

## NITRIDATION OF Pt-TiO<sub>2</sub> NANOPARTICLE AND THEIR CHARACTERISTICS AS A VISIBLE LIGHT PHOTOCATALYST

*Soo-Keun Lee, Soonhyun Kim*

*Division of Nano-Bio Technology, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Samsung Financial Plaza, Duksan-dong 110, Jung-gu, Daegu 700-010, Korea  
[laser@dgist.ac.kr](mailto:laser@dgist.ac.kr)*

TiO<sub>2</sub> photocatalyst has been extensively studied with regard to its application in degradation of various organic pollutants [1-3]. However, because of the size of its band gap, TiO<sub>2</sub> is active only under UV irradiation, which accounts for less than 5 % of solar light energy. Therefore, there have been many efforts to make a TiO<sub>2</sub> photocatalyst that would be active under visible irradiation. One approach is to prepare impurity doped TiO<sub>2</sub> [4]. Impurity doping material would substitute the Ti<sup>4+</sup> ion or O<sup>2-</sup> ion in the TiO<sub>2</sub> lattice and form the intraband states, which could be responsible for the visible absorption of impurity doped TiO<sub>2</sub>. Previously, Kim et al. [5] investigated that Pt-ion-doped TiO<sub>2</sub> photocatalysts showed the efficient photocatalytic activities under visible irradiation. In that case, the Pt ions substituted in the TiO<sub>2</sub> lattice were present mainly in the Pt(IV) state. In this work, the nitrated Pt-TiO<sub>2</sub> nanoparticle was prepared for the enhancement of photocatalytic activity under visible irradiation. We have investigated the physicochemical properties and photocatalytic activities of nitrated Pt-TiO<sub>2</sub> for 4-chlorophenol (4-CP) and dichloroacetate (DCA) degradation.

Pt-TiO<sub>2</sub> was prepared by a sol-gel method as reported previously [5]. 2.5 ml of TTIP dissolved in 50 ml of ethanol was dropwise to 450 ml of chloroplatinic acid solution (0.08 mM for 0.5 atom% Pt doping) whose pH was adjusted at 1.5 with nitric acid. The resulting colloidal suspension was stirred overnight. For nitridation, Pt-TiO<sub>2</sub> or TiO<sub>2</sub> nanocolloid solution was directly mixed with an excess of TEA and vigorously stirred [6]. The nanocolloid solution rapidly forms a yellowish mixture. All nanocolloid solution was evaporated at 40 °C using a rotavapor. The obtained powder was calcined at 673 K for 3 hr under air atmosphere. The photocatalytic activities were evaluated for the photocatalytic degradation of 4-CP and DCA. TiO<sub>2</sub> was dispersed in distilled water (0.5 g/L) and an aliquot of the substrate stock solution (1 mM) was subsequently added to the suspension to give a desired substrate concentration. Photoirradiation employed a 300-W Xe arc lamp (Oriol) as a light source. Light passed through a 10-cm IR water filter and a UV cutoff filter (>420 nm for visible irradiation), then the filtered light was focused onto a 30-mL Pyrex reactor with a quartz window. The degradation of 4-CP was monitored using a high performance liquid chromatograph (HPLC: Agilent 1100 series) equipped with a UV detector and a ZORBAX 300SB C18 column (4.6×150 mm).

Nitridation treatment changed the physicochemical properties of TiO<sub>2</sub> and Pt-TiO<sub>2</sub>. The primary particle size of nitrated samples was slightly smaller than that of unnitrated samples (Fig. 1) and the anatase to rutile phase transformation was seen to be retarded by the nitridation treatment. The visible light absorption of n-Pt-TiO<sub>2</sub> was more extended than that of Pt-TiO<sub>2</sub> and Pt ion state of n-Pt-TiO<sub>2</sub> was higher than that of Pt-TiO<sub>2</sub>. Furthermore, surface area of nitrated samples was more than twice that of unnitrated samples. From these changes of physicochemical properties, we expected the enhanced photocatalytic activities of nitrated samples. However, their photocatalytic activities were restrictively enhanced and significantly affected by the kind of substrates. For 4-CP degradation, n-Pt-TiO<sub>2</sub> showed the enhanced photocatalytic activity under visible irradiation. For DCA degradation, the enhancement effect of nitridation treatment was not observed under visible irradiation. Above observations indicate that photocatalytic degradation activities of photocatalysts are depended on the kind of substrate as reported by Ryu and Choi [7]. Although they compared the photocatalytic activities

