



## Hydrophilic and photocatalytic activities of Nd-doped titanium dioxide thin films

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Received 27 October 2014; accepted 27 April 2015

**Abstract:** The Nd-doped TiO<sub>2</sub> thin films with higher hydrophilic and photocatalytic activities were prepared on glass slides by an acid-catalyzed sol–gel method. The effects of Nd doping on crystalline phase, surface composition and optical property were investigated by means of techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), optical contact angle tester and UV-Vis spectroscopy. The results show that Nd doping obviously influences the hydrophilic and photocatalytic activities of TiO<sub>2</sub> thin films. Nd doping could cause the TiO<sub>2</sub> lattice distortion, inhibit phase transition from anatase to rutile, cause red shift of the absorption spectrum edge, produce hydroxyl radicals ( $\cdot\text{OH}$ ), and accelerate surface hydroxylation, which result in a significant improvement in the hydrophilicity and photoreactivity of Nd-doped TiO<sub>2</sub> thin films. When the content of Nd is 0.1% (mass fraction), TiO<sub>2</sub> thin films achieve the smallest grain size (about 15 nm), and the hydrophilic and photocatalytic activities of TiO<sub>2</sub> thin film reach the maximum, the contact angle is only 8.1°, and 92% of methylene blue is finally degraded. Moreover, the modification mechanism of Nd doping was also discussed.

**Key words:** TiO<sub>2</sub>; Nd doping; sol–gel method; hydrophilicity; photocatalysis

### 1 Introduction

As a promising semiconductor photocatalyst, TiO<sub>2</sub> has attracted worldwide interest for its good chemical stability, strong oxidizing power, non-toxicity and low-cost related in environmental problems such as water and air purification or pollution control [1–3]. One-dimensional TiO<sub>2</sub>, such as nanopowder and nanofilms, becomes the focus of considerable interest due to their unique properties and their potential applications, such as nanoelectronics and photo-electrochemical applications. Due to the self-cleaning and antifogging effects, TiO<sub>2</sub> thin films have been widely used in material industry as coating glasses [4,5]. It is known that the self-cleaning and antifogging effects are attributed to the photocatalytic and hydrophilic activities, respectively.

However, it is reported that there are still some applications limited by two defects of TiO<sub>2</sub>: firstly, it absorbs near UV light, and its band-gap ( $E_g=3.3$  eV)

does not match with solar light very well; secondly, the photocatalytic efficiency of TiO<sub>2</sub> is not high, as the recombination of photogenerated electron–hole pairs results in low photo quantum efficiency [6]. Therefore, many methods have been undertaken to improve the photocatalytic activity of TiO<sub>2</sub> [7–9]. Transitional metal ions [9–12] and rare earth elements [13,14] are usually employed by the researchers as catalyst for the incompletely occupied 4f and empty 5d orbits, which can trap the electrons and/or holes and eliminate the recombination of electron–hole pairs significantly. Therefore, this results in the extension of their wavelength response toward the visible region, and consequently improving the photo-reactivity. In particular, doping with lanthanide metal ions (Nd<sup>3+</sup>) has proved to be an efficient route to alter the photoactivity of TiO<sub>2</sub> for selected reactions [13]. Such variation in property might be due to the increase of oxygen vacancies and a large number of hydroxyl groups with enhanced polarity, which tended to make the surface hydrophilicity. In the past two decades, numerous efforts

have been devoted to the TiO<sub>2</sub> powders, while few researchers dealt with the surface property of TiO<sub>2</sub> thin films modified by rare earth ions. Thus, the main aim of the work is to fabricate an effective photocatalyst by doping TiO<sub>2</sub> thin films with lanthanide metal ions (Nd<sup>3+</sup>), and to discover the surface property of Nd-doped TiO<sub>2</sub> thin films for its interesting and useful features.

As is known to all, many different methods and techniques have been developed to fabricate the doped TiO<sub>2</sub> thin films. Among them, the sol-gel method has been reported to be the most powerful technique due to the simplicity of the synthesis and the fact that the nanofilms can be obtained by simple, cost-effective and environmentally innocuous route.

