the bare and N-doped TiO₂ thin films are shown in Fig. 5(a). The undoped TiO₂ thin films (TiO₂-Q and TiO₂-G) present no absorption in the visible light region. However, due to the presence of Ti³⁺ in the structure of N-doped TiO₂ thin films (Fig. 4(b)), which acts as a color center for absorption of visible light [48], these samples show a

weak absorption in the visible region. In addition, compared with the pure TiO₂ thin films, there is a remarkable red shift in the absorption edge of N-doped TiO₂ samples.

Figure 5(b) depicts the plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ (Tauc plots) for the prepared thin films. The band gap energies of the TiO₂-Q, TiO₂-G, NTiO₂-Q, and NTiO₂-G thin films were estimated to be 3.29, 3.19, 2.81, and 2.76 eV, respectively. The decrease of the band gap of N-doped TiO₂ thin films can be attributed to the mixing of the N 2p and O 2p states and presence of occupied localized N 2p states above the valence band of TiO₂ [48–50]. Therefore, it can be concluded that the presence of occupied localized N 2p states above the valence band of TiO₂ is responsible for the band gap narrowing of N-doped TiO₂, and the presence of Ti³⁺ (which acts as a color center) creates a weak absorption band in the visible region. However, it must be noticed that, according to the XPS results, the presence of N in TiO₂ induces the formation of Ti³⁺ in N-doped TiO₂, and the amount of Ti³⁺ in N-doped TiO₂ is directly related to the amount of N present in this sample. In the case of the thin films with nanocube morphology on glass substrate (i.e., TiO₂-G and NTiO₂-G samples), the decrease of band gap in comparison to the samples with irregular spherical morphology on quartz substrate (i.e., TiO₂-Q and NTiO₂-Q samples), is resulted from the defect formation on the sharp corners and edges of such structures [51].

In order to investigate the transparency of the prepared thin film samples, transmittance spectra of the samples were studied, and the results are shown in Fig. 6. By analyzing the results of this figure, the transparency of the TiO₂-Q, TiO₂-G, NTiO₂-Q, and

Fig. 5 (a) UV–Vis absorption spectra of the prepared thin films samples and (b) band gap energy calculation from Tauc plots.

Fig. 6 Transmittance spectra of the prepared thin film samples.

NTiO₂-G thin films in visible region (wavelength of 400–800 nm) are estimated to be 84.02%, 70.83%, 75.74%, and 64.10%, respectively. Because of the higher visible light absorption of N-doped TiO₂ samples than undoped ones, the undoped thin films have high transparency. Therefore, the prepared thin films have high transparency in visible region [52].

3.4 Photoluminescence

Photoluminescence (PL) spectroscopy could be used as an effective tool to get insight into the efficiency of charge carrier trapping and transfer, and to understand the recombination rate of photogenerated electron–hole pairs [53]. In this spectroscopy, the PL intensity of a photocatalyst sample is directly proportional to the electron–hole recombination rate on its surface, that is, the higher PL intensity indicates a higher recombination rate, and vice versa [54]. To study the effect of N doping on the recombination rate of photo-induced electron–hole pairs, PL spectra of the prepared thin films were investigated (Fig. 7). As the results of this experiment in Fig. 7 demonstrate, among the N-doped and undoped TiO₂ thin film samples, the N-doped TiO₂ thin films have low PL intensity, and consequently low charge carrier recombination rate. In comparison between thin films deposited on glass and quartz substrates, the films deposited on a glass substrate have low electron–hole recombination rate. This effect could be related to the special nanocube morphology of these samples and enhanced charge separation on their sharp edges and corners [55]. Furthermore, as reported in the literature [56], Ti³⁺ sites can act as hole trapping center to convert to Ti⁴⁺ and, in this way, reduce the electron–hole recombination rate. As the results of XPS experiments indicate in comparison with the

Fig. 7 PL spectra of the prepared thin film samples.

N-doped TiO₂ thin film on a quartz substrate, the N-doped TiO₂ thin film on a glass substrate has a high amount of Ti³⁺ in its structure, and for this reason, has low electron–hole recombination rate.

3.5 Photocatalytic activity

The photocatalytic performance of the prepared thin films for visible light photocatalytic degradation of paraoxon can be seen in the C_t / C_0 versus irradiation time plots as shown in Fig. 8(a), where C_t is the remaining concentration of paraoxon at the irradiation time of t and C_0 is its concentration after the adsorption–desorption equilibrium. As this figure demonstrates, there is no remarkable degradation of paraoxon under visible light irradiation in the absence of any thin film photocatalyst; however, in the presence of the prepared thin films, especially the NTiO₂-G sample, the photocatalytic degradation process significantly enhances.

Based on the pseudo-first-order kinetic model, the reaction rate constant (k) for the photocatalytic degradation of an organic pollutant can be obtained using the following equation:

$$-\ln(C_t / C_0) = kt \quad (2)$$

The value of the reaction rate constant (k) for visible light photocatalytic degradation of paraoxon over TiO₂-Q, TiO₂-G, NTiO₂-Q, and NTiO₂-G thin films can be estimated from the slope of $-\ln(C_t / C_0)$ versus irradiation time (t) plots, as Fig. 8(b) shows. The estimated reaction rate constants for visible light photocatalytic degradation of paraoxon on TiO₂-Q, TiO₂-G, NTiO₂-Q, and NTiO₂-G thin films are 0.0044, 0.0063, 0.0125, and 0.0228 min^{−1}, respectively. According to these results, it can be concluded that among the prepared thin films, the N-doped TiO₂ thin films have higher photocatalytic activity than pure

Fig. 8 (a) Visible light photocatalytic activity of the different thin films in degradation of paraoxon, and (b) calculation of the corresponding reaction rate constant (k) based on the pseudo-first-order kinetic model.

