

Effective nitrogen doping into TiO₂ for visible light response photocatalysis by ion implantation technique

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Photocatalytic reactions at the surface of titanium dioxide (TiO₂) under UV light irradiation have been attracting much attention in view of their practical applications to environmental cleaning such as self cleaning of tiles, glasses, and windows. Recently, Asahi *et al.* reported that the doping of nitrogen into TiO₂ contributes to band gap narrowing to provide visible-light response [1].

In the present study, the thickness-controlled TiO₂ thin films were fabricated by the pulsed laser deposition (PLD) method. These samples functioned as photocatalysts under UV light irradiation and the reaction rate depended on the TiO₂ thickness, i.e., with an increase of thickness, it increased to the maximum, followed by decreasing to be constant. Such variation of the reaction rate was fundamentally explained by the competitive production and annihilation processes of photogenerated electrons and holes in TiO₂ films, and the optimum TiO₂ thickness was estimated to be ca. 10 nm

We also tried to dope nitrogen into the effective depth region (ca. 10 nm) of TiO₂ by an ion implantation technique. The nitrogen doped TiO₂ enhanced photocatalytic activity under visible-light irradiation. XANES and XPS analyses indicated two types of chemical state of nitrogen, one photo-catalytically active N substituting the O sites and the other inactive NO_x ($1 \leq x \leq 2$) species (Fig.1). In the valence band XPS spectrum of the high active sample, the additional electronic states were observed just above the valence band edge of a TiO₂. The electronic state would be originated from the substituting nitrogen and be responsible for the band gap narrowing, i.e., visible light response of TiO₂ photocatalysts.

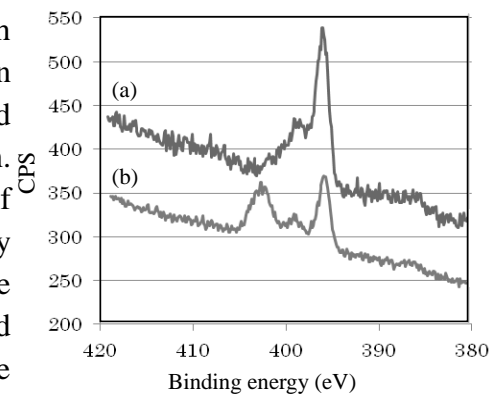


Fig. 1 XPS spectra of the N 1s region for (a) photocatalytic active sample and (b) photocatalytic inactive sample.

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[1] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science* **293**, 269 (2001).