

## Visible-photoresponsive Nitrogen-Doped Mesoporous TiO<sub>2</sub> Films for Photoelectrochemical Cells

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Nitrogen-doped TiO<sub>2</sub> (TiO<sub>2</sub>:N) nano-particles with a pure anatase crystalline structure were successfully synthesized through the hydrolysis of TiCl<sub>4</sub> in an ammonia aqueous solution. The samples were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), N<sub>2</sub>-sorption, and UV-vis diffuse reflectance spectra (UV-vis DRS) techniques. The absorption edge of nitrogen-doped TiO<sub>2</sub> shifted into the visible wavelength region. The photoelectrochemical (PEC) performances were investigated for the TiO<sub>2</sub> mesoporous electrodes doped with different nitrogen concentrations. The TiO<sub>2</sub>:N electrodes exhibited much higher PEC responses compared to the pure TiO<sub>2</sub> electrode because of the significantly enhanced visible-photoresponsibility of the TiO<sub>2</sub>:N electrodes.

**Key Words:** Nitrogen-doped TiO<sub>2</sub>, Visible-photoresponsive, Photoelectrochemical cells, Mesoporous electrodes

### Introduction

Titanium dioxide (TiO<sub>2</sub>) has attracted considerable interest for use as a photoelectrode in photoelectrochemical (PEC) cells such as PEC water-splitting cells and dye-sensitized solar cells because of its relatively low cost, non-toxicity, and long-term stability against corrosion.<sup>1-3</sup> However, TiO<sub>2</sub> has a wide band gap (3.2 eV for anatase and 3.0 eV for rutile),<sup>4</sup> which allows it to absorb ultraviolet light (~4% of solar energy) and be transparent for most solar irradiation.<sup>5</sup> Many groups have investigated methods to enhance its photoactivity under visible light illumination. Impurity doping is one of the typical approaches for extending the spectral response of titania into the visible light region. These doping techniques can either substitute other metals, such as Fe<sup>6</sup>, Ni<sup>7</sup>, and Cr<sup>8</sup>, etc., into a Ti site or nonmetals, such as B<sup>9</sup>, C<sup>10</sup>, N<sup>11</sup>, and F<sup>12</sup>, in order to efficiently extend the photo-response from the UV region to the visible light region. The simplest and most feasible TiO<sub>2</sub> modification approach for achieving visible-light-driven PEC systems seems to be nitrogen-doping.

As early as 1986, Sato<sup>13</sup> reported that the calcination of NH<sub>4</sub>Cl or NH<sub>4</sub>OH with titanium hydroxide caused the photocatalytic sensitization of TiO<sub>2</sub> into the visible light region due to the NO<sub>x</sub> impurity. Later studies showed that TiO<sub>2</sub> could be doped with nitrogen using various physical and chemical methods.<sup>14-17</sup> The traditional synthetic method of nitrogen-doped TiO<sub>2</sub> was followed by calcining TiO<sub>2</sub> in an ammonia atmosphere at high temperature. In addition to the energy waste caused by heating the sample, the treatment under high temperature usually induces particle agglomeration, leading to decreased surface area.<sup>18</sup>

In this study, nitrogen-doped anatase TiO<sub>2</sub> was successfully synthesized using a wet method, i.e., a hydrolysis process, which did not need a high calcination temperature. Nitrogen-doped TiO<sub>2</sub> was prepared through the simple addition of ammonia water to an aqueous solution, and exhibited a good photoactivity

in the visible light region, a good crystallinity, and a high BET specific surface area. TiO<sub>2</sub> photoelectrodes with various concentrations of nitrogen were tested for H<sub>2</sub> water-splitting in order to confirm the effect of nitrogen doping on the PEC activity of prepared TiO<sub>2</sub>. These results proved that the nitrogen-doped TiO<sub>2</sub> electrodes can potentially be beneficial to PEC cells in the visible light region.

### Experimental Section

**Preparation of nitrogen-doped TiO<sub>2</sub> particles.** Titanium tetrachloride (99.9%, TiCl<sub>4</sub>) was used as the main starting material and was used without any further purification. TiCl<sub>4</sub> was dissolved in doubly distilled water (0.7 mol/L) in an ice-water bath. This aqueous solution was then mixed with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (for preparation of anatase phase) in a temperature-controlled bath with continuous stirring at 90 °C for 24 h. Subsequently, ammonia water was added to prepare nitrogen-doped TiO<sub>2</sub>. Three different mole ratios of ammonia to TiCl<sub>4</sub> (i.e., N/Ti) of 10, 15, and 20 were used. After continuous stirring for 6 h, the precipitated TiO<sub>2</sub> was separated from the solution by using centrifugation and repeatedly washed with distilled water. The hydrous TiO<sub>2</sub> was dried at 80 °C under vacuum and ground into a fine powder. Then the samples were calcined at 400 °C for 3 h. For comparison, pure TiO<sub>2</sub> nanoparticles (N/Ti = 0) were synthesized using the same technique without the addition of ammonia water.

