Facet-dependent Deposition of Metal Particles and their Stability on Decahedral-shaped Titania Particles

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It has been proposed that faceted titanium(IV) oxide (titania) particles, e.g., decahedral-shaped anatase titania particles (DAPs) exposing two {001} and eight {101} facets, show high-level photocatalytic activity, presumably because photoexcited electrons and positive holes migrate to {101} and {001} facets, respectively, to result in charge separation.[1,2] This speculation seemed to be based on the observations by scanning electron microscopy and/or transmission electron microscopy in which most metal and metal-oxide particles deposited on DAPs, through photocatalytic reduction and oxidation of their precursors, were seen on {101} and {001} facets, respectively.[1,2] However, these studies may include some problems, e.g., (1) there were no statements on the number of metal/metal-oxide particles deposited on the two kind of facets, only showing a single or few microscopic images, and (2) deposited metal (or oxide) particles could be desorbed and re-adsorbed on the {101} or {001} facets. In this study, metal particles were deposited on DAPs using two methods and observed by scanning electron spectroscopy (SEM). Facet-dependent deposition was quantitatively and precisely measured.

DAPs were prepared by a gas-phase reaction of titanium(IV) chloride ($TiCl_4$) with oxygen.[3] Platinum or gold particles were deposited on the DAPs by (1) photocatalytic reduction of hexachloroplatinic acid (H_2PtCl_6) or tetrachloroauric acid ($HAuCl_4$), respectively or (2) mixing a gold or platinum colloid solution with DAPs suspensions in the dark or under mercury-lamp irradiation.

Figure 1 shows an SEM image of the platinum colloid-deposited DAPs under mercury-lamp irradiation. By counting the number of the metal particles (on more than 100 DAPs), a ratio of deposition density (*s*) was calculated as a measure of facet-selective metal deposition using a equation: $s = D_{\{001\}} / D_{\{101\}}$,where $D_{\{001\}}$ and $D_{\{101\}}$ are the density of deposited metal particles on each facets. In the case of the photocatalytic metal deposition from H_2PtCl_6 or $HAuCl_4$, *s* was smaller than 1, i.e., metal particles tended to be deposited preferentially on the {101} facet, as was reported previously. On the other hand, in the case of mixing of a gold or platinum colloid both under irradiation and in the dark, *s* was also smaller than 1, i.e., even without photocatalytic reaction, mixing of a metal colloid in the dark exhibited {101}-facet selectivity. These results suggest the difference in ability of metal-particle adsorption or desorption between {101} and {001} facets.

Influence of stirring under dark condition after photodeposition was examined to check the stability of photodeposited metal particles. As a result, {001} facet-selective desorption was observed, and therefore in the case of photodeposition, it can be hypothesized that facet-selective metal deposition was caused by desorption of metal particles once deposited on {001} facets and adsorption on {101} facets.

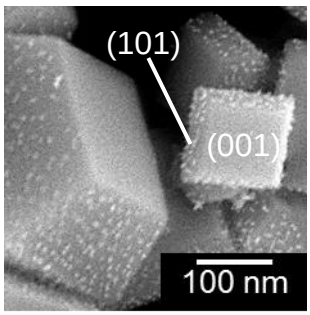

Fig. 1 An SEM image of DAPs with platinum particles (white) deposited from a colloid under irradiation

REFERENCES

[1] C. Liu, X. Han, S. Xie, Q. Kuang, X. Wang, M. Jin, Z. Xie and L. Zheng, *Chem. Asian. J.*, **8**, 282 (2013).
[2] T. Ohno, K. Sarukawa and M. Matsumura, *New J. Chem.*, **26**, 1167 (2002).
[3] M. Janczarek, E. Kowalska and B. Ohtani. *Chem. Eng. J.*, **289**, 502 (2016).