In this work, the pure TiO<sub>2</sub> and the Nd-doped TiO<sub>2</sub> thin films were prepared by the sol-gel method. And hydrophilic and photocatalytic activities of Nd-doped TiO<sub>2</sub> thin films were investigated in detail.

## 2 Experimental

To prepare Nd-doped TiO<sub>2</sub> thin films, two kinds of solutions (Solutions A and B) were prepared first. Solution A was made from tetrabutyl titanate and ethanol in a mass ratio of 1:4, then 1 mL acetylacetone (Acac) and 2 mL polyethylene glycol (PEG) were added dropwise into Solution A under vigorous stirring, and pH of the solution was adjusted to 2.5 with HNO<sub>3</sub>. Acac and PEG were used as hydrolysis inhibitor and film-forming agent, respectively. Solution B was made from Nd(NO<sub>3</sub>)<sub>3</sub>, which was dissolved with deionized water. Solution B was added dropwise into Solution A under vigorous stirring, and the content of Nd was between 0.1% and 0.9% (mass fraction). Consequently, a light yellowish solution was obtained and then gelatinized for 3 h to form TiO<sub>2</sub> gel. The glass slides (25 mm × 50 mm × 1 mm) were used as the substrates. The slides were pulled from the gel at a speed of 2 mm/min by dip-coating instrument, dried at 90 °C for 0.5 h, and then the dry gel precursor was calcined at 550 °C for 2 h. Finally, TiO<sub>2</sub> thin films were obtained. In the meantime, pure TiO<sub>2</sub> as a blank catalyst was also prepared using the same procedure except that Solution B was substituted by deionized water. All the chemicals used in the experiments were of analytical grade.

Multifunctional X-ray diffractometer (XRD, Bede), scanning electron microscope (SEM), transmission electron microscope (TEM, JEM-2100) and Fourier transform infrared spectrometer (Nicolet 5700) were used to characterize the phase structure, the surface morphology and the composition of the samples, respectively. The hydrophilic properties were observed on the optical contact angle measuring instrument (Zheke, DSA 100). The photocatalytic activity of thin films was

measured by the UV-Vis spectrophotometer (Shimadzu, 2501 PC).

To measure the photocatalytic activity, the solution of methylene blue was prepared. The standard solutions of methylene blue with the concentration of 1–11 mg/L had a good linear relationship with absorbance [15], so 4 mg/L methylene blue was chosen as degradation model. The concrete steps were as follows: 15 mL methylene blue (4 mg/L) was taken into the beaker at room temperature, the thin films were put into the beaker, and then a 25 W ultraviolet light was turned on. The absorbance of residual methylene blue was detected every 1 h. The degradation rate of methylene blue ( $\eta$ ) was calculated as follows:

$$\eta = (c_0 - c) / c_0 \times 100\% = (A_0 - A) / A_0 \times 100\% \quad (1)$$

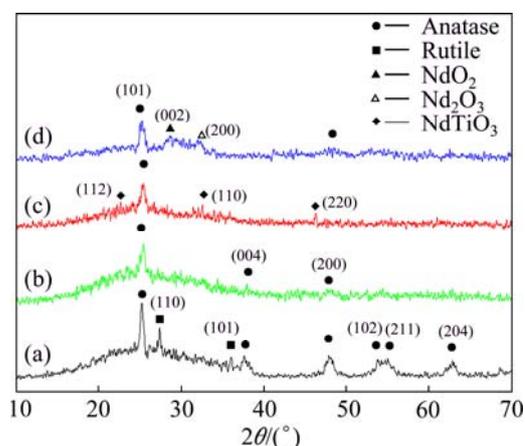
where  $c_0$  and  $A_0$  are the initial concentration and absorbance of methylene blue solution at 664 nm, respectively.  $C$  and  $A$  are the concentration and the absorbance of methylene blue solution at 664 nm under UV light irradiation with different time, respectively.

Both blank and dark experiments emended disturbance produced from ultraviolet radiation and adsorption of the thin films, respectively.

