**In situ** TEM study of platinum electrode catalysts with 80kV-1MV accelerating voltage

K. Yoshida¹,²,³, A. Carlsson⁴, J. R. Jinschek⁴, D. J. Stokes⁴, P. L. Gai², S. Arai³, K. Saitoh¹ and N. Tanaka¹,³

¹ Nanostructures Research Laboratory, Japan Fine Ceramics Center, Atuta-ku, Nagoya, 456-8587, Japan
² Department of Chemistry and The York JEOL Nanocentre, University of York, Heslington, York, YO10 5DD, UK
³ Ecotopia Science Institute, Nagoya University, Chikusa-ku, Nagoya, 464-8603, Japan
⁴ FEI COMPANY, PO Box 80066, 5600 KA, Eindhoven, The Netherlands

E-mail: k_yoshida@jfcc.or.jp

**Abstract.** We perform transmission electron microscopy (TEM) at different accelerating voltages for analysis of complex nano-structures of platinum (Pt) nanoparticle catalysts synthesized on titanium dioxide. TEM images obtained at 80, 200, 300, and 1000kV are carefully compared. The particle size, density and volume of the Pt nanoparticles deposited under different conditions are evaluated using electron tomography. The atomic structures of Pt nanoparticles on the TiO₂ and amorphous carbon a surfaces are also investigated using spherical aberration corrected TEM in order to study the diffusion of these Pt nanoparticles and atoms.

1. **Introduction**

Platinum supported on titanium dioxide (Pt/TiO₂) exhibits remarkably high activity towards the decomposition reaction of organic molecules such as acetaldehyde and carboxylic acid. Recently, Pt/TiO₂–Carbon catalyst has been synthesized for proton exchange membrane fuel cells [1]. In such catalytic applications, the importance of reducing size and increasing density of Pt nanoclusters on anatase titanium dioxide has attracted strong interest. In contrast, the size of the TiO₂ support particles has been kept at sub-micron sizes to ensure stability at high temperature. The TiO₂ surface has also been modified to form a heterogeneous nanostructure. Transmission electron microscopy (TEM) is one of the most effective methods to analyze such complex nanostructures. Electron tomography allows reconstruction and quantification of the three-dimensional (3D) morphology [2-4]. Spherical aberration corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) imaging has been widely used for measuring size distributions of the catalyst nanoparticles, clusters and single atoms active in various reaction processes [5]. Although it is clear that these complex nanocatalysts can be visualized at typical voltages such as 200kV, switching between several accelerating voltages (progressive electron microscopy) provides much better data about the sample structure.
Here we report a progressive electron microscopy study of such heterogeneous catalysts using accelerating voltages of 80 kV to 1 MV. Switching voltages is also essential for estimating the beam effect when performing environmental transmission electron microscopy (ETEM). We present aberration-corrected ETEM images of Pt/TiO$_2$ photocatalysts taken over this range of accelerating voltages.

2. Experimental Procedure

The platinum (Pt) nanoparticles were prepared on titanium dioxide by the photo-electrocrytallization in the two-phase liquid solution of water and hydrophobic ionic liquid. Titanium oxide powder (Ishihara Sanngyou Co.), hydrophobic ionic liquid N,N,N-Trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA TFSI, Kanto Reagent) and tetrachloroauric acid were aged after adding to water. UV light (10W × 2, $\lambda = 310 \sim 400$nm) was used to irradiate the mixture under stirring at 300K for 5 minutes. The mixture was filtered off and the recovered solid was thoroughly washed with ethanol and acetone and oven dried with UV irradiation for 12 hours.

The samples were characterised using a double spherical aberration corrected environmental TEM/STEM (JEM-2200FS, The University of York) [6], a spherical aberration corrected environmental TEM (Titan ETEM, FEI COMPANY) [7] and Ultra-High Voltage environmental TEM (JEM-1000K RS, Nagoya University) [8].

3. Results and discussion

Figure 1 is a schematic diagram showing the heterogeneous catalyst with wide range in size. Electron tomogram visualizes the complicated structure of the present Pt/TiO$_2$ samples. Figure 2 shows reconstructed 3D structures of Pt/TiO$_2$ prepared in water solution (PTA) and water/ionic liquid solution (PTB), respectively. We can observe clearly fine Pt nanodots about 1-3 nm diameter located on the TiO$_2$ surface without showing artefacts, which occur from a missing wedge or digital quantum noise. After 3D reconstruction based on the back-projection method, we have analyzed quantitatively Pt nanoparticle structures in terms of size, volume and number of nanodots for each unit area on the titania surface by using the IMOD [9] and in-house measurement programs [3]. In Table 1, the morphology of the Pt/TiO$_2$ samples are summarised. In the present study, electron tomography was firstly applied to the 3D analysis of the shapes and 3D distribution of Pt nanoparticles (PTA; 2.89 nm and PTB; 2.20nm in diameter) on the TiO$_2$ surface. Density and volume were accurately measured in real space.

Figure 3 are spherical aberration corrected TEM (AC-TEM) images of PTB. The surface structure of the Pt particle and an organic network (adsorbed IL molecules) are successfully observed by 80kV.
AC-TEM and agreed well with image simulation. On the other hand, a 300 kV accelerating voltage provided clearer lattice imaging of the TiO$_2$ supporting particles. For in situ study of reduction/deactivation process of the Pt/TiO$_2$, transmittance of Ultra-High Voltage EM showed big advantage for visualizing nanoparticles, which aggregated on grain boundaries of sintered TiO$_2$, as shown in Figure 4. We also present an in situ AC-TEM study of Pt nanoparticle on anatase TiO$_2$, amorphous carbon and amorphous silicon nitride surfaces (Figure 5). The nano-step structure working as trapping site of Pt nanoparticle and reactionsite had been observed with deposited nanoparticle at same time. The present results indicated that adsorbed ionic molecules prevent sintering of nanoparticle and improve robustness.

**Figure 2.** Reconstructed 3D structure of the Pt/TiO$_2$ of (a) PTA and (b) PTB. The scale bar is an estimate only.

**Figure 3.** AC-TEM image of Pt/TiO$_2$ obtained with (a) 80 keV and (b) 300 keV by Titan ETEM.

**Figure 4.** In situ observation of reduction process of Pt/TiO$_2$ by Ultra-High Voltage EM.
4. Conclusion
In order to analyze such complex nanostructures of Pt/TiO$_2$–C catalysts, Cs corrected TEM with various accelerating voltage and electron tomography was applied.

The Small and uniform Pt crystallites 2-3nm in diameter were measured in real space using electron tomography. A numbers of nanoclusters and nanoparticles were indicated on PTB. In the 80 kV TEM image, selective lattice imaging of the Pt nanoparticle was achieved. Greater contrast was obtained in comparison with a conventional 200 kV image. On the other hand, a 300 kV accelerating voltage provided clearer lattice imaging of the TiO$_2$ supporting particles. In addition, we achieved single atom imaging of platinum on amorphous carbon using 300kV AC-TEM and studied the behavior of Pt atomic species dynamically. Single atoms, clusters (<1nm) and nanoparticles (<3nm) were successfully visualized in the same region at the same time. The time resolution (0.2s) is similar to that reported in a previous in-situ AC-STEM study [10].

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