Photocatalytic equipment with nitrogen-doped titanium dioxide for air cleaning and disinfecting

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Received 14 November 2013
Accepted for publication 29 January 2014
Published 28 February 2014

Abstract
Nitrogen-doped TiO₂ nanoparticle photocatalysts were synthesized by a sol–gel procedure using tetra-n-butyl orthotitanate as a titanium precursor and urea as a nitrogen source. Systematic studies for the preparation parameters and their impact on the material’s structure were carried out by multiple techniques: thermogravimetric and differential scanning calorimetric analysis, x-ray diffraction, scanning electron microscope, transmission electron microscopy, energy dispersive x-ray spectroscopy and UV–Vis diffuse reflectance spectrophotometry showed that the nitrogen-doped TiO₂ calcined at 500°C for 3 h exhibited a spherical form with a particle size about 15–20 nm and crystal phase presented a mixture of 89.12% anatase. The obtained product was deposited on a porous quartz tube (D = 74 mm; l = 418 mm) to manufacture an air photocatalytic cleaner as a prototype of the TIOKRAFT company’s equipment. The created air cleaner was able to remove 60% of 10 ppm acetone within 390 min and degrade 98.5% of bacteria (total aerobic bacteria and fungi, 300 cfu m⁻³) within 120 min in a 10 m³ box. These photodegradation activities of N-TiO₂ are higher than that of the commercial nano-TiO₂ (Skyspring Inc., USA, particle size of 5–10 nm).

Keywords: N-doped TiO₂, photocatalytic, air cleaner, oxidation effectiveness

1. Introduction

Recently, the problem of air pollution caused by inorganic and volatile organic compounds (VOC), bacteria in hospitals, public buildings has become urgent, so the indoor air quality has received immense attention. According to WHO, air pollution has caused approximately 3.3 million deaths a year worldwide. There are many traditional methods for air pollution treatment such as adsorption, separation or using chemical disinfectants, but they all have the same weakness: pollutants just move from one place to another one without being thoroughly resolved or by-products toxic for human health are created. Lately, the photocatalytic pollution treatment method using nano-TiO₂ material has been discovered and is considered as a breakthrough solution [1–5]. When photocatalyst TiO₂ absorbs ultraviolet (UV) with energy higher than the band gap of TiO₂ (~3.3 eV for the anatase phase), the electrons from the valence band are excited to the conduction band, therefore produce the electron–hole pairs [6]. The free e⁻ and h⁺ react with O₂ and water vapor in the atmosphere to produce superoxide ions (O₂⁻) and hydroxyl radicals (OH). Both O₂⁻ and OH are extremely powerful agents in destroying chemical compounds as well as bacterial cells to CO₂ and H₂O [7–12].

After the discovery of photoinduced decomposition of water on TiO₂ electrodes by Fujishima and Honda [11], the photocatalysis process began to be extensively researched, particularly for the treatment of water and air polluted by
organic and inorganic compounds. Most of these researches have focused on photocatalytic activity of TiO$_2$ under the UV light (λ < 387 nm) which is only a small part (3–5%) of solar irradiation, so its practical applications have been limited [12]. To overcome this drawback, the next studies have aimed to enhance the visible light absorption ability and thus, photocatalytic reactions have occurred more effectively. Asahi et al [13] have successfully fabricated nitrogen-doped (N-doped) TiO$_2$ with a visible light absorption. Although N-doping is considered more effective and widely studied, the photocatalytic mechanisms under visible light are still debatable with three main views: band gap narrowing (the N$_2$p state hybridizes with the O$_2$p states in anatase TiO$_2$ doped with nitrogen and thus the band gap of N-doped TiO$_2$ is narrowed and able to absorb visible light) [13], impurity energy levels (the TiO$_2$ oxygen sites substituted by the nitrogen atom form isolated impurity energy levels above the valence band) [14, 15] and oxygen vacancies (the oxygen-deficient sites formed in the grain boundaries accept electrons excited by visible light and N-doped nearly oxygen-deficient sites block up the reoxidation) [16–19].