## 3 Results and discussion

### 3.1 Structural properties

Figure 1 shows the effects of neodymium on the phase compositions of the Nd-doped TiO<sub>2</sub> thin films. For comparison, the pattern of pure TiO<sub>2</sub> thin film is also shown in Fig. 1. The pure TiO<sub>2</sub> thin film exists as the coexistence of anatase and rutile. However, the rutile phase cannot be found in the Nd-doped TiO<sub>2</sub> thin films. When the content of Nd<sup>3+</sup> is 0.1% (mass fraction), only the anatase can be found. When the content of Nd<sup>3+</sup> increases to 0.5%, three weak diffraction peaks of NdTiO<sub>3</sub> are found. With the content of Nd increasing

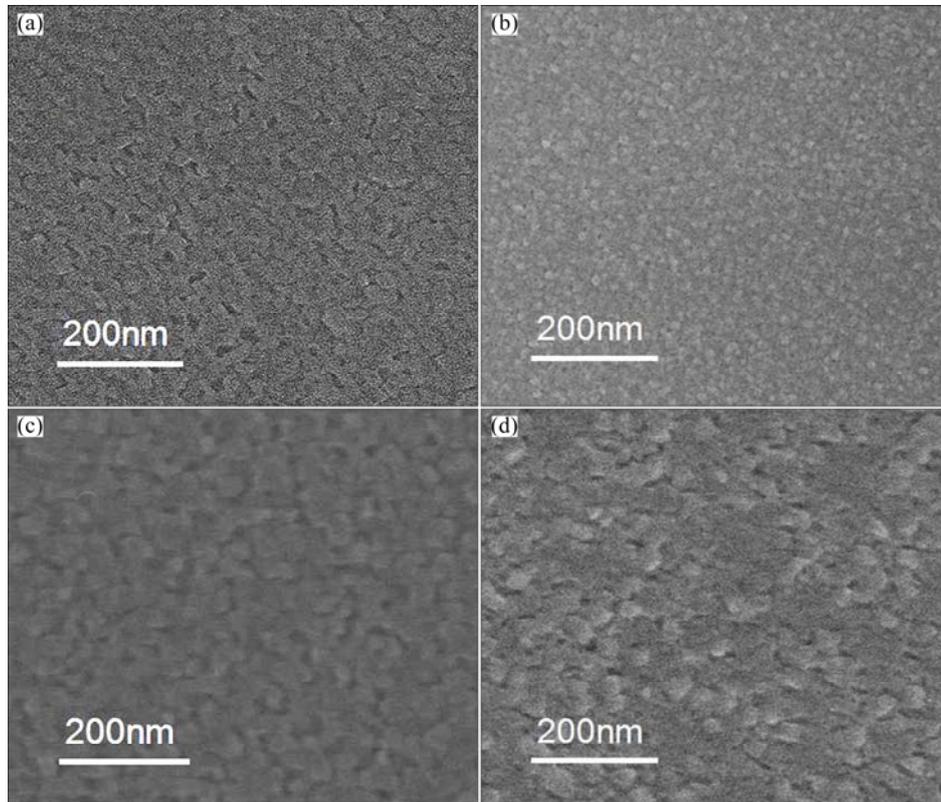


**Fig. 1** XRD patterns of pure TiO<sub>2</sub> (a), 0.1% Nb-doped (b), 0.5% Nb-doped (c) and 0.9% Nb-doped (d) TiO<sub>2</sub> thin films