TiO_2 thin films due to the decrease of their band gap energy and reduced electron–hole recombination rate on their surface. Moreover, in comparison with the thin films deposited on quartz substrate, the films on glass substrate have higher photocatalytic performance, because of the special nanocube morphology of the thin films deposited on glass substrate. As reported in previous works, because of the sharp corners and edges of photocatalysts with nanocube morphology and increased exposure of high-energy (001) facets in such structure, the photocatalysts with such morphology have higher photocatalytic activity [22–26,57].

Higher visible light absorption of N-doped TiO_2 samples than the undoped ones, results in the low transparency of these samples. However, on the other hand, this effect along with the low recombination rate of the charge carriers (due to the presence of Ti^{3+} as hole trapping center) in the N-doped samples may cause the high yield of electron–hole pairs under visible light irradiation. These effects, in turn, may contribute in the higher visible light photocatalytic activity of the N-doped TiO_2 thin film.

Prasad *et al.* [58] reported the k value of 0.0069 min^{-1} for photocatalytic degradation of paraoxon on TiO_2 thin film. In another work, Kongsong *et al.* [59] reached a maximum k value of 0.0067 min^{-1} for photocatalytic degradation of glyphosate pesticide on N-doped $\text{SnO}_2/\text{TiO}_2$ thin film under simulated solar irradiation, and in Mamane *et al.*'s work [60], the calculated k value for photocatalytic degradation of carbamazepine on N-doped TiO_2 thin film is 0.0176 min^{-1} . Therefore, in comparison with these work, the N-doped TiO_2 thin film on glass substrate in our work has higher photocatalytic activity.

One of the important characteristics of photocatalyst

systems for practical applications is their stability and reusability under the reaction condition. For this reason, the reusability of the NTiO_2 -G thin film was examined by a series recycle experiments on the visible light photocatalytic degradation of paraoxon. After each experiment, the thin film was separated from the reaction solution and washed with acetone and deionized water and then dried at 60°C in an oven, and then reused for the next experiment. Figure 9 shows the results of this experiment. As this figure indicates, even after five times of recycling, the NTiO_2 -G thin film maintains 97% of its initial activity, and there is a slight decrease in its photocatalytic activity. Therefore, it can be concluded that this thin film has remarkable stability under the reaction condition and can be used for several times.

During the photocatalytic degradation of organic pollutants, some intermediates with high toxicity may be produced. Therefore it is necessary to evaluate the complete mineralization of these compounds and their intermediates. In this regard, in this work, the TOC

Fig. 9 Reusability of the NTiO_2 -G thin film for visible light degradation of paraoxon.

Fig. 10 TOC removal efficiency of the N-TiO₂-G photocatalyst for visible light degradation of paraoxon.

(total organic carbon) test was done in order to explain the mineralization of paraoxon over the N-TiO₂-G thin film under visible light irradiation. As the result of this test in Fig. 10 indicates, paraoxon and its photocatalytic degradation intermediates are completely mineralized after about 540 min and converted to the inorganic compounds like H₂O, PO₄³⁻, NO₃⁻, and CO₂. Therefore, by using the N-TiO₂-G thin film and by visible light irradiation, the paraoxon contaminated water can be successfully de-polluted.

4 Conclusions

The growing use of organophosphorus pesticides such as paraoxon in agriculture industry has raised significant environmental concerns by contamination of soils and groundwater. Therefore, there is a high demand for developing efficient methods for removing of these poisonous pollutants from contaminated resources. Transparency is an important property in photoactive coatings on glass of vehicles and buildings. In this regard, in the current study, nanostructured TiO₂ and N-doped TiO₂ thin films with high transparency were deposited on glass and quartz substrates through sonochemical–chemical vapor deposition (CVD) method and were used in the visible light photocatalytic degradation of paraoxon pesticide. The prepared thin films on a glass substrate have nanocubic morphology, and the films deposited on quartz substrate have nanospherical morphology. The presence of N atoms in the structure of TiO₂ results in a decrease in the band gap energy of TiO₂. Furthermore, N doping induces formation of Ti³⁺ species in the N-doped TiO₂ thin films and the presence of Ti³⁺, which can act as a color

center, increases visible light absorption in these samples. According to the PL spectroscopy results, among the prepared samples, the N-doped TiO₂ thin film deposited on a glass substrate has the lowest photogenerated electron–hole recombination rate, which can be related to the formation of Ti³⁺ species as hole trapping centers because of the substitution of O atoms with N ones and tendency of Ti³⁺ to convert to its stable oxidation state of Ti⁴⁺. Among the prepared thin films, the N-doped TiO₂ thin films have higher photocatalytic activity than pure TiO₂ thin films. Moreover, in comparison with the thin films deposited on a quartz substrate, the films on a glass substrate have higher photocatalytic performance. Because of the special nanocube morphology of the thin films deposited on glass substrate, and the presence of the sharp corners and edges in this morphology, the films with nanocube morphology have higher photocatalytic activity than the films with nanospherical morphology.

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