Nitrogen-doped TiO₂ (TiO₂:N) nano-particles with a pure anatase crystalline structure were successfully synthesized through the hydrolysis of TiCl₄ in an ammonia aqueous solution. The samples were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), N₂-sorption, and UV-vis diffuse reflectance spectra (UV-vis DRS) techniques. The absorption edge of nitrogen-doped TiO₂ shifted into the visible wavelength region. The photoelectrochemical (PEC) performances were investigated for the TiO₂ mesoporous electrodes doped with different nitrogen concentrations. The TiO₂:N electrodes exhibited much higher PEC responses compared to the pure TiO₂ electrode because of the significantly enhanced visible-photoresponsibility of the TiO₂:N electrodes.

**Key Words:** Nitrogen-doped TiO₂, Visible-photoresponsive, Photoelectrochemical cells, Mesoporous electrodes

**Introduction**

Titanium dioxide (TiO₂) 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. However, TiO₂ has a wide band gap (3.2 eV for anatase and 3.0 eV for rutile), which allows it to absorb ultraviolet light (~4% of solar energy) and be transparent for most solar irradiation. 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 Fe⁶, Ni⁷, and Cr⁸, into a Ti site or nonmetals, such as B⁹, C¹⁰, N¹¹, and F¹², in order to efficiently extend the photo-response from the UV region to the visible light region. The simplest and most feasible TiO₂ modification approach for achieving visible-light-driven PEC systems seems to be nitrogen-doping.

As early as 1986, Sato reported that the calcination of NH₄Cl or NH₄OH with titanium hydroxide caused the photocatalytic sensitization of TiO₂ into the visible light region due to the NOₓ impurity. Later studies showed that TiO₂ could be doped with nitrogen using various physical and chemical methods. The traditional synthetic method of nitrogen-doped TiO₂ was followed by calcining TiO₂ 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.

In this study, nitrogen-doped anatase TiO₂ was successfully synthesized using a wet method, i.e., a hydrolysis process, which did not need a high calcination temperature. Nitrogen-doped TiO₂ 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. TiO₂ photoelectrodes with various concentrations of nitrogen were tested for H₂ water-splitting in order to confirm the effect of nitrogen doping on the PEC activity of prepared TiO₂. These results proved that the nitrogen-doped TiO₂ electrodes can potentially be beneficial to PEC cells in the visible light region.

**Experimental Section**

**Preparation of nitrogen-doped TiO₂ particles.** Titanium tetra-chloride (99.9%, TiCl₄) was used as the main starting material and was used without any further purification. TiCl₄ was dissolved in doubly distilled water (0.7 mol/L) in an ice-water bath. This aqueous solution was then mixed with (NH₄)₂SO₄ (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 TiO₂. Three different mole ratios of ammonia to TiCl₄ (i.e., N/Ti) of 10, 15, and 20 were used. After continuous stirring for 6h, the precipitated TiO₂ was separated from the solution by using centrifugation and repeatedly washed with distilled water. The hydrated TiO₂ was dried at 80 °C under vacuum and grind into a fine powder. Then the samples were calcined at 400 °C for 3 h. For comparison, pure TiO₂ 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 Kα radiation (40 kV, 25 mA) at step size of 0.02°/s over a range from 20°< θ<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 (Hitach H-7100) with an accelerating
voltage of 120 kV. The N$_2$-adsorption isotherms were measured at 77 K on a nitrogen adsorption apparatus (Quantachrome QUADRASORB SI). The volume of adsorbed N$_2$ 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$_4$ 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$_2$:N films (active area: 0.25 cm$^2$) were used as the working electrodes. A Pt sheet and an 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$^2$. 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$_2$ which consists of anatase and rutile phases was also investigated with comparison to that of synthesized TiO$_2$.

**Results and Discussion**

**Crystalline structure of nitrogen-doped TiO$_2$.** Nitrogen-doped TiO$_2$ (TiO$_2$:N) nanoparticles were synthesized by the hydrolysis of TiCl$_4$ 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$_2$ (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$^{21}$ in Equation (1) to the anatase (101) diffraction peaks:

$$L = K\lambda / \beta \cos \theta$$

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 Ka = 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$_2$ and nitrogen-doped TiO$_2$ are shown in Table 1. The crystallite size slightly increased after nitrogen doping. In a typical wet process, the TiO$_2$ materials were synthesized through the competition between the nucleation and the growth. In the strong acidic environment generated by the hydrolysis of TiCl$_4$, the nucleation and the growth of TiO$_2$ 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 equilibrium.$^{19}$ 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$_2$ was larger than pure TiO$_2$ because the nitrogen doping had a stabilizing effect on the colloidal particles, which inhibited particle agglomeration.$^{20}$

**Morphology of nitrogen-doped TiO$_2$.** The morphology of the pure TiO$_2$ and nitrogen-doped TiO$_2$ powders were investigated using the TEM images in Figure 2. The images (Figure 2a and b) revealed that the pure TiO$_2$ and nitrogen-doped TiO$_2$ (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$_2$. Figure 3 shows the diffuse reflectance spectra of pure TiO$_2$ and nitrogen-doped TiO$_2$ with different doping concentrations. The pure TiO$_2$ 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.$^{21,22}$

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.
Visible-photoresponsive Photoelectrochemical Cells

Figure 2. TEM images of (a) pure TiO₂ and (b) nitrogen-doped TiO₂ (N/Ti = 15).

Figure 3. UV-vis diffuse reflectance spectra of nitrogen-doped TiO₂ with various N/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 TiO₂ and TiO₂: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 TiO₂ electrode composed of P25 powders. The TiO₂ film synthesized in this study exhibited a superior PEC performance compared to the P25 TiO₂ electrode. Previous reports have shown that P25 is composed of a mixture of anatase and rutile TiO₂ and has a BET of around 65 - 70 m²/g. On the contrary, the synthesized TiO₂ exhibited only an anatase phase, and its BET surface area was much higher than P25. Therefore, the improved PEC performance of the synthesized TiO₂ mesoporous film was attributed to the much higher surface area and the strictly anatase structure.

Figure 4 also clearly shows that the N-doped TiO₂ electrode exhibited a much higher PEC response than undoped TiO₂. As shown in Table 1, the BET surface area of TiO₂:N (N/Ti = 15) was slightly higher than undoped TiO₂, indicating that the significantly enhanced PEC performance of TiO₂: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, the improved PEC responses of the TiO₂: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 later 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 TiO₂ 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 TiCl₄ hydrolysis in an ammonia aqueous solution at low temperature. UV-vis DRS spectra depicted the visible light absorption of nitrogen-doped TiO₂, which continued above 500 nm. The TiO₂:N mesoporous electrode exhibited a much higher PEC performance than those of the undoped TiO₂ and P25 electrodes because of its visible-photosensitivity and slightly increased surface area.

Acknowledgments. This research was supported by the Yeungnam University research grant (209-A-054-030) for the PEC application.

References