Quantitative high-resolution microscopy of size-controlled metallic nanodots on titania photocatalysts

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Abstract. We applied the cryo-HAADF-STEM tomography (cryogenic Tecnai G2 Plara) for analysing three-dimensional nano-structures of platinum (Pt) and gold (Au) nanodots synthesised on titanium dioxide. The structural parameters such as particle size, density and volume were successfully evaluated and compared between macroscopic properties (methylene blue dissolution and CO oxidation). The atomic structures of metallic clusters on the TiO2 surface were also carefully investigated by using double aberration corrected TEM/STEM (double AC JEOL JEM-2200FS) in order to study the quantum size effect of these noble metals.

1. Introduction
Oxides supporting precious metals act as oxidation catalysts. Platinum supported on titania (Pt/TiO2) is an especially high-active oxidation photocatalyst. Photocatalytic processes such as aqueous photo-degradation, antibacterial activity and environmental cleanup are already applied to a lot of products familiar with the public. Since the early 19th century, many researchers have tried to develop methods to achieve high photocatalytic activity by controlling nano-structures of platinum-supported titania, e.g., producing fine particles or porous configurations with large surface areas and the size of Pt clusters on the TiO2 surface as effective reaction sites [1]. However, analysing nm-sized Pt dots on TiO2 particles of several hundred nm’s diameter has been difficult by spectroscopic methods including X-ray diffraction.

Transmission electron microscopy (TEM) is one of the most effective methods to analyse such supported nanodot structures, though information obtained from images is limited to two-dimensions (2D). In 1992, “electron tomography” was proposed in order to obtain three-dimensional (3D) structural information from 2D TEM images [2]. In electron tomography, 3D structures of samples are reconstructed by many TEM images taken from various directions, in the same manner as the computed tomography (CT) by X-rays. In recent years, electron tomography using high angle annular dark field scanning TEM (HAADF-STEM) images is shown to be a more powerful method to observe 3D structures of crystalline materials than using TEM images [3-6].
In the present study, cryogenic high-angle annular dark field scanning transmission electron microscopy (Cryo-HAADF STEM) tomography has been used to obtain 3D structural information of metallic nanodots on TiO\textsubscript{2} particle surfaces.

2. Experimental Procedure

The platinum (Pt) and gold (Au) nanodots were prepared on titanium dioxide by the photo-electrocrystallization in the two-phase liquid solution as water and hydrophobic ionic liquid. Titanium oxide powder (Ishihara Sanngyou Co.), hydrophobic ionic liquid N,N,N-Trimethyl-N-propylammomium bis(trifluoromethanesulfonyl)imide (TMPA TFSI, Kanto Reagent) and tetrachloroauric acid were aged after adding water. Subsequently, the mixture was irradiated with UV light (10W × 2, $\lambda = 310 \sim 400$nm), while stirring it at 300K for 5 minutes. The mixture was then filtered and the recovered solid was thoroughly washed with ethanol and acetone, and dried in an oven with UV irradiation for 12 hours.

The STEM images were recorded with tilt angles ranging from -76 to +74 degrees with 1 degree increments in cryogenic HAADF-STEM (FEI Tecnai G2 Plara). A HAADF detector of 100 mrad as the inner angle was used for obtaining Z-contrast images. By using a Howie detector, which excludes Bragg scattering, one can use actively incoherent thermal diffuse scattering (TDS) electrons and obtain Z-contrast STEM tilt series [7]. The IMOD suite of programs [8,9] was used for 3D reconstruction of the HAADF-STEM tilt series. After adjusting experimental data, including image sizes, orientation and image drift, 3D reconstruction was performed. By calculating three-dimensional coordinates and intensities of the images, the pore size, volume fraction of pores and specific surface area of the porous structures could be analysed in real space using IMOD and in-house programs. In addition, the atomic structure of Pt clusters on the TiO\textsubscript{2} surface and the interface structure were carefully investigated by using a double aberration corrected TEM/STEM (double AC JEOL JEM-2200FS). The 2AC-JEOL 2200FS (S)TEM, configured to have a larger gap (HRP) objective lens polepiece [10] to enable tilting of the sample for alignment into a zone axis orientation, was used for nanostructural studies.

3. Results and discussion

Figure 1 shows a tilt series of the Pt/TiO\textsubscript{2}. Figure 1(a)-(g) are HAADF-STEM images corresponding to the tilted sample with tilt angles of -70, -35, 0, 35 and 75 degrees from the position of zero degree. Figure 2(a)-(g) are HAADF-STEM images of Au/TiO\textsubscript{2} with tilt angles of -60, -30, 0, 30 and 70 degrees from the position of zero degree.

Figure 3 shows reconstructed 3D structures of a Pt/TiO\textsubscript{2} and Au/TiO\textsubscript{2} prepared in water solution. We can clearly observe fine Pt nanodots about 1-3 nm diameter located on the TiO\textsubscript{2} surface without any visible artefacts, which can occur from a missing wedge or digital quantum noise. After 3D reconstruction based on the back-projection method, we have quantitatively analysed Pt nanodot structures, including size, volume and number of nanodots for each unit area on the titania surface by using the IMOD and in-house measurement programs. The 3D morphologies of nanodots are shown in Table 1. Average particle size of Pt nanodots was found to be less than 3nm. The Pt nanodots are small compared to the TiO\textsubscript{2} support of 150nm in diameter. It is usually not possible to see nanodots by HRTEM because of strong Fesnel’s interference from the thick supporting material.

Figure 4 is a spherical aberration corrected (Cs-corrected) TEM image of the Pt/TiO\textsubscript{2} sample. Pt lattice spacing of (111) and (200) planes were observed at white arrowed areas. Crystal size observed was in good agreement with that quantified by HAADF-STEM tomography. The high-resolution observation have elucidated the single crystallite of Pt nanoparticle (atomic number; Z = 78), which exhibit stronger contrast than the anatase substrate (atomic number, gray atom approximation; Z = 12.7).

4. Conclusion

In the present study, electron tomography was applied to the 3D analysis of metallic nanodots on titania photocatalysts. The shapes and 3D distribution of nanodots (Pt particles of 2.89 nm and Au particles of 18.4 nm in diameter) on the modified TiO\textsubscript{2} surface were successfully reconstructed. The
volume fraction and the density of the nanodots were also accurately measured in real space. The results and the data of Methylene Blue degradation indicate that smaller dots, produced via a solution containing ionic liquids have considerably greater number of effective reaction sites than nanodots produced by the conventional electrocrystallization method. Our results have shown that 3D analysis of nanostuctures using electron tomography is an effective method of studying the influence of the synthesis process on the photocatalytic activity of metal nanodot/TiO₂ photocatalysts.

Figure 1. Tilt series of the Pt/TiO₂.

Figure 2. Tilt series of the Au/TiO₂.

Figure 3. Reconstructed 3D structure of the Pt/TiO₂(left) and Au/TiO₂ (right). The black, red and blue arrows show the incident axis of the electron beam (Z axis), the rotation axis of tomography (Y axis) and another X axis, respectively.
Table 1. Structural parameters of metal nanodots synthesized in water and water/ 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$^2$ |

Figure 4. TEM image of the Pt/TiO$_2$ using double Cs corrected thermal field-emission HRTEM (JEOL: JEM-2200FS).

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6. References
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