**Materials characterization.** The powder XRD patterns were collected using a powder diffractometer (PANalytical X'pert PRO MRD) with Cu K $\alpha$  radiation (40 kV, 25 mA) at step size of 0.02°/s over a range from 20° < 2θ < 80°. The samples were prepared as thin layers on metal slides. For the TEM observations, powder specimens were preground, deposited onto a grid with a holey carbon film, and then rapidly transferred to a transmission electron microscope (Hitachi H-7100) with an accelerating

voltage of 120 kV. The N<sub>2</sub>-adsorption isotherms were measured at 77 K on a nitrogen adsorption apparatus (Quantachrome QUADRASORB SI). The volume of adsorbed N<sub>2</sub> was normalized using standard temperature and pressure. Prior to the experiments, the samples were dehydrated at 200 °C for 2 h. The specific surface area was determined from the linear portion of the BET equation ( $P/P_0 = 0.05 - 0.30$ ). The UV-vis diffuse reflectance spectra were obtained from dry-pressed disk samples using a UV-vis-NIR spectrophotometer (Varian Cary 100) that was equipped with an integrating sphere assembly, with BaSO<sub>4</sub> as the reflectance sample.

**Fabrication and measurement of PEC photoelectrode.** The PEC measurements were performed in a three-electrode cell with a flat quartz window to facilitate the illumination of the photoelectrode surface. The mesoporous TiO<sub>2</sub>:N films (active area: 0.25 cm<sup>2</sup>) were used as the working electrodes. A Pt sheet and a Ag/AgCl electrode (with saturated KCl) were used as the counter and reference electrodes, respectively, with a 1 M KOH basic aqueous solution as the electrolyte. The PEC response was measured using a photodiode power meter and a Xe lamp (150 W) with a light intensity of 100 mW/cm<sup>2</sup>. The photocurrent-voltage performances were measured under chopped light on/off illumination during a potential sweep (scan rate: 5 mV/s). The PEC performance of Degussa P25 TiO<sub>2</sub> which consists of anatase and rutile phases was also investigated with comparison to that of synthesized TiO<sub>2</sub>.

## Results and Discussion

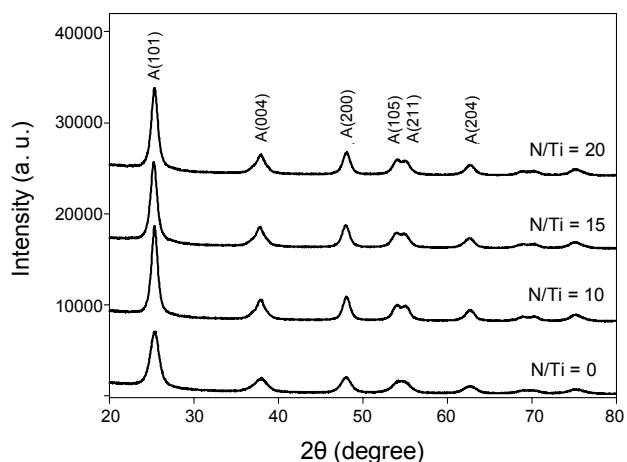
**Crystalline structure of nitrogen-doped TiO<sub>2</sub>.** Nitrogen-doped TiO<sub>2</sub> (TiO<sub>2</sub>:N) nanoparticles were synthesized by the hydrolysis of TiCl<sub>4</sub> in an ammonia aqueous solution. Figure 1 shows the XRD results that were used to investigate the crystalline structure of the samples. The patterns of all the samples were indexed to only the anatase phase of TiO<sub>2</sub> (JCPDS 21-1272). Therefore, the anatase phase was retained without phase change after nitrogen doping.

The crystallite sizes of the samples were calculated by applying the Debye-Scherrer formula<sup>22</sup> in Equation (1) to the anatase (101) diffraction peaks:

$$L = K\lambda / \beta \cos\theta, \quad (1)$$

In this equation,  $L$  is the crystallite size in angstroms,  $K$  is a constant equal to 0.89 for this study,  $\lambda$  is the wavelength of the X-ray radiation (Cu K $\alpha$  = 0.15406 nm),  $\beta$  is the corrected band broadening after the subtraction of the equipment broadening, and  $\theta$  is the diffraction angle. The values of the crystallite sizes are provided in Table 1 along with other physical properties.

