Synthesis of Pt/TiO_{2-x} Photocatalyst via Reduction Assisted by Hydrogen Spillover and Formation Mechanism of Surface-exposed Ti^{3+}

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Defect engineering is one of the important strategies in the field of heterogeneous catalysts. Reduced metal cation and concomitant oxygen vacancy (V_O) in semiconductor oxide, as represented by TiO_{2-x} including Ti^{3+} and V_O, play an important role in various catalytic and photocatalytic reactions.[1] In the application of TiO_{2-x} photocatalyst, the introduced defects form donor level below the conduction band, thereby providing remarkable photocatalytic performance by improvement of the electron conductivity and narrowing its inherent bandgap. Although the effect of defects on the photocatalytic activity and the development of facile reduction method is one of the hot topics of research, the formation mechanism of defects has caught less attention.

In this study, we synthesized Pt deposited TiO_{2-x} photocatalyst via a reduction treatment assisted by hydrogen spillover from rutile, anatase, or brookite TiO_2 as a starting material.[2] As a result of ESR measurement, surface-exposed Ti^{3+} and V_O were observed in rutile and brookite Pt/TiO_{2-x} after the reduction treatment. Notably, rutile Pt/TiO_{2-x} included a more amount of defects, therefore photocatalytic activity was enhanced by the reduction treatment. In contrast, anatase Pt/TiO_{2-x} included V_O but not surface-exposed Ti^{3+}. During the reduction treatment, Ti^{4+} was reduced to Ti^{3+} by an electron donation from spillover H atom to TiO_2 conduction band and V_O formation occurred via dehydration (**Fig. 1**). The obtained results suggest that the depth of the inherent midgap states, depending on the crystal phases, influences the formation of surface-exposed Ti^{3+}.

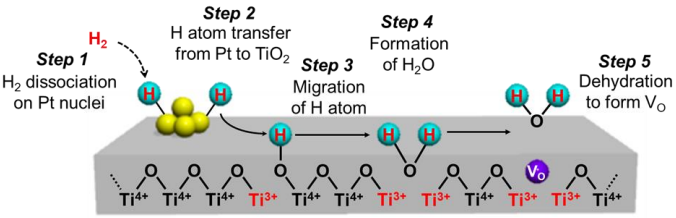

Fig. 1. Possible scheme of defect formation by the reduction assisted by hydrogen spillover.

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