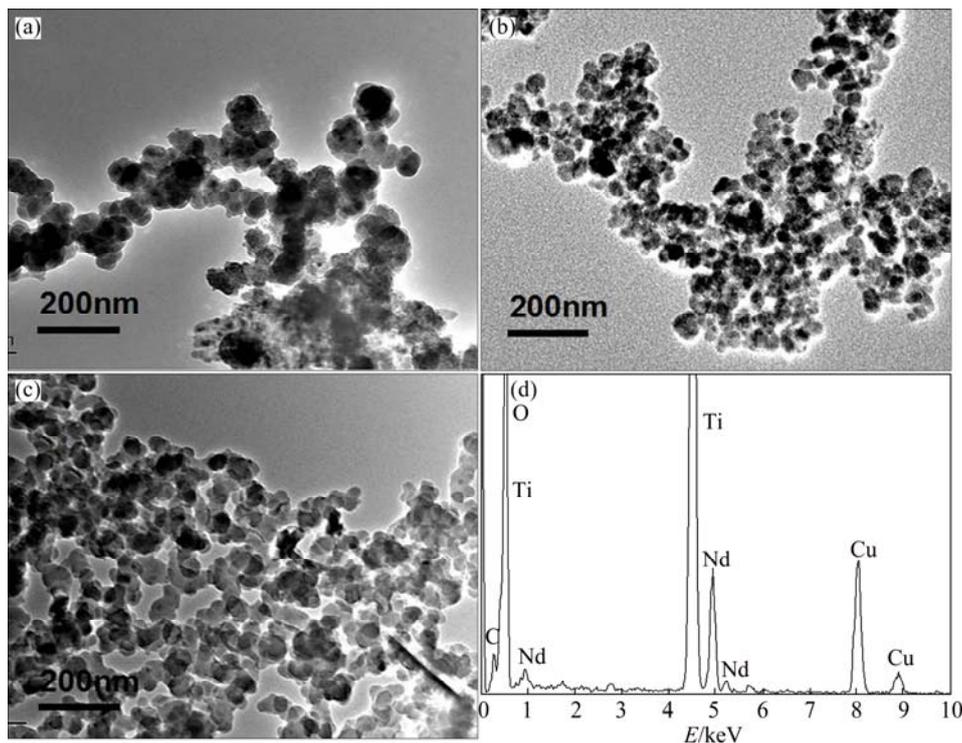
continuously from 0.5% to 0.9%, the weak peaks of  $\text{Nd}_2\text{O}_3$  and  $\text{NdO}_2$  appear in the pattern.

The SEM and TEM micrographs of pure  $\text{TiO}_2$  and Nd-doped  $\text{TiO}_2$  thin films prepared at 550 °C are shown

in Fig. 2 and Fig. 3, respectively. It can be observed that all samples have a granular morphology without particle agglomeration and a relatively uniform particle diameter distribution. Meanwhile, Nd-doped  $\text{TiO}_2$  thin films



**Fig. 2** SEM images of pure  $\text{TiO}_2$  (a), 0.1% Nd-doped (b), 0.5% Nd-doped (c) and 0.9% Nd-doped (d)  $\text{TiO}_2$  thin films prepared at 550 °C



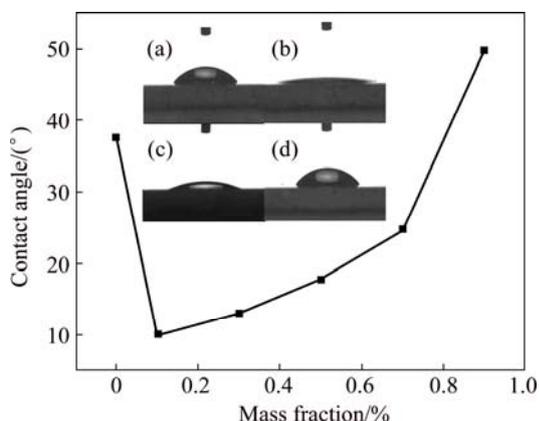
**Fig. 3** TEM images of pure  $\text{TiO}_2$  (a), 0.1% Nd-doped (b), 0.5% Nd-doped (c) and EDS spectrum of 0.1% Nd-doped (d)  $\text{TiO}_2$  thin films prepared at 550 °C

appear to have smaller grains, a corresponding smoother and denser surface than pure TiO<sub>2</sub> thin films. And 0.1% Nd-doped thin film presents the smallest grains and the size is about 15 nm. With the content of Nd increasing continuously from 0.1% to 0.9%, the size of crystalline phase increases from about 15 to 40 nm, but the particle diameters of pure TiO<sub>2</sub> thin films are 50–60 nm. Thus, the presence of Nd modifies the texture of the TiO<sub>2</sub> surfaces.

