Study on formation process of the N-doped TiO₂ photocatalyst by Ambient Pressure X-ray Photoelectron Spectroscopy

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Introduction
To utilize solar energy efficiently, development of visible-light-response photocatalyst with TiO₂ has been paid much attention[1-3]. Among them, the nitrogen doping by heating under NH₃ atmosphere is known to be an efficient approach[2,3]. Although a number of reports are available for the N-doped TiO₂ prepared by this method, there is no concrete conclusion for its formation process and structure. Here, we studied the formation process of the N-doped TiO₂ under NH₃ atmosphere by means of real-time monitoring with ambient pressure x-ray photoelectron spectroscopy (AP-XPS).

Experimental
All the experiments were performed with an AP-XPS system at the soft x-ray station, BL-7A and BL-13A. To prepare the N-doped TiO₂, a TiO₂(110) single crystal was heated at 820 K under 0.2 Torr of NH₃ atmosphere. During the reaction, Ti 2p, N 1s and valence band XPS spectra were measured to monitor the formation process of the N-doped TiO₂. All the binding energies of the XPS spectra were calibrated with the Ti 2p 3/2 peak top position as 458.6 eV.

Results and Discussion
Fig.1 shows the valence band XPS spectra measured before, during and after the NH₃ treatment. Under 0.2 Torr of NH₃ atmosphere, the top edge of the valence band shifted gradually with heating time. After 3 hours heating at 820 K, the energy shift reached approximately 0.8 eV. The N 1s XPS spectra (Fig.2) measured at the same time show two peaks associated with N-containing species. The peak at around 398.7 eV(site 1) is attributed to chemisorbed NH₃ and this peak intensity was reduced during the reaction. On the other hand, the intensity of the peak at around 399.8 eV(site 2), which appeared after the ignition of the reaction, increased gradually with heating time. This seems to be evidence for the progress of nitrogen doping into the TiO₂(110) single crystal.

From these results, we conclude that nitrogen doping into the TiO₂ proceeds gradually with heating time. The top of the valence band exhibits a gradual shift concomitantly with the increase of doped N. This is interpreted as an appearance of N2p-derived band above the top of original O 2p valence band (~1.7 eV), which was supported by resonance photoemission spectroscopy measurements.

References
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