In this paper, the N-doped titania was produced through a simple sol–gel method at room temperature. The N-doped TiO$_2$ was characterized using thermogravimetric and differential scanning calorimetry analysis (TG-DSC), x-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), energy dispersive x-ray spectroscopy (EDX) and UV–Vis diffuse reflectance spectrophotometry. The prepared N-doped TiO$_2$ was deposited inside a quartz tube and the latter was then installed in an air cleaner. The air cleaner was evaluated inside an environmental chamber by oxidation of acetone which was selected as a model VOC molecule and by bacterial degradation.

2. Materials and methods

2.1. N-doped TiO$_2$ synthesis and characterization

The N-doped nano-TiO$_2$ using tetra-n-butyl orthotitanate (Ti(OBu)$_4$ 99% Merck, Germany) as a titanium precursor and urea ((NH$_2$)$_2$CO, MP company, French) as a nitrogen source was synthesized by a sol–gel process at room temperature (overall protocol shown in figure 1). The mixture containing 20 ml Ti(OBu)$_4$ and 500 ml ethanol (C$_2$H$_5$OH, Merck, Germany) was treated with ultrasonic at about 30 min, 20 kHz (solution A); the mixture containing urea, 60 ml ethanol and 1 ml nitric acid (65% Merck) was treated with ultrasonic at about 30 min, 20 kHz (solution B). Solution B was then drop-wise added in solution A under stirring for 0.5 h and aged for 1 day, the pH of the mixture was controlled was then drop-wise added in solution A under stirring for 20 kHz (solution A); the mixture containing urea, 60 ml ethanol and 1 ml nitric acid (65% Merck) was treated with ultrasonic at about 30 min, 20 kHz (solution B). Solution B was then drop-wise added in solution A under stirring for 0.5 h and aged for 1 day, the pH of the mixture was controlled.

Figure 1. Overall protocol used for preparing the N-doped TiO$_2$ by the sol–gel method.

Morphology and size of the nanoparticles were examined using SEM (JEOL-JSM 5410, Japan) and TEM (JEOL-JEM1010, Japan). The EDX analysis (Oxford Instruments Ltd) was carried out to study the chemical composition of the samples. Absorbance spectra of samples were recorded in the diffuse reflectance mode using a JASCO-V670 UV–Vis spectrometer.

2.2. Air cleaner

As shown in figure 2, our air cleaner of 25 m$^3$ h$^{-1}$ capacity is equipped with a pre-filter, photocatalytic filter tube (PFT) and activated carbon filter. The pre-filter is made of a synthetic polymer to keep the particles larger than 0.5 µm. PFT was prepared by deposition of N-TiO$_2$ thin films on a quartz tube fabricated by the TIOKRAFT company (Russia) (D = 74 mm, l = 418 mm, $S_{\text{surface}} = 971.3$ cm$^2$). Illumination was provided by a 36 W ultraviolet lamp (UVA, 1.84 mW cm$^{-2}$ at 360 nm, Phillip) placed in the center of the PFT. A 30 W axial fan is used to draw air at the bottom of the air cleaner and exhausted on the top, as indicated by the airflow directions in figure 2. The activated carbon filter is installed to absorb and eliminate odors.

2.3. Air purification ability of the cleaner

The air cleaner was placed in a closed box (10 m$^3$ of volume). The air-purification ability was evaluated by oxidation of acetone which was selected as a model VOC molecule and by bacterial degradation. The obtained results were compared with the air cleaner using a commercial nano-TiO$_2$ (Skyspring Inc., USA).

0.5 ml of acetone (C$_3$H$_6$O, Merck) was injected inside the box. The concentrations of acetone at various times was measured by gas sensor TGS2602 (FIGARO). To truly evaluate the removal efficiency of acetone using N-doped TiO$_2$ and nano-TiO$_2$ Skyspring Inc., we used the removal efficiency, $E_{\text{ac}}$ defined by the following equation:

$$E_{\text{ac}} = \frac{C_0 - C}{C_0} \times 100\%,$$

where $C_0$ and $C$ are the initial and final acetone concentration inside the environmental chamber.
4. Ultraviolet lamp
5. Fan
6. Activated carbon filter

Figure 2. Air cleaner with a capacity of 25 m$^3$ h$^{-1}$.

Figure 3. TG and DSC curves of N-doped TiO$_2$.

