

## Use of co-spray pyrolysis for synthesizing nitrogen-doped TiO<sub>2</sub> films

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**Abstract.** Nitrogen-doped nanocrystalline TiO<sub>2</sub> is well known as the most promising photocatalyst. Despite many years after discovery, seeking of efficient method to prepare TiO<sub>2</sub> doped with nitrogen still attracts a lot of attention. In this paper, we present the result of using co-spray pyrolysis to synthesize nitrogen-doped TiO<sub>2</sub> films from TiCl<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub>. The grown films were subjected to XRD, SEM, photocatalysis, absorption spectra and visible-light photovoltaic investigations. All the deposited films were of nanosized polycrystal, high crystallinity, pure anatase and porosity. Specific characteristics involved nitrogen doping such as enhanced photocatalytic activity, bandgap narrowing, visible light responsibility and typical correlation of the photoactivity with nitrogen concentration were all exhibited. Obtained results proved that high photoactive nitrogen-doped TiO<sub>2</sub> films can be synthesized by co-spray pyrolysis.

**Keywords.** TiO<sub>2</sub>; co-spray pyrolysis; nitrogen-doping; photocatalytic activity; visible light responsibility.

### 1. Introduction

It was found that the photocatalytic activity of TiO<sub>2</sub> in UV and visible range of the light spectrum can be obviously enhanced by means of doping with nitrogen (Suda *et al* 2005; Chiu *et al* 2007; Huang *et al* 2007; Valentin *et al* 2007; Lui *et al* 2009; Sasikala *et al* 2010; Zhai *et al* 2010) or by co-doping such as N–Cu co-doping (Song *et al* 2008), N–In co-doping (Sasikala *et al* 2010), N–B co-doping (Zhou *et al* 2011), N–S co-doping (Shi *et al* 2012). It was also proved that the nitrogen-doping for TiO<sub>2</sub> heightened efficiency of the photoelectrochemical solar cell (Guo *et al* 2011; Zhang *et al* 2011; Umar *et al* 2012; Yun *et al* 2012).

Nitrogen-doped TiO<sub>2</sub> has been prepared by different routes. The techniques include thermal treatment of TiO<sub>2</sub> in nitrogen atmosphere (Wang *et al* 2009), ion-implantation (Batzill *et al* 2007), plasma surface modification (Pulsipher *et al* 2010), reactive magnetron sputtering (Chiu *et al* 2007), laser deposition (Somekawa *et al* 2008), microwave-assisted process (Zhai *et al* 2010), oxidation (Zhou *et al* 2011) and sol–gel synthesis (Nolana *et al* 2012). However, the achieved performance and explanations of underlying questions such as photocatalytic mechanism, bandgap narrowing, N 1s XPS assignment were shown to be strongly different among researchers (Shen *et al* 2007; Zaleska 2008a, b; Wang *et al* 2009; Pulsipher *et al* 2010; Viswanathan and Krishanmurthy 2012) that made difficulties for the effective development of nitrogen-doped TiO<sub>2</sub> materials.

Nitrogen impurities introduce new energy levels in the bandgap of TiO<sub>2</sub> (Zhang *et al* 2011) that increase the photo-induced electron–hole pairs favourable to enhanced efficiency of photocatalytic and photovoltaic effects. But they could also generate crystal defects and create recombination centres at a high doping level (Pore *et al* 2006; Qin *et al* 2008; Wang *et al* 2009; Sasikala *et al* 2010; Guo *et al* 2011) which negatively affect the photoactivity of the doped material. Because of these opposite effects, the photoactivity and involved properties strongly depend on the doping condition and technology. So the development of method for incorporating nitrogen into TiO<sub>2</sub> structure with minimum doping defects is a rational approach to the high performance nitrogen-doped TiO<sub>2</sub>.

Nitrogen-doped TiO<sub>2</sub> is considered as a ternary compound formulated as TiO<sub>2–x</sub>N<sub>x</sub>. It can be synthesized from elements instead of introducing nitrogen into TiO<sub>2</sub> crystals. This is a theoretical way to limit the crystallinity reduction and can be considered as synthesis doping. Using the synthesis doping such as laser technique (Suda *et al* 2005), atomic layer deposition (Pore *et al* 2006), solvothermal process (Yin *et al* 2006), reactive magnetron sputtering (Chiu *et al* 2007), nitrogen-treating amorphous TiO<sub>2</sub> (Li *et al* 2007), gas-phase synthesis (Braun *et al* 2010), plasma processing (Pulsipher *et al* 2010), interaction between nitrogen dopant sources and TiO<sub>2</sub> precursors (Nolana *et al* 2012), nitrogen-doped TiO<sub>2</sub> has been successfully prepared and exhibited to be a strong photocatalyst.