Some of the structural characteristics of pure TiO<sub>2</sub> and nitrogen-doped TiO<sub>2</sub> are shown in Table 1. The crystallite size slightly increased after nitrogen doping. In a typical wet process, the TiO<sub>2</sub> materials were synthesized through the competition between the nucleation and the growth. In the strong acidic environment generated by the hydrolysis of TiCl<sub>4</sub>, the nucleation and the growth of TiO<sub>2</sub> clusters were both at intermediate rates. After adding the ammonia solution, the growth rate accelerated and the nucleation and the growth were no longer at equili-



**Figure 1.** XRD patterns of nitrogen-doped TiO<sub>2</sub> with various N/Ti ratios.

**Table 1.** Physical properties of pure TiO<sub>2</sub> and nitrogen-doped TiO<sub>2</sub>

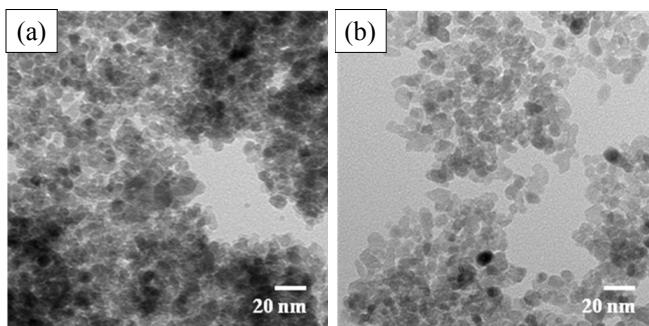
Sample	Crystallite size (nm)	d spacing (Å)	BET (m <sup>2</sup> /g)
N/Ti = 0	7.3	3.51	166
N/Ti = 10	10.6	3.51	173
N/Ti = 15	9.8	3.52	176
N/Ti = 20	9.9	3.51	203

brium.<sup>19</sup> Additionally, the “ $d$ ” space values did not change, implying that, the nitrogen was introduced into the lattice of the nitrogen-doped samples without changing the average unit cell dimension. The BET surface area of nitrogen-doped TiO<sub>2</sub> was larger than pure TiO<sub>2</sub> because the nitrogen doping had a stabilizing effect on the colloidal particles, which inhibited particle agglomeration.<sup>20</sup>

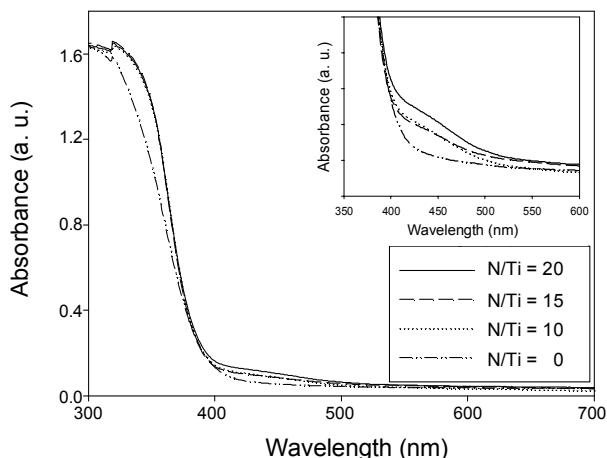
**Morphology of nitrogen-doped TiO<sub>2</sub>.** The morphology of the pure TiO<sub>2</sub> and nitrogen-doped TiO<sub>2</sub> powders were investigated using the TEM images in Figure 2. The images (Figure 2a and b) revealed that the pure TiO<sub>2</sub> and nitrogen-doped TiO<sub>2</sub> (N/Ti = 15) samples consisted of agglomerates of the primary particles with average diameters of 7 - 10 nm, which were in agreement with the crystallite sizes calculated from the XRD patterns.

**Photo-absorption and PEC properties.** Usually, nitrogen doping has an obvious effect on the light absorption characteristics of TiO<sub>2</sub>. Figure 3 shows the diffuse reflectance spectra of pure TiO<sub>2</sub> and nitrogen-doped TiO<sub>2</sub> with different doping concentrations. The pure TiO<sub>2</sub> sample did not absorb visible light, however, the nitrogen-doped absorption spectrum extended into the visible range of 400 - 500 nm. Furthermore, the absorption strengthened with increasing doping concentration because nitrogen doping contributed to the localized N 2p states in the band structure in the form of substituted and interstitial N states.<sup>21,22</sup>

Figure 4 shows the photocurrent-voltage performances of the films that were undoped and doped with nitrogen at a ratio of N/Ti = 15. The photoelectrochemical response was measured under light on/off illumination in order to confirm whether the photocurrent was specifically generated by only the absorbed photons without any dark current component.



