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

K. Yoshida,*,*** P.L. Gai,** S. Sueda,*** N. Tanaka*,***

* Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan
** The Nanocentre, Department of Chemistry, Department of Physics and Department of Electronics, The University of York, York Y010 5DD, U.K.
*** Department of Crystalline Materials Science, Ecotopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

Page Gold (Au) and silver (Ag) nanoparticles supported on titanium dioxide (TiO_2) are characterized using the Z-contrast of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and the 3D morphologies of Au and Ag on TiO_2 catalysts are carefully quantified by developed measurement programs. The Au and Ag nanoparticles on TiO_2 are well known as high active oxidation catalysts, and much 3D research of these TiO_2 catalysts has been reported [1-3]. HAADF-STEM tomography has proven to be a quite effective tool for analyzing such catalytic nanomaterials [4,5]. This study is also interested in the high contrast imaging of HAADF-STEM.

In contrast, the convergent electron beam of HAADF-STEM sometimes damages samples. This effect can be an especially serious problem in tomography, because a lengthy observation is required in order to obtain tilt series for 3D reconstruction. In fact, degradation of 3D reconstructed data was a concern because of the diffusion and coalescence of metallic nanoparticles on oxide support or the destruction of the TiO_2 support [6]. In the present study, a cryogenic technique, which has been commonly used in electron tomography for biological samples, was employed in order to avoid such irradiation damage. The metallic nanoparticles and TiO_2 support were quite stable under the cryogenic conditions at 78 K even when electron irradiation was performed for 3 or more hours. The present results clearly indicate that the cryogenic system is advantageous for electron tomography of inorganic materials.

FIG.1(a) is a slice image of the 3D reconstructed image, and FIG.1(b) is a histogram of the intensity distribution in the slice. This histogram shows that there are four types of peaks, which are larger than the case of Au/TiO_2. This means that two different types of metallic nanoparticles were supported on TiO_2. Threshold values are determined in order to distinguish such different types of nanoparticles. The first threshold value [a] between Au and Ag was determined as a value that gives the deepest valley in intensity distribution between the peak near 160 and the other near 100 [arbitrary units]. Next, the second threshold value [b] between Au and TiO_2 and threshold value [c] between TiO_2 and vacuum were similarly determined as values that give the deepest valley between each peak in the histogram.

All nanoparticles have intensity gradients from the centre to the edge; the intensity of the Au edge overlaps the intensity of the Ag centre. However, the intensity of the Au centre is different from the intensity of the Ag centre; therefore, the maximum intensity of each nanoparticle is very important for distinguishing Au from Ag. When the maximum intensity of one nanoparticle exceeds the threshold value [a], the surrounding voxels whose intensities are over the threshold value [c] were coded as a light grey colour for Au. In the same way, Ag nanoparticles were coded as a light grey colour by measuring their maximum intensities. A color-coded tomogram of Au/Ag/TiO_2 is shown in FIG.1(c). The present electron tomography visualized the heterogeneous diffusion of photoexcited electrons dominating a reduction process in the photocatalysis. We can see Au nanoparticles, which surround a previously deposited Ag nanoparticle. Such localized Au deposition was not observed in the Au/TiO_2 sample. It is an important result to study the heterogeneous catalytic reaction, which is achieved only by HAADF-STEM tomography. In TABLE 1, the 3D morphologies of Au and Ag nanoparticles are summarized.

References
[1] S.P. Ahrenkiel et al., *J. Electron. Microsc.* 230 (2008) 382.
[2] K. Kaneko et al., *Material Sci. Eng.* A 403 (2005) 32.
[3] K. Yoshida et al., *J. Appl. Phys.* 99 (8) (2006) 084908.
[4] J.C. Gonzales et al., *Angew. Chem.* 48 (2009) 5313.
[5] A.B. Hungria et al., *Catal. Today* 143 (2009) 225.
[6] Y. Chen et al., *Langmuir*, 22 (2006) 2851.

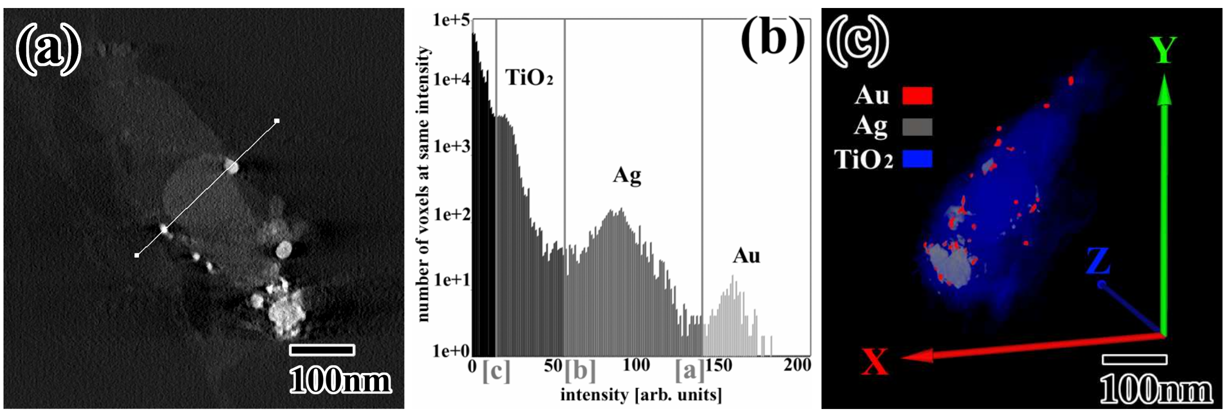

FIG. 1. (a) Z-slice image of Au/Ag/TiO_2 obtained by STEM tomography. (b)Histogram at Fig. 8a. Two different high intensities show that Au and Ag can be discriminated by STEM tomography. Determining three threshold values between Au and Ag, Ag and TiO_2, TiO_2 and vacuum, 3D morphologies can be measured by the TCC method. (c)Colour coded tomogram using multiple threshold values.

TABLE 1. 3D morphologies about Au/Ag/TiO_2 obtained by the TCC method.

	total volume [nm^3]	total surface area [nm^2]	largest thickness [nm]	average nearest-neighbour distance [nm]	average particle volume [nm^3]
Au	6.5×10^5	1.4×10^5	77	108	9.2×10^3
TiO_2	1.3×10^8	1.9×10^7	650	——	——

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