

Title	TEM Analysis of Pt-particles Embedded on TiO ₂ Exhibiting High Photocatalytic Activity (STATES NAD STRUCTURES-Crystal Information Analysis)
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Citation	ICR annual report (2000), 6: 6-7
Issue Date	2000-03
URL	http://hdl.handle.net/2433/65247
Right	
Type	Article
Textversion	publisher

TEM Analysis of Pt-particles Embedded on TiO₂ Exhibiting High Photocatalytic Activity

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For fine particles of semiconductive rutile TiO₂ supporting ultra-fine particles of Pt which were prepared by decomposing a colloidal organic-Pt complex, the structural aspects of the high photoactivity were examined by high resolution imaging, X-ray mapping by energy dispersive spectroscopy and electron energy-loss spectroscopy. As a result, the Pt particles with nm-sizes were found to grow epitaxially on rutile, which supports an