

## Atomic Structures of Pt nanoparticles on TiO<sub>2</sub> (110)

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Platinum nanoparticles dispersed on TiO<sub>2</sub> exhibits unique catalytic activity for the oxidation of carbon oxide. The catalytic performance of the supported Pt nanoparticles not only depends on their shapes and sizes, but also on the types of support oxides. To fully understand their functionality, it is important to understand the metal nanoparticle-support interactions on a nanometer scale<sup>2,3</sup>. Recently, the structure of Pt clusters, its nucleation and growth behavior, as well as the preferential site on TiO<sub>2</sub> (110) surface for Pt atoms adsorption have been studied by scanning tunneling microscopy. However, the effects of the TiO<sub>2</sub> support on the initial stage of Pt nanoparticles growth, especially when the nanoparticles are quite small with size less than 2 nm, as well as the interaction between Pt atoms and TiO<sub>2</sub> supports, have not been well addressed. In this study, we use aberration-corrected scanning transmission electron microscopy (STEM) to directly observe the atomic structures of Pt nanoparticles on the TiO<sub>2</sub> (110) surface. The atomic-resolution of STEM enables us to understand the influence of TiO<sub>2</sub> surface structures on Pt nanoparticles growth, and the insight into Pt-TiO<sub>2</sub> interactions at atomic-scale.

The TEM specimens with clean, atomically flat TiO<sub>2</sub> (110) surface was prepared under standard procedure as described in the previous reports<sup>2,3</sup>. High-purity Pt atoms were then evaporated onto the TEM specimen surfaces by vacuum evaporation at room temperature. For comparison, we also evaporate Pt atoms onto amorphous carbon micro-grids at exactly the same evaporation condition. HAADF STEM images were then obtained using JEM-ARM200CF equipped with the aberration corrector operated at 200kV and low-dose condition with the probe size of about 0.8 Å and the beam current of about 10 pA.

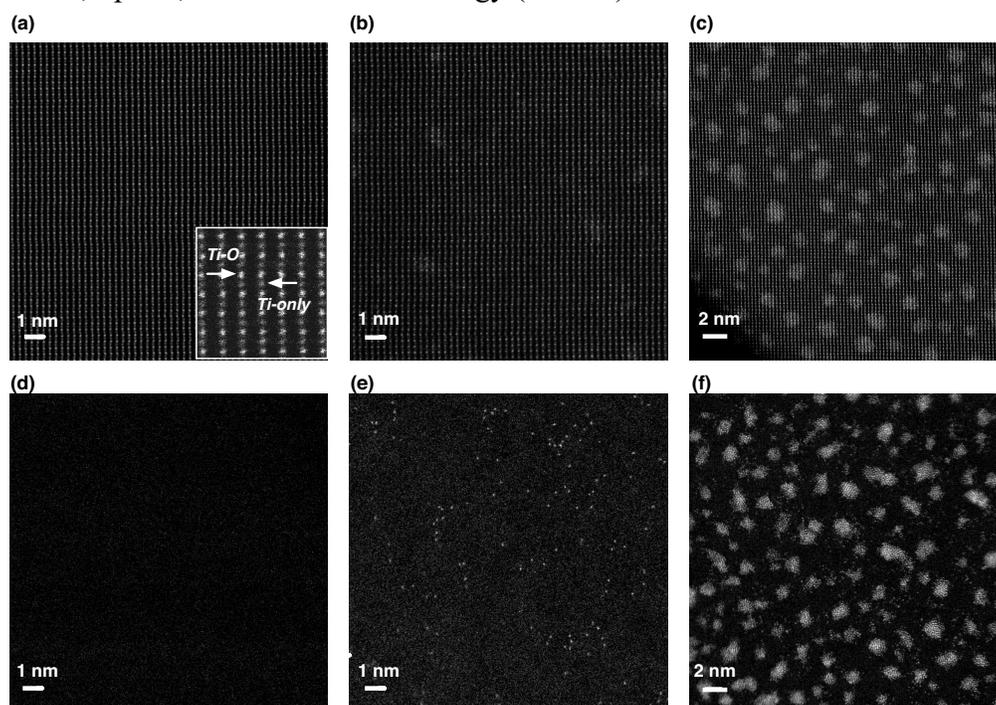
Figure 1(a) shows typical HAADF-STEM images of rutile TiO<sub>2</sub> crystal observed along the [110] zone axis as well as its magnified image (inset) showing the typical Ti-O and Ti-only columns. In Fig. 1(b), Pt nanoparticles with the size less than 1 nm were clearly observed with the evaporation time of 45 s. Fig. 1 (c) shows, after growth for 1200 s, Pt nanoparticles spread over the surface with their sizes no larger than 2 nm. Fig. 1(d)-1(f) show that the Pt atoms are evaporated as single atoms, diffuse on the amorphous surface and then coalesce into larger nanoparticles. While having the same evaporation time of 1200 s, the size and shape of the Pt nanoparticles appear to be more random on the amorphous carbon surface than on the crystalline TiO<sub>2</sub> (110) surfaces.