Furthermore, the EDS pattern of 0.1% Nd-doped thin film is also shown in Fig. 3. From this EDS spectrum, a very weak signal for Nd and a very strong signal for Ti can be observed. This is consistent with the nominal amount of doped Nd. Elements Cu and C are also detected, which are originated from the supporting copper grid. From Figs. 1–3, it can be concluded that Nd can enter the TiO<sub>2</sub> lattice in Nd-doped TiO<sub>2</sub> thin films. It is known that the ionic radii of Ti<sup>4+</sup> and Nd<sup>3+</sup> are 0.061 and 0.098 nm, respectively. The ionic radius of Nd<sup>3+</sup> is larger, so the doping of Nd will cause the TiO<sub>2</sub> lattice distortion. As a result, the growth of TiO<sub>2</sub> crystalline phase decreases, as shown in Fig. 1(b) and Fig. 2(b), the peak intensity and the size of TiO<sub>2</sub> crystalline phase decrease. On the other hand, the densities of rutile and anatase are 4.22 and 3.84 g/cm<sup>3</sup>, respectively. The rutile has higher stacking density than anatase. After Nd enters the TiO<sub>2</sub> lattice, it is difficult to form high stacking density because of the lattice distortion. As shown in Fig. 1, compared with the pure TiO<sub>2</sub> thin films, the diffraction peaks of rutile TiO<sub>2</sub> can be rarely found in Nd-doped TiO<sub>2</sub> thin films. This means that the content of rutile crystalline phase is very little in the Nd-doped TiO<sub>2</sub> thin films. Consequently, it can be concluded that Nd doping can inhibit phase transition from anatase to rutile.

### 3.2 Hydrophilicity

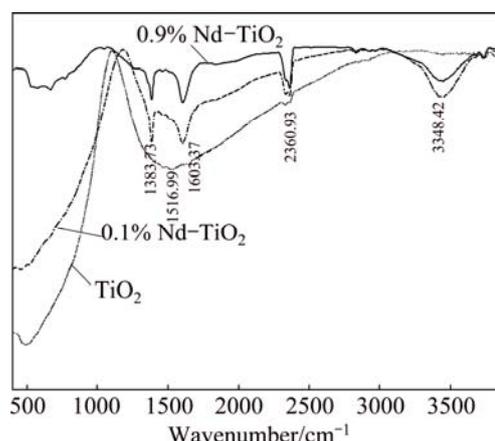
Figure 4 shows the hydrophilic property of Nd-



**Fig. 4** Hydrophilic property of Nd-doped TiO<sub>2</sub> thin films prepared at 550 °C for 2 h (Inset: images of contact angle of pure TiO<sub>2</sub> (a), 0.1% Nd-doped (b), 0.5% Nd-doped (c) and 0.9% Nd-doped (d) thin films at 550 °C

doped thin films. When the content of Nd is 0.1%, the hydrophilicity of TiO<sub>2</sub> thin film reaches the maximum, as shown in the inset Fig. 4(b), the contact angle is only 8.1°. With the content of Nd increasing continuously from 0.1% to 0.9%, the hydrophilicity decreases gradually. When the content of Nd is 0.9%, the contact angle goes up to 49.2°, higher than that of pure TiO<sub>2</sub> thin film. It can be concluded that the content of Nd has an important effect on the hydrophilicity.

Figure 5 shows the FT-IR spectra of thin films. Absorption at 450–800 cm<sup>-1</sup> is assigned to the stretching vibrations of Ti—O—Ti, Ti—O, and O—Ti—O bonds [16]. The absorption bands at about 1383.73 and 1603.37 cm<sup>-1</sup> are attributed to the bending vibration of H—O—H bonds, which are assigned to the chemisorbed water. Compared with pure TiO<sub>2</sub>, Nd-doped TiO<sub>2</sub> thin films have the strong stretching vibration of O—H absorption peak at 3348.42 cm<sup>-1</sup> and the characteristic absorption peak of CO<sub>2</sub> at 2360.93 cm<sup>-1</sup>. Obviously, Nd-doped TiO<sub>2</sub> thin films have a higher ability of absorbing water than pure TiO<sub>2</sub> thin films, which results in more hydroxyls on the surface of Nd-doped TiO<sub>2</sub>.

