

## Reply to the Comment on "Electron Source in Photoinduced Hydrogen Production on Pt-Supported TiO<sub>2</sub> Particles"<sup>†</sup>

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We wish to reply to the Comment stated by Perkins et al. for our published paper in *J. Phys. Chem. B*.

In the paper, the most important point we have reported is that stoichiometric O<sub>2</sub> and H<sub>2</sub> formations on Pt-supported TiO<sub>2</sub> (P-25 was used) (TiO<sub>2</sub>/Pt) cannot take place under UV irradiation, and only H<sub>2</sub> formation was observed. In addition, a long-term photolysis by TiO<sub>2</sub>/Pt showed that the H<sub>2</sub> formation stops almost after 600 h irradiation. Although the TiO<sub>2</sub> were reused in a photocatalytic H<sup>+</sup> reduction by adding methanol as an electron donor after recovering the photocatalyst used in the long-term reaction, no H<sub>2</sub> formation was observed, showing that the TiO<sub>2</sub>/Pt particles have entirely lost their photocatalytic activity after the long-term reaction. These results revealed that TiO<sub>2</sub> itself has been changed to lose its photocatalytic activity after the long-term photochemical reaction.

As for the electron donor to cause the photoinduced H<sub>2</sub> formation on the TiO<sub>2</sub>/Pt, we investigated various possibilities. We took into account also the possibilities such as the

contamination by (1) inorganic impurities, (2) Ti<sup>3+</sup>, and/or (3) organic impurities, as suggested in the above Comment by Perkins et al. However, we believe that the entire deactivation of TiO<sub>2</sub>/Pt could exclude such possibilities and that only one possible interpretation would be a structural change of the TiO<sub>2</sub>.

As for the structural change of TiO<sub>2</sub>, we proposed as one of the possibilities the oxidation of Ti<sup>4+</sup> to 5+ as a most probable mechanism. We did not mention the entire change to 5+, but the activity has been lost entirely after one-third of the Ti is changed, as calculated from the total amount of evolved H<sub>2</sub>, suggesting that an intermediate state (probably one positive charge is delocalized between three Ti<sup>4+</sup>), whose average composition is (Ti<sub>2</sub>O<sub>5</sub>)(TiO<sub>2</sub>)<sub>2</sub>, is stabilized to realize a stable Ti<sup>5+</sup> apparent state.

We do not hesitate to accept any other possibilities of other electron source or other structural change of the TiO<sub>2</sub> if supporting data for such are available. For example, Arakawa's groups carried out a recent experiment of water photolysis with layered and platinized TiO<sub>2</sub> nanosized particles to find also only H<sub>2</sub> formation (K. Sayama, J. Augustynski, and H. Arakawa, Poster in the 3rd NIMC International Symposium on Photoreaction Control and Photofunctional Materials held in Tsukuba, Japan, in March 2000). They are proposing also structural change of TiO<sub>2</sub>, but an oxidized structure such as the formation of Ti—O—O—Ti bondings. We welcome further discussion about the real photochemical reaction process on TiO<sub>2</sub>.

As pointed in the above Comment, it was our mistake that both refs 10 and 11 were missing in the paper. They are added here.

## References and Notes

- (10) Ohtani, B.; Okugawa, Y.; Nishimoto, S.-I.; Kagiya, T. *J. Phys. Chem.* **1987**, *91*, 3550.
- (11) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron spectroscopy*; Chastain, J., Ed.; Physical Electronics Division, Perkin-Elmer Corp.: MN, 1992.

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