Although precise estimation of the height of Pt nanoparticles along beam direction is challenging, we estimated the relative intensity  $I'$  (obtained by subtracting the nearby intensity of substrate from the intensity of nanoparticle), which enables us to relatively compare the image intensities of Pt on different supports. Figure 2 presents the histogram of  $I'$  in three cases, showing that the  $I'$  of TiO<sub>2</sub> (110) support with 1200 s deposition time has similar intensity as the case of 45 s Pt deposition and its distribution is confined in a much narrower range than the case of amorphous carbon support. This result suggests that at the initial stage of growth, Pt grows in a 2-dimensional manner on the TiO<sub>2</sub> (110) surface, and in a 3-

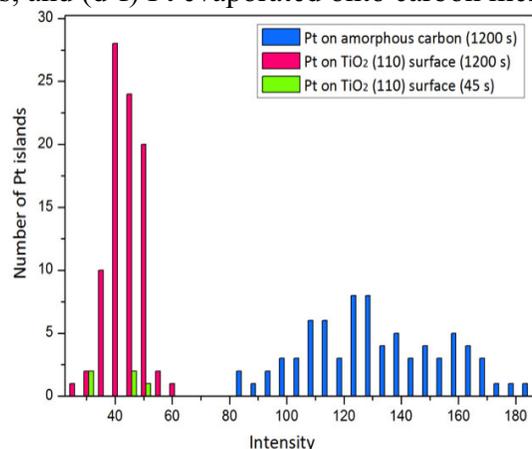
dimensional manner on the amorphous carbon, indicating that the effects of supports on Pt growth are much stronger in the case of the TiO<sub>2</sub> (110) surface than in the amorphous carbon surface<sup>4</sup>. In the present talk, we will show the direct determination of atomic-scale stable adsorption sites of Pt atoms on the TiO<sub>2</sub> (110) surface.

#### References:

- [1] N. Shibata *et al*, Physical Review Letters 102 (2009), p. 136105  
 [2] T.-Y. Chang, Y. Ikuhara, N. Shibata *et al*, Applied Physics Express 6 (2013), p. 025503.  
 [3] This work was conducted in Research Hub for Advanced Nano Characterization, the University of Tokyo, supported under “Nanotechnology Platform” (Project No. 12024046) by the Ministry of Education, Culture, Sports, Science and Technology (MEXT).



**Figure 1.** HAADF-STEM images of (a) rutile TiO<sub>2</sub> along [110] direction, (b, c) Pt evaporated onto TiO<sub>2</sub> for (b) 45 and (c) 1200 s, and (d-f) Pt evaporated onto carbon mesh for (d) 0, (e) 45, and (f) 1200 s.



**Figure 2.** Histogram showing the relative intensity of Pt nanoparticles on different substrates.