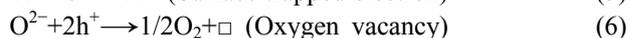


**Fig. 5** FT-IR spectra of TiO<sub>2</sub> thin films

The hydrophilic processes of Nd-doped TiO<sub>2</sub> thin films can be expressed as follows:



When a UV photon is absorbed by TiO<sub>2</sub> thin films, an e/h<sup>+</sup> pair is produced according to Eq. (2). On the surface of TiO<sub>2</sub> thin films, the holes react with surface hydroxyl groups (OH<sup>-</sup>) and adsorbed H<sub>2</sub>O, to form hydroxyl radicals (·OH). The basis of hydrophilic state is related to the production of very active ·OH obtained primarily according to Eqs. (2), (3), and (4).



Nd doping can form the dopant level near the valence band of  $\text{TiO}_2$  [17]. The electronic transition from the modified dopant band to the conduction band will be effectively improved, and the hole–electron recombination will decrease. The electrons tend to reduce the  $\text{Ti(IV)}$  cations to the  $\text{Ti(III)}$  state, and the holes oxidize the  $\text{O}_2^-$  anions. In the process, oxygen atoms are ejected and oxygen vacancies are created. Thus, more  $\text{Ti}'_{\text{Ti}}$  defects and oxygen vacancies are procured [18]. Then, water molecules can occupy these oxygen vacancies, producing adsorbed  $-\text{OH}$  groups, which tend to make the surface hydrophilic.

Furthermore, there is an important influence of the surface chemical groups on the performances of the thin films. As shown in Fig. 5, Nd-doped  $\text{TiO}_2$  thin films have more hydroxyls, which can form hydrogen bonds with water, so, the surface property of the doping samples is significantly enhanced.

On the other hand, when the dopants are excessive, as shown in Fig. 1(d), the rest of Nd cannot enter the  $\text{TiO}_2$  lattice but cover on the surface of  $\text{TiO}_2$ , and form heterogeneity junction. The valence bands and conduction bands of two crystals maybe link paratactically, and charge capture centers may become recombination center [19], so hydrophilic activity is reduced. The reaction equation can be described as follows:



### 3.3 Photocatalytic activity

Figure 6 shows the UV–Vis patterns of  $\text{TiO}_2$  and Nd-doped  $\text{TiO}_2$  thin films prepared at  $550^\circ\text{C}$ . It can be seen that the absorption edge shifts toward longer wavelength for Nd-doped  $\text{TiO}_2$  thin films, which means that the light absorption ability is greatly improved. The absorption peaks remain almost at the same position, while the peaks of Nd-doped  $\text{TiO}_2$  thin films become steep. When the content of Nd is 0.1%, the ultraviolet absorption ability of  $\text{TiO}_2$  thin films increases to the greatest (about 3.7). This indicates that Nd doping can not only influence the band gap of the sample, but also enhance the light absorption.

Figure 7(a) shows the adsorption spectra of methylene blue solution after the photocatalysis process. It can be observed that the strongest absorption peak of methylene blue is at about 664 nm. Compared with the original solution, the absorbance intensity of methylene blue solution decreases obviously under UV irradiation, which indicates that methylene blue has been photodegraded. Furthermore, the absorbance of methylene blue solution photodegraded by 0.1% Nd-doped  $\text{TiO}_2$  thin film is the lowest. Figure 7(b) shows

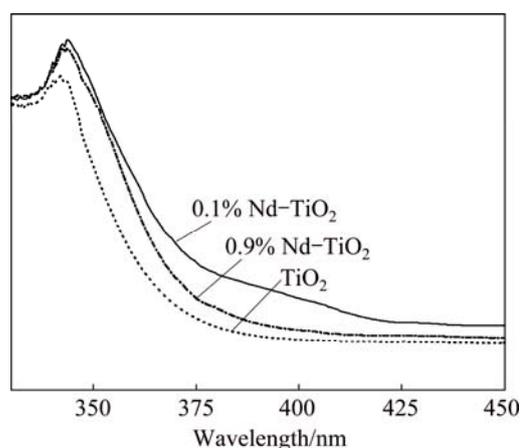


Fig. 6 UV–Vis patterns of  $\text{TiO}_2$  thin films prepared at  $550^\circ\text{C}$