Figure 4. XRD patterns of N-doped TiO$_2$ calcined at 500 °C using different urea concentrations (A: anatase, R: rutile): (a) 1 M, (b) 2 M, (c) 3 M, (d) 4 M, (e) 5 M and (f) 6 M.

Table 1. Influence of urea concentration on particle size and crystal phase of N-TiO$_2$.

| Urea (M) | Anatase (%) | Rutile (%) | Average particle size (nm) |
|---------|-------------|------------|---------------------------|
| 1       | 89.12       | 10.88      | 16.32                     |
| 2       | 84.68       | 15.32      | 16.86                     |
| 3       | 81.36       | 18.64      | 18.28                     |
| 4       | 77.16       | 22.84      | 19.96                     |
| 5       | 72.06       | 27.94      | 24.40                     |
| 6       | 46.50       | 53.50      | 25.14                     |

The total aerobic bacteria and fungi were selected as a model microorganism to evaluate bacterial degradation ability of the air cleaner. The standard plate count method using plate count agar (PCA) (Merck) was carried out to enumerate the total aerobic bacteria (after incubation at 37 °C for 24 h) and the total fungi after incubation at 37 °C for 48 h). Microbial counts were expressed as log CFU m$^{-3}$. For each experiment, we took five samples at five specific positions in the box and each experiment was repeated three times.

3. Results and discussion

3.1. N-doped TiO$_2$ synthesis

3.1.1. Effect of calcination temperatures. TG-DSC analysis was performed on xerogel N-TiO$_2$ prepared by protocol in figure 1 without calcination and TG-DSC curves are shown in figure 3. The decrease in weight up to 220 °C (loss of 18.484%) can be attributed to desorption of the physisorbed water and ethanol (confirmed by two endothermic peaks on the DSC curve at about 67.27 °C and 190.03 °C) [20–22].

A large exothermic peak at about 259.93 °C is possibly caused by decomposing NH$_4$NO$_3$ to produce N$_2$O [23]. A small endothermic peak at about 300.1 °C possibly resulted from the desorption of unhydrolyzed Ti(OC$_3$H$_7$)$_2$ remained in the N-doped TiO$_2$ xerogel [22]. The DSC curve also shows a small exothermic peak at about 410 °C, which is possible because of the phase transformation from amorphous to anatase [22, 24]. Above 500 °C, the change in weight was very small and a peak at about 648.2 °C could be due to a loss of nitrogen [20]. So, we chose to calcine xerogels at 500 °C.

3.1.2. Effect of urea concentration. Figure 4 depicts the XRD patterns of N-doped TiO$_2$ prepared with varying urea concentration.

The average crystallite size of the N-TiO$_2$ calculated from the XRD data, according to Scherrer’s equation and anatase/rutile phase percentage are summarized in table 1. Clearly, urea content plays a significant role in the formed crystal structure and particle size: the higher urea concentration favors the growth of rutile structure and produces N-doped TiO$_2$ nanoparticles with larger particle size. This result can be explained as follows. The N atom replaces the O atom in the TiO$_2$ crystal lattice to form an N–T–N bond [25] and the increase of nominal nitrogen content leads to the presence of N atom not only in the TiO$_2$ crystal lattice but also on crystal surface, hence increases the particle size. This finding is in agreement with the works...
Figure 5. EDX pattern of N-doped TiO$_2$ prepared with a 1 M urea and calcined at 500 $^\circ$C.

Figure 6. SEM (a) and TEM (b) image of N-doped TiO$_2$ prepared with a 1 M urea and calcined at 500 $^\circ$C.

reported by Yang et al [26]. Consequently, urea concentration of 1 M was chosen.

3.1.3. Characterization of N-doped TiO$_2$. After studying the influence of calcination temperature and urea concentration, we prepared the N-doped TiO$_2$ at the optimum conditions. EDX, TEM and SEM were used to study, respectively, the elemental distribution and morphologies of the synthesized N-doped TiO$_2$ material.

The energy dispersive x-ray spectrum of the sample (figure 5) reveals the presence of nitrogen in the N-doped TiO$_2$ sample, indicating that the N element was doped into the TiO$_2$ nanoparticles and the peak of energy at 0.75 keV is attributed to nitrogen N. Also, this sample contains the major elements such as Ti, O.