Spray pyrolysis is a simple method for preparation of pure TiO<sub>2</sub> films. This paper, for the first time, reports the use of co-spray pyrolysis for synthesizing nitrogen-doped TiO<sub>2</sub> from inexpensive materials.

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## 2. Experimental

### 2.1 Preparation of films

TiO<sub>2</sub> films were deposited on the surface of a glass slide, heated by a low thermal inertia furnace. The heater of the furnace is 1000 W halogen lamp powered by electronic equipment using OMRON temperature controller. The system allows presetting temperature and keeps it constant during the entire preparation process. The spraying system consisted of a reservoir of pressurized air, an electromagnetic gas valve and a glass atomizer. The electromagnetic valve was operated using an electronic pulse generator. The frequency and width of the pulse can be adjusted to establish optimum conditions.

Preparation began with investigation of the possibility of using spray pyrolysis to form TiO<sub>2</sub> films. TiCl<sub>4</sub> (99%, Merck) was dissolved in ethanol. A suitable amount of the solution was loaded into the atomizer and sprayed by 0.75 atm. air streams in about 15 min. Spraying equipment created pulses of 40 cycles/min. Each pulse lasted for 0.5 s. To determine conditions under which TiO<sub>2</sub> films can be formed on the glass substrates, concentration of precursor solutions and substrate temperature were varied. The film prepared by spray pyrolysis from only TiCl<sub>4</sub> was denoted as P-TiO<sub>2</sub>.

Based on the P-TiO<sub>2</sub> preparation, co-spray pyrolysis was carried out from TiCl<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub>—a rich nitrogen source when being decomposed. TiCl<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> dissolved in separate solutions, then both solutions were mixed at the predetermined ratio and stirred vigorously before spraying. Substrate temperature was 380 °C which is suitable both for preparation of high performance TiO<sub>2</sub> film and pyrolysis of NH<sub>4</sub>NO<sub>3</sub>. To find optimum conditions, the content of NH<sub>4</sub>NO<sub>3</sub> in the mixture was varied from 0 to 50% with a step size of 10%. Obtained films were denoted as CP-TiO<sub>2</sub>.

### 2.2 Material analysis

The phase and crystallinity of products were analysed by XRD using a BRUKER D8 ADVANCE. Surface morphologies of samples were characterized by scanning electron microscope (SEM) using a JEOL-540LV.

### 2.3 Photocatalytic test

The photocatalytic activity (PA) was evaluated via the degradation of methylene blue (MB) in water solution using a xenon light source that could excite both P-TiO<sub>2</sub> and CP-TiO<sub>2</sub>. The films were immersed in petri dishes containing 5 ml of 0.5% MB solution. The solutions were stirred during the treatment process by an electromechanical spin system and irradiated by a 35 W xenon lamp at a distance of 10 cm. The decrease of MB concentration was determined via absorption measurements using a spectrometer UV-VIS-NIR JASCO-V-579.