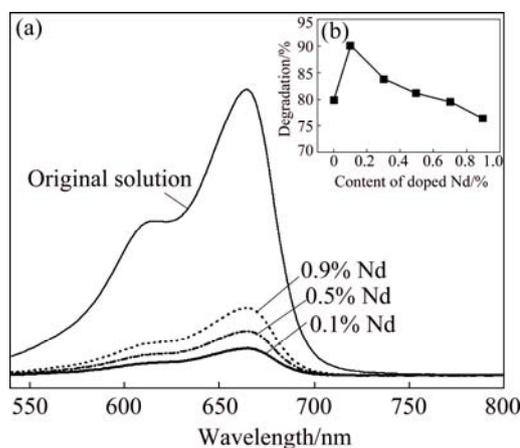


Fig. 7 UV–Vis adsorption spectra of methylene blue solution (a) and effect of Nd doping on photocatalytic activity of  $\text{TiO}_2$  thin films (b) after 6 h photocatalytic reaction

the effect of Nd doping on the photocatalytic activity of  $\text{TiO}_2$  thin film. As shown Fig. 7(b), when the content of Nd is 0.1%, the photocatalytic activity reaches the maximum, and the photodegradation is 92%. However, a decrease in photocatalytic activity appears when the content of Nd becomes too high. The basic law of data change is in good agreement with the conclusion above. Therefore, Nd doping can enhance the photocatalytic activity of  $\text{TiO}_2$  thin films and 0.1% Nd doping exhibits the highest photocatalytic activity.

As we know,  $\text{TiO}_2$  is a semiconductor. UV light can excite electron–hole pairs (Eq. (2)). The photogenerated electrons react with molecular oxygen ( $\text{O}_2$ ) to produce superoxide radical anions ( $\text{O}_2^-$ ) (Eq. (10)), and the photogenerated holes react with water to produce hydroxyl ( $\cdot\text{OH}$ ) radicals (Eq. (4)) [20]. And hydroxyl radicals ( $\cdot\text{OH}$ ) produced during photocatalysis have been reported to be detected by the photoluminescence (PL) technique [21,22].



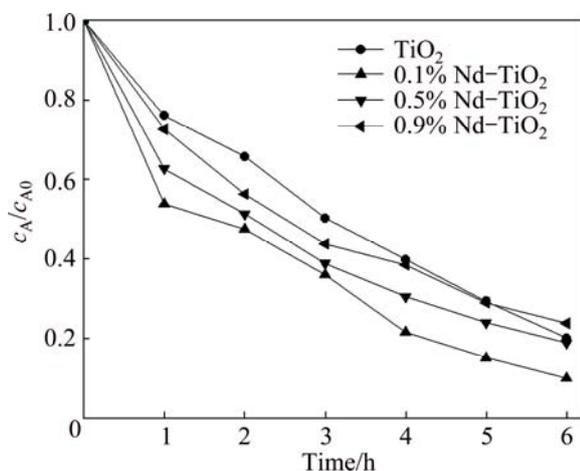
Both holes and hydroxyl radicals ( $\cdot\text{OH}$ ) have been proposed as the oxidizing species responsible for the degradation of the organic substrates. Then, these two types of reactive radicals decompose organic compounds together. When Nd is doped into  $\text{TiO}_2$  thin films, Nd ions may act as an electron trap agent, thus promoting electron separation and transfer effects [6]:



Moreover, an appropriate content of Nd may form more hydroxyls, which can trap more photogenerated holes and improve the separation of electrons and holes. As a result, Nd doping is responsible for an enhancement in its photocatalytic activity.

But when the concentration of Nd becomes too high, Nd may be served as a mediator of interfacial charge transfer or as a recombination center [23], and in our case the optimal content of Nd is 0.1%, above which the photocatalytic activity decreases.

