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Quantitative Electron Tomography of Size-controlled Metallic Nanodots on Sintered Titania Photocatalysts

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Oxides supporting precious metals act as oxidation catalysts. Platinum supported on titania (Pt/TiO_2) is an especially high-active oxidation photocatalyst. The photocatalyses such as aqueous photo-degradation, antibacterial activity and environmental cleanup are already applied to a lot of products familiar with the public. Since early 19th century, many researchers have tried to develop methods to achieve high photocatalytic activity by controlling nano-structures of the platinum-supported titania, e.g., producing fine particles or porous configurations with large surface areas and size-controlling of Pt clusters on the TiO_2 surface as effective reaction sites [1]. It has been, however, rather difficult that nm-sized Pt dots on TiO_2 particles of several hundreds nm diameter are analyzed by spectroscopic methods including X-ray diffraction.

Transmission electron microscopy (TEM) is one of the most effective methods to analyze such supported nanodot structures, though information obtained from the images is limited to two-dimensional (2D). In 1992, "electron tomography" was proposed in order to obtain three-dimensional (3D) structure information from 2D TEM images [2]. In the electron tomography, 3D structures of samples are reconstructed by many TEM images taken from various directions, in the same manner of the computed tomography (CT) by X-ray. In the recent years, electron tomography using high angle annular dark field scanning TEM (HAADF-STEM) images has been expected as a more powerful method to observe 3D structures of crystalline materials than using TEM images [3]. In the present study, we have applied the STEM method to analysis of 3D nano-structures of Pt/TiO_2. The STEM images were recorded at each tilt angles from -76 to +74 degree by Tecnai Polara G^2 (FEI Co.). HAADF detector of 100 mrad was used for Z-contrast images [4]. The IMOD software was used for 3D reconstruction of the HAADF-STEM tilt series [5].

Figure 1 shows reconstructed 3D structures of a Pt/TiO_2 sample prepared in water solution of Pt ions with TiO_2 particles. We can observe clearly fine Pt nanodots about 1-3 nm diameter locating on the TiO_2 surface without showy artifacts, which occur from a missing wedge or digital quantum noise. The influence of Fresnel contrast was researched especially in detail compared with reconstructed 3D structures by TEM. The reconstructed 3D structures are available for inspection at http://sirius.cirse.nagoya-u.ac.jp/~tanakalab/kenta/newpage0801.html. After 3D reconstruction based on the back-projection method, we have analyzed quantitatively Pt nanodots structures such as size, volume and number of nanodots for each unit area on the titania surface by using the IMOD and original measurement programs. These parameters of Pt/TiO_2 and other Au/TiO_2 are shown in Table I in comparison for with/without ionic liquid [6]. In the present study, size-controlled Pt and Au nanodots were three-dimensionally analyzed by HAADF-STEM tomography. Comparison between the structural parameters and macroscopic properties (MB dissolution and CO oxidation) suggested the quantum size effect of these noble metals on such macroscopic photocatalysis.

References

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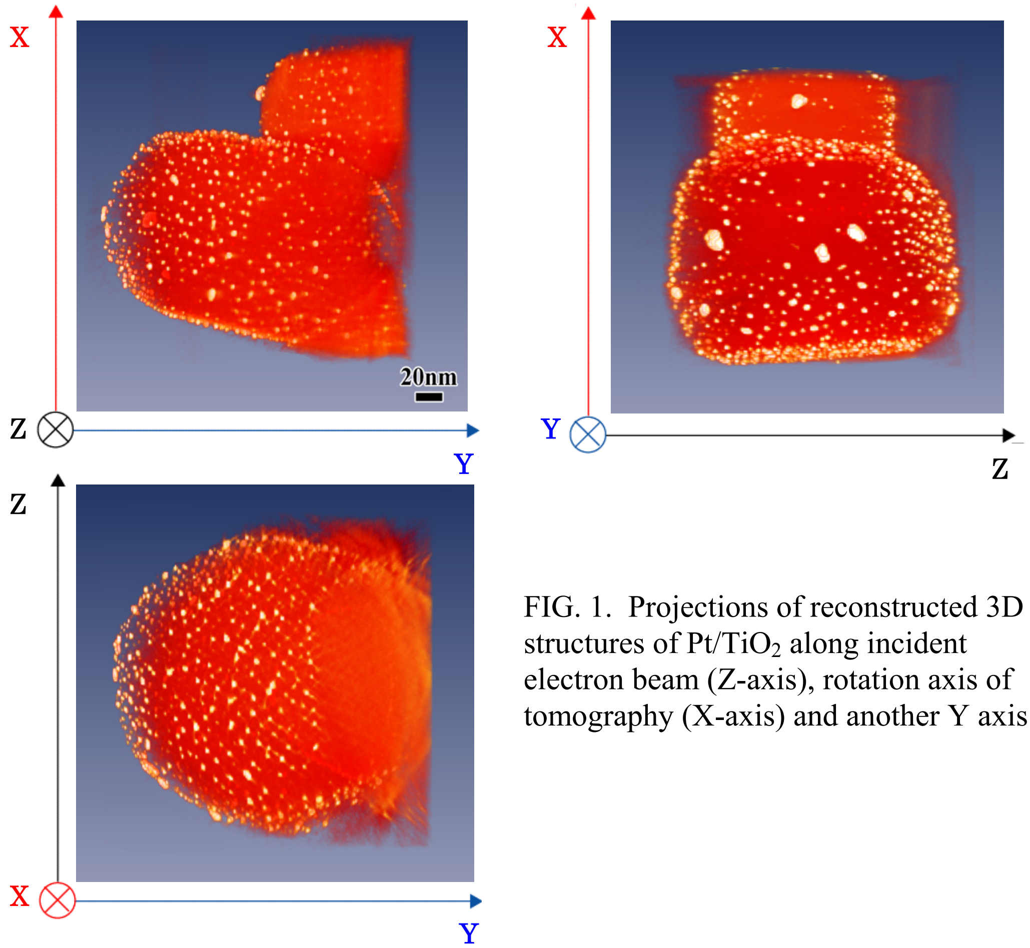

FIG. 1. Projections of reconstructed 3D structures of Pt/TiO_2 along incident electron beam (Z-axis), rotation axis of tomography (X-axis) and another Y axis.

TABLE 1. Structural parameters of metal nanodots synthesized in water and water/ionic liquid(IL).

Solvent	Supported Metal	Particle size	Density	Volume
Water	Au	18.4nm	$1.80 \times 10^{16}/m^2$	$9.64 \times 10^{-3} g/m^2$
	Pt	2.89nm	$2.75 \times 10^{16}/m^2$	$17.7 \times 10^{-3} g/m^2$
Water + IL	Au	3.70nm	$3.10 \times 10^{16}/m^2$	$3.52 \times 10^{-3} g/m^2$
	Pt	2.20nm	$4.50 \times 10^{16}/m^2$	$2.68 \times 10^{-3} g/m^2$