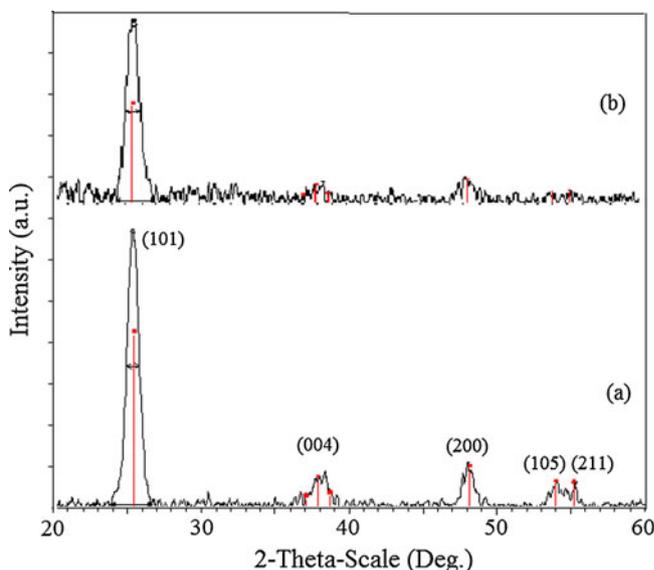
### 2.4 Visible light responsive test

The visible light responsibility of prepared materials was determined via bandgap narrowing and photovoltaic effect on a photoelectrochemical cell similar to Grätzel cell (Grätzel 2001). The active electrode of the cell comprised of CP-TiO<sub>2</sub> film coated on a transparent conductive oxide (SnO<sub>2</sub>:F of 15 Ω/sq and 80% visible light transparency). The counter-electrode was SnO<sub>2</sub>:F activated with Pt deposited by vacuum technology. Substrates of the electrodes were 1.2 mm thick microscope glass slides. The 0.3 mm intervening space between both electrodes was filled up with I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox electrolyte from Solaronix. The cells of 5 × 5 mm<sup>2</sup> active area were irradiated with visible light of 50 W halogen lamp at a distance of 15 cm. The open circuit voltage (V<sub>oc</sub>) of the cell was used as an indicator of the visible light responsibility.

## 3. Results and discussion

### 3.1 Material characterization

Material characterization showed that the P-TiO<sub>2</sub> films have been deposited on the glass substrates at temperatures in the range of 350–450 °C and from 0.01 to 0.15 M TiCl<sub>4</sub> solutions. All the films were polycrystalline TiO<sub>2</sub> formed without the need for post-deposition annealing. Figure 1(a) presents XRD pattern of the P-TiO<sub>2</sub> film prepared at 380 °C from 0.03 M TiCl<sub>4</sub> solution. As a result, all of the diffraction peaks corresponding to TiO<sub>2</sub> anatase appeared. No peak from other crystal phase was detected. The average crystal size of the films was ~7–10 nm calculated using Scherrer equation. The clear and sharp diffraction peaks as seen in figure 1(a) also



**Figure 1.** XRD patterns of P-TiO<sub>2</sub> film prepared at 380 °C from TiCl<sub>4</sub> solution (a) and CP-TiO<sub>2</sub> prepared from solution consisting of 30% NH<sub>4</sub>NO<sub>3</sub> (b).

appeared in diffraction patterns of all the samples prepared under above mentioned conditions.

Figure 1(b) shows XRD pattern of CP-TiO<sub>2</sub> prepared from mixed solution containing 30% NH<sub>4</sub>NO<sub>3</sub> at 380 °C as the representative of CP-TiO<sub>2</sub> films. It can be seen that the films have also been deposited in pure anatase form. The crystallinity of CP-TiO<sub>2</sub> film was lightly lower than that of P-TiO<sub>2</sub>. This reduction may be caused by the additional gas release during pyrolysis of NH<sub>4</sub>NO<sub>3</sub>.

Surface morphology of sample represented in figure 2 shows porous characteristic of the deposited films. This porosity originated from evaporation of solvent and it is a common property of TiO<sub>2</sub> films prepared by pyrolysis from sprayed solutions.

### 3.2 Photocatalytic activity test

Figure 3 shows absorption spectra of MB solutions before (reference) and after 2 h photocatalytic treatment. As a result, the obvious difference in absorption between MB solutions treated over P-TiO<sub>2</sub> and CP-TiO<sub>2</sub> was exhibited.

In the visible region of light spectrum, MB has two absorption peaks assigned to the absorption of dimer (at 600 nm) and monomer (at 660 nm). The monomer is highly chemical-active. Consequently its concentration changed more when treated with TiO<sub>2</sub> as seen in figure 3. So, for the best accuracy of PA determination, the absorption intensity of treated solutions at 660 nm was taken into account.