under UV irradiation their conclusions could apply to the photocatalytic activities under visible irradiation. In our case, the synergetic effect of n-Pt-TiO<sub>2</sub> was showed in 4-CP degradation but it was not observed in DCA degradation. The synergetic effects of n-Pt-TiO<sub>2</sub> for 4-CP degradation under visible irradiation seem to be due to enhancement of surface area by nitriding. For DCA degradation, surface area enhancement of TiO<sub>2</sub> might not affect on the visible activity of TiO<sub>2</sub>. Although nitridation treatment significantly affected the physiochemical properties of Pt-TiO<sub>2</sub> and we expected the enhanced visible activities for the degradation of organic substances, as previously discussed, its positive effects were limited to the degradation of 4-CP.

This work was supported by DGIST basic research program of the MOST.

## References:

- [1] A. Mills and S. -K. Lee, J. of Photochem. & Photobiol., A: Chemistry, **152** (2002) 233-247.
- [2] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, Chem. Rev. **95** (1995) 69-96.
- [3] W. Choi, Catal. Surv. Asia **10** (2006) 16-28.
- [4] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science **293** (2001) 269-271.
- [5] S. Kim, S.-J. Hwang, W. Choi, J. Phys. Chem. B **109** (2005) 24260-24267.
- [6] J. L. Gole, J. D. Stout, C. Burda, Y. Lou, X. Chen, J. Phys. Chem. B **108** (2004) 1230-1240.
- [7] J. Ryu, W. Choi, Environ. Sci. Technol. **42** (2008) 294-300.

## Figures:

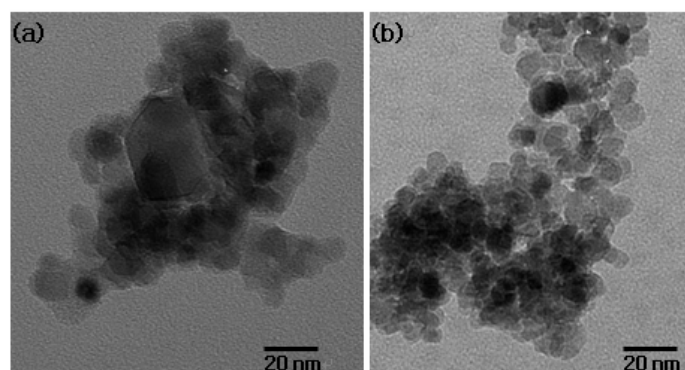


Fig. 1 TEM images of various TiO<sub>2</sub> samples. (a) TiO<sub>2</sub>, (b) n-Pt-TiO<sub>2</sub>.

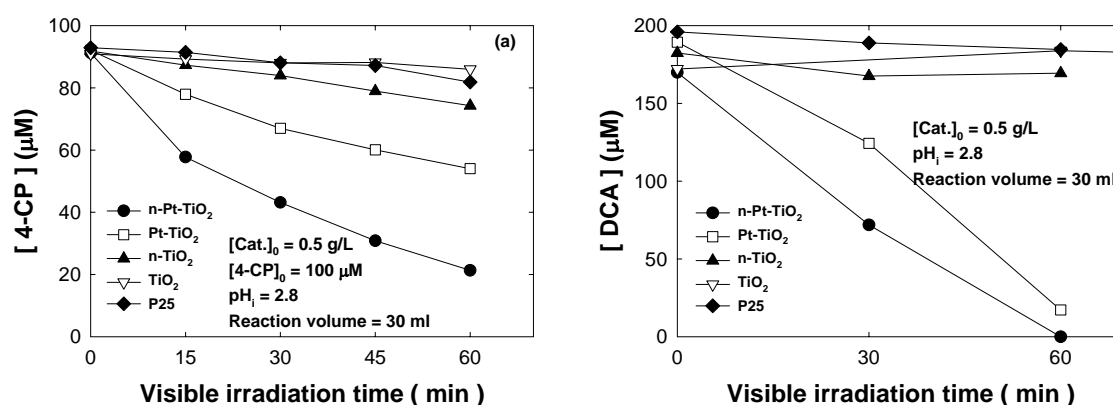


Fig. 2 Photocatalytic degradation of 4-chlorophenol (a) and DCA (b) under visible irradiation.