Figure 6 shows the SEM and TEM images of the sample. It can be seen that the size of the N-doped TiO$_2$ is in the range of nanometer. The particles have a spherical form and uniform size about 15–20 nm, which agreed with the results from the XRD patterns. Our catalyst has the same morphology and size as the N-doped titania synthesized by Qin et al [20].

3.2. Air purification ability of the cleaner

3.2.1. Acetone oxidation activity. Figure 7 shows the acetone removal efficiencies under UV-A light of the air cleaners based on the synthesized N-doped TiO$_2$ and commercial TiO$_2$ (Skyspring Inc., USA). A higher acetone degradation efficiency was observed for synthesized N-TiO$_2$, 60% of 10 ppm acetone is removed within 390 min, which is 5% higher than using nano-TiO$_2$ Skyspring Inc. though the particle size of N-doped TiO$_2$ (15–20 nm) is larger than that of TiO$_2$ Skyspring Inc. (5–10 nm). This may be due to the N impurity energy levels in the TiO$_2$ band gap [14, 15] and thus electron–hole pairs are easily produced. As a consequence, a large amount of O$_2^-$ and OH$^-$ are created and so the acetone removal efficiency is enhanced.

Indeed, figure 8 illustrates the light absorption properties of TiO$_2$ Skyspring Inc. and N-doped TiO$_2$, and the visible absorption spectra show that the N-doped titania is a photocatalyst sensitive with respect to visible light irradiation. The band gap of the samples was determined by the following equation [27]:

$$E_g = 1239.8/\lambda,$$

where $E_g$ is the band gap (eV) and $\lambda$ is the wavelength of the absorption edge in the spectrum.

The absorption edge of pure the TiO$_2$ (curve (a)) sample is observed at about 380 nm, corresponding to the band gap energy of 3.2 eV. After the N doping in the TiO$_2$ sample, the absorption spectrum (curve (b)) shows that the absorption edge is shifted slightly toward the visible region with a band edge of 420 nm ($E_g = 2.95$ eV). This change demonstrates a
strategy for shaping photocatalysis by an atomic-level doping for nanocatalyst. This phenomenon can be explained in terms of the formation of an intra-band gap located above the valence band, due to substitution of oxide centers by nitride centers and/or to the interstitial introduction of nitride into the oxide lattice [28]. In addition, the absorption spectrum of the N-doped TiO$_2$ sample also showed a stronger absorption than TiO$_2$ Skyspring Inc. under UV irradiation, indicating that N-doping could be a promising approach for increasing the catalytic activity. The increase of the catalytic activity upon N-doping is different from the previous study [10, 29]. This difference could result from our different preparation route and nitrogen source.

3.2.2. Bacterial degradation activity. Table 2 summarizes the bactericidal efficiency under UV-A light of the air cleaner using a synthesized N-doped TiO$_2$ and a commercial nano-TiO$_2$ (Skyspring Inc., USA). 98.5% of bacteria (total aerobic bacteria and fungi) are removed within 120 min by synthesized N-doped TiO$_2$ while 95.93%—by nano-TiO$_2$ Skyspring Inc. This possibly results from the formation of isolated impurity energy levels as discussed above. This result is consistent with [30].

4. Conclusion

The N-doped TiO$_2$ prepared by the sol–gel method calcined at 500°C for 3h using tetra-n-butyl orthotitanate (99%) as a titanium precursor and 1 M urea as the nitrogen source are spherical particles with a uniform crystallite size about 15–20 nm and crystal phase presents a mixture of anatase (89.12%) and rutile (10.88%). An air cleaner of 25 m$^3$ h$^{-1}$ capacity installed with photocatalytic filter using prepared N-doped TiO$_2$ deposited on a porous quartz tube and UV-A lamp can remove 60% of acetone within 390 min and degrade 98.5% of bacteria within 120 min in a 10 m$^3$ box. This result is higher than that of the commercial nano-TiO$_2$ (Skyspring Inc., USA). Therefore, this air cleaner can be used in the home or office (volume up to 40 m$^3$) to purify indoor air.

Acknowledgment

The financial support from the Ministry of Science and Technology Vietnam is appreciated.

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