Figure 4 presents the family of  $C/C_0$  curves calculated from absorption measurements of MB solutions treated over CP-TiO<sub>2</sub> films vs NH<sub>4</sub>NO<sub>3</sub> concentrations in starting solutions, where  $C$  is current and  $C_0$  is initial concentrations. The rapid reduction of MB during photocatalytic decomposition demonstrated a strong increase in PA gained by the co-spray pyrolysis. At the end of decomposition process, the changes of  $C/C_0$  were slowly down due to exhaustion of MB in the solution. So the slope of  $C/C_0$  plot vs exposure time at initial stage of the experiment could be considered as an indicator

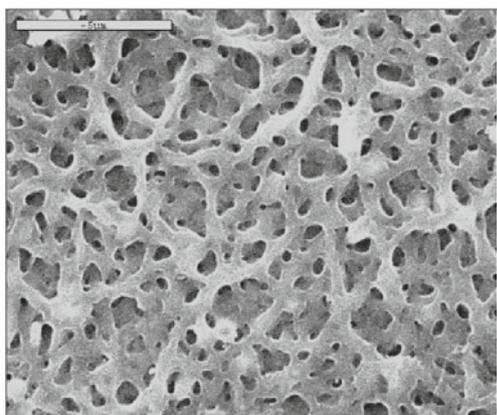


Figure 2. 16 × 13 μm SEM image of CP-TiO<sub>2</sub> film.

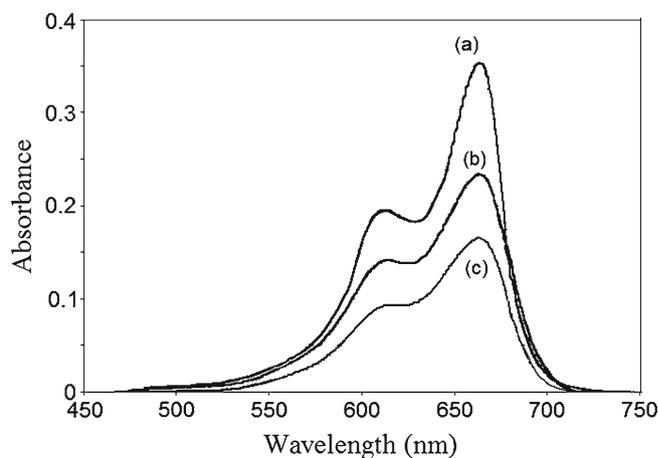


Figure 3. Absorption spectra of MB solutions: reference (a), after photocatalytic treatment over P-TiO<sub>2</sub> (b) and CP-TiO<sub>2</sub> (c).

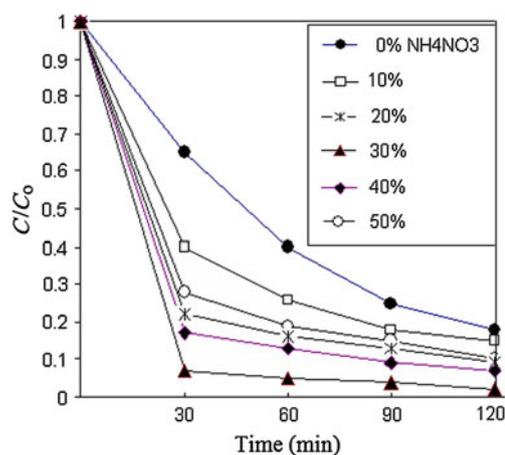


Figure 4. Photodegradation of MB solution over CP-TiO<sub>2</sub> prepared with NH<sub>4</sub>NO<sub>3</sub> concentration ranging from 0 to 50%.

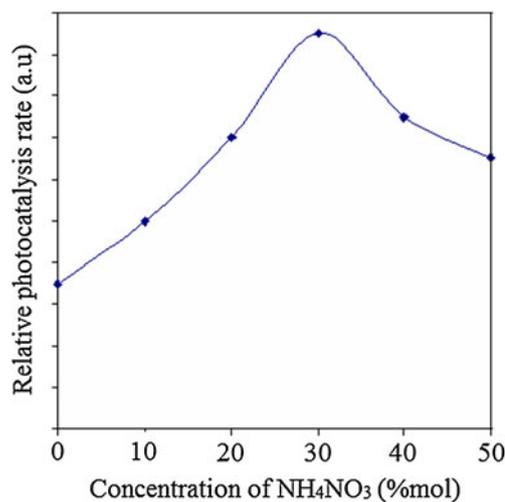


Figure 5. Correlation between relative photocatalysis rate of CP-TiO<sub>2</sub> films and NH<sub>4</sub>NO<sub>3</sub> concentration in precursor solutions.

of PA and called as relative photocatalysis rate ( $R$ ), which is defined as follows:

$$R = -d(C/C_0)/dt.$$

Figure 5 presents  $R$  of CP-TiO<sub>2</sub> films vs NH<sub>4</sub>NO<sub>3</sub> concentration in the starting solution. It can be seen that, according to increment of nitrogen concentration, PA of CP-TiO<sub>2</sub> first was raised then reduced. This result was similar to earlier reports (Wong *et al* 2006; Chiu *et al* 2007; Shen *et al* 2007; Qin *et al* 2008; Somekawa *et al* 2008; Braun *et al* 2010), which correctly reflected the interaction between contrary effects of nitrogen doping.

The enhanced PA of CP-TiO<sub>2</sub> over P-TiO<sub>2</sub> due to co-spray pyrolysis of TiCl<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> can be considered as a result of nitrogen doping. The rate of increment in PA may be considered as the doping efficiency. If we define efficiency as  $k$ , we have:

$$k = \frac{R_N}{R_O}, \quad (1)$$

where  $R_N = -d(C/C_0)_N/dt$  is the relative photocatalysis rate of CP-TiO<sub>2</sub> and  $R_O = -d(C/C_0)_O/dt$  is the relative photocatalysis rate of P-TiO<sub>2</sub>.

Applying (1) to the optimum condition of our experiments,  $k$  is calculated to be 2.7. This means that when using co-spray pyrolysis, PA reached upto 2.7 times. Estimation of  $k$  in some other techniques shows that, for example, in introducing nitrogen into TiO<sub>2</sub>  $k = 1.25$  (Silveyra *et al* 2005), reactive magnetron sputtering:  $k = 2.0$  (Chiu *et al* 2007), sol-gel:  $k = 2$  (Huang *et al* 2007), laser technology:  $k = 1.25$  (Somekawa *et al* 2008), N-Cu co-doped:  $k = 2.25$  (Song *et al* 2008), N-In co-doped:  $k = 2.1$  (Sasikala *et al* 2010). It can be seen that the doping efficiency of co-spray pyrolysis is not lower than that of complicated methods.

### 3.3 Bandgap narrowing determination

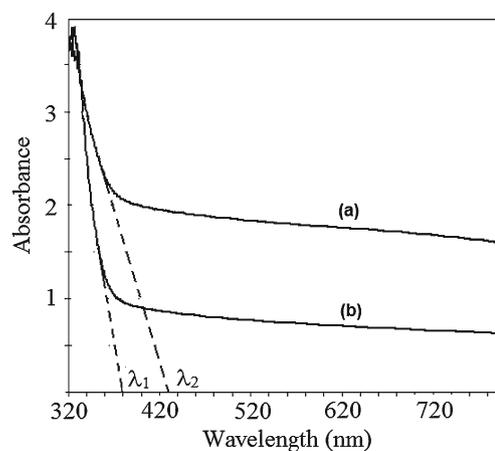
The bandgap narrowing is also an evidence of nitrogen-doped TiO<sub>2</sub>. It could be theoretically calculated and experimentally determined when nitrogen content was high enough (Valentin *et al* 2007; Wang *et al* 2009; Pulsipher *et al* 2010). Figure 6 presents absorption spectra of P-TiO<sub>2</sub> and CP-TiO<sub>2</sub> films prepared with 30% NH<sub>4</sub>NO<sub>3</sub> in starting solution. There was an obvious shift in absorption edge between P-TiO<sub>2</sub> ( $\lambda_1 = 380$  nm) and CP-TiO<sub>2</sub> ( $\lambda_2 = 427$  nm). Applying a calculation presented in Huang *et al* (2007), the bandgap was narrowed from 3.2 to 2.9 eV.