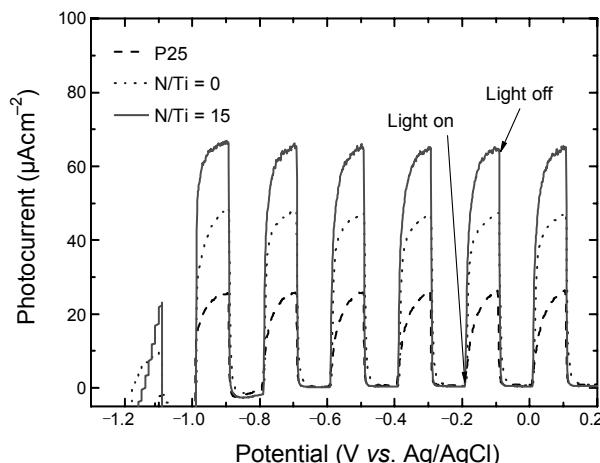
**Figure 2.** TEM images of (a) pure  $\text{TiO}_2$  and (b) nitrogen-doped  $\text{TiO}_2$  ( $\text{N}/\text{Ti} = 15$ ).



**Figure 3.** UV-vis diffuse reflectance spectra of nitrogen-doped  $\text{TiO}_2$  with various  $\text{N}/\text{Ti}$  ratios.

The dark current under light-off conditions hardly changed across the potential range compared to the photoresponse under light-on conditions. Therefore, the photocurrents of the  $\text{TiO}_2$  and  $\text{TiO}_2:\text{N}$  films were generated only by the absorbed photons under light illumination without any contributions from the dark current. For comparison, the PEC response was also measured for a widely used  $\text{TiO}_2$  electrode composed of P25 powders. The  $\text{TiO}_2$  film synthesized in this study exhibited a superior PEC performance compared to the P25  $\text{TiO}_2$  electrode. Previous reports have shown that P25 is composed of a mixture of anatase and rutile  $\text{TiO}_2$  and has a BET of around  $65 - 70 \text{ m}^2/\text{g}$ . On the contrary, the synthesized  $\text{TiO}_2$  exhibited only an anatase phase, and its BET surface area was much higher than P25. Therefore, the improved PEC performance of the synthesized  $\text{TiO}_2$  mesoporous film was attributed to the much higher surface area and the strictly anatase structure.

Figure 4 also clearly shows that the N-doped  $\text{TiO}_2$  electrode exhibited a much higher PEC response than undoped  $\text{TiO}_2$ . As shown in Table 1, the BET surface area of  $\text{TiO}_2:\text{N}$  ( $\text{N}/\text{Ti} = 15$ ) was slightly higher than undoped  $\text{TiO}_2$ , indicating that the significantly enhanced PEC performance of  $\text{TiO}_2:\text{N}$  could not be explained by this factor alone. Figure 3 showed that the optical absorption extended into a longer wavelength region (or visible region for 400 to 500 nm) with increasing N content. Therefore,



**Figure 4.** Current-voltage performances of N-doped  $\text{TiO}_2$ ,  $\text{TiO}_2$  and P25, respectively, measured under chopped light on/off illumination.

the improved PEC responses of the  $\text{TiO}_2:\text{N}$  films were attributed to the higher visible-photosensitivity as well as the slightly increased surface area because the former increased the photo-generation of the electron-hole pairs, and the latter provided a higher number of electrochemical reaction sites. The comparative PEC performance tests were repeated many times to confirm that the results were reproducible.

## Conclusions

Nitrogen-doped  $\text{TiO}_2$  nanoparticles synthesized by a hydrolysis process were used as photoelectrodes in photoelectrochemical cells for solar water splitting. The samples with a homogeneous anatase phase were easily synthesized through  $\text{TiCl}_4$  hydrolysis in an ammonia aqueous solution at low temperature. UV-vis DRS spectra depicted the visible light absorption of nitrogen-doped  $\text{TiO}_2$ , which continued above 500 nm. The  $\text{TiO}_2:\text{N}$  mesoporous electrode exhibited a much higher PEC performance than those of the undoped  $\text{TiO}_2$  and P25 electrodes because of its visible-photoresponsibility and slightly increased surface area.

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