The concentration ratio of methylene blue solution ( $c_A/c_{A0}$ ) versus degradation time is shown in Fig. 8, where  $c_{A0}$  and  $c_A$  are the initial concentration of methylene blue solution and the concentration at different illumination time, respectively. It can be seen that Nd doping significantly improves the photocatalytic activity of  $\text{TiO}_2$  under UV light. Firstly, the photocatalytic activity of Nd-doped  $\text{TiO}_2$  thin films is improved along with the increase of doping amount from 0 to 0.1%, but it switches to decrease when Nd content is above 0.1%, which demonstrates that Nd-doped amount is an important factor for photocatalytic activity and there is an optimal dosage. According to the photocatalytic results, it can be concluded that the optimal dosage of Nd doping is 0.1%, and the degradation rate of methylene blue solution can achieve 92% under UV light irradiation time of 6 h.



**Fig. 8** Variation of  $c_A/c_{A0}$  of methylene blue solution with photocatalytic time

Secondly, an appropriate amount of Nd can form the surface chemical groups, such as  $\text{O}-\text{H}$ , which can be found in Fig. 5. Due to the strong electron-withdrawing property of these groups, hydroxyl can accelerate the photocatalytic process of  $\text{TiO}_2$  thin films and improve their photocatalytic activities. As shown in Fig. 8, at the initial stage, the surface chemical groups can react with the organic compounds; both the surface chemical groups and  $\text{TiO}_2$  have an important influence on the photocatalytic activity, thus the photocatalytic process is accelerated. But the surface chemical groups will be depleted as the reactions progress; only the intrinsic mechanism of photo-catalysis has effects on the photocatalytic activity, as shown in Fig. 8. When the reactive time is above 1 h, the photocatalytic activities of the Nd-doped thin films decrease, and their activities are similar to those of pure  $\text{TiO}_2$ . In a word, Nd-doped  $\text{TiO}_2$  thin films have higher photocatalytic activity at the initial stage.

## 4 Conclusions

1) Pure  $\text{TiO}_2$  and Nd-doped  $\text{TiO}_2$  thin films were prepared on glass slides by sol-gel method. The results show that Nd can enter the  $\text{TiO}_2$  lattice, which causes the  $\text{TiO}_2$  lattice distortion and inhibits phase transition from anatase to rutile. And 0.1% Nd-doped  $\text{TiO}_2$  thin film presents the smallest grains (about 15 nm) and the most uniform surface.

2) Nd doping can cause red shift of the absorption spectrum edge and accelerate surface hydroxylation, which results in a significant improvement in the hydrophilicity and photoreactivity of Nd-doped  $\text{TiO}_2$  thin films. The possible mechanism of enhanced hydrophilicity may be that Nd doping can produce more oxygen vacancies and hydroxyl, both of them can form hydrogen bonds with water.

3) The enhanced photocatalytic activity may be mainly attributed to the enhancement of photogenerated electron-hole pair separation. And Nd-doped  $\text{TiO}_2$  thin films have higher activity at the initial stage because of the existence of the surface chemical groups. When the content of Nd is 0.1%, the hydrophilic and photocatalytic activity of  $\text{TiO}_2$  thin film reaches the maximum, the contact angle is only  $8.1^\circ$ , and 92% of methylene blue is finally degraded.

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## 钕掺杂氧化钛薄膜的亲水和光催化性能

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**摘要:** 通过酸催化溶胶–凝胶法在玻璃基板上制备具有高亲水性和光催化活性的 Nd 掺杂 TiO<sub>2</sub> 薄膜。用 XRD、SEM、TEM、FT-IR、光学接触角测量仪和紫外可见分光光度计研究 Nd 掺杂对薄膜的晶体结构、组成和光学性能的影响。结果表明, Nd 掺杂对薄膜的亲水性和光催化性能有重要影响。Nd 掺杂导致 TiO<sub>2</sub> 晶格变形, 抑制氧化钛由锐钛矿相向金红石相转变、紫外吸收光谱的红移, 产生大量氢氧自由基(-OH)并加速表面的羟基化反应。当 Nd 掺杂量为 0.1% (质量分数)时, 薄膜颗粒尺寸最小, 约为 15 nm, 薄膜的亲水性能最佳, 接触角仅为 8.1°, 且 92% 的亚甲基蓝被光催化分解。此外, 对 Nd 掺杂的改性机理进行讨论。

**关键词:** 氧化钛; 钕掺杂; 溶胶–凝胶法; 亲水性; 光催化

(Edited by Wei-ping CHEN)