### 3.4 Visible light responsibility

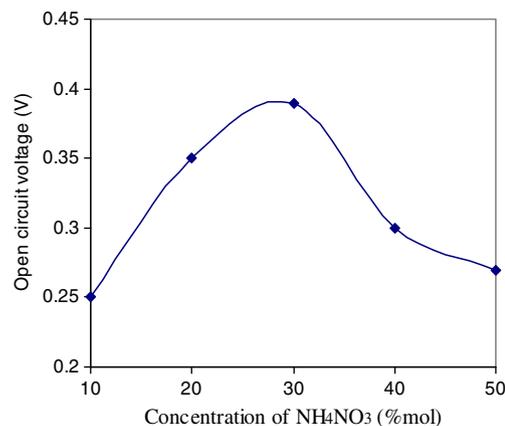
The most expected characteristic of nitrogen doped TiO<sub>2</sub> is possibility to be activated with visible light. Because nitrogen energy levels are lower than bandgap energy, nitrogen doped TiO<sub>2</sub> can be excited by the visible light to produce electron-hole pairs. In photoelectrochemical cell interface between CP-TiO<sub>2</sub> photoanode and electrolyte separates the pairs to

generate a photo-emf if any, which can be measured as open circuit voltage ( $V_{oc}$ ) of the cell. Due to identical structure and illumination condition, the  $V_{oc}$  is principally proportional to photoinduced electron-hole pairs concentration and so obtained  $V_{oc}$  more correctly reflects nitrogen doping for CP-TiO<sub>2</sub>. Figure 7 presents  $V_{oc}$  of the film prepared from solutions consisting of various NH<sub>4</sub>NO<sub>3</sub> concentrations. The measured  $V_{oc}$  shows that CP-TiO<sub>2</sub> is a strong visible light responsive material and  $V_{oc}$  was sensitive to nitrogen source as reported in earlier works (Zhang *et al* 2011; Umar *et al* 2012).

The relationship between  $V_{oc}$  with NH<sub>4</sub>NO<sub>3</sub> concentration is similar to the case of PA as seen from figures 5 and 7. The rise of  $V_{oc}$  and PA can be explained by an increasing photoinduced electron-hole density proportional to nitrogen doping. At high NH<sub>4</sub>NO<sub>3</sub> concentrations, more recombination centres were formed resulting in the reduction of electron-hole life time. Consequently  $V_{oc}$  and PA were down. The contrary effects of doping led into appearance of optimums of  $V_{oc}$  and PA as obtained in other works and generalized in a review article (Viswanathan and Krishnamurthy 2012).



**Figure 6.** Absorption spectra of (a) CP-TiO<sub>2</sub> and (b) P-TiO<sub>2</sub> films.



**Figure 7.** Open circuit voltages of photoelectrochemical cell vs NH<sub>4</sub>NO<sub>3</sub> concentrations.

In comparison with other methods, co-spray pyrolysis described in this paper was characterized by: (i) co-spray pyrolysis simultaneously released titanium, nitrogen and oxygen in chemically active states that allows synthesizing nitrogen-doped TiO<sub>2</sub> at higher doping level without crystal destruction. The higher concentration of nitrogen generates more photoinduced electron-hole pair, (ii) by controlling substrate temperature and spraying regime it was possible to attain a high crystallinity of deposited CP-TiO<sub>2</sub> films. For compound crystal as TiO<sub>2</sub>, crystallinity reflects not only perfect structure but also stoichiometry of obtained films so that these facts reduced generation of recombination centres and (iii) co-spray pyrolysis created a porous morphology. This porosity can be adjusted by changing concentration of solution, substrate temperatures and spraying regime to increase the specific surface of photoactive materials.

High nitrogen doping level, high crystal perfect and porosity are demands for enhanced photocatalytic activity and efficiency of electrochemical solar cell. All of them can be attained by the described co-spray pyrolysis.

#### 4. Conclusions

Obtained high enhancement of PA, clear bandgap narrowing, strong visible-light photovoltaic effect and correlation of PA,  $V_{oc}$  with nitrogen source are the specific characteristics of the nitrogen doping for TiO<sub>2</sub>, which allowed us to conclude that by co-spray pyrolysis from mixture of TiCl<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> the nitrogen-doped TiO<sub>2</sub> films are successfully synthesized.

Controlled co-spray pyrolysis helped to reach a high nitrogen-doping level of TiO<sub>2</sub> films with pure anatase phase, nanosized perfect crystal and macro porosity, which were the decisive factors for application to the advanced photocatalyst and photoelectrochemical solar cell.

Co-spray pyrolysis can achieve a high performance of nitrogen-doped TiO<sub>2</sub> with low production cost. It deserves to be a promising method for research and development of photoactive materials and devices based on the nitrogen-doped TiO<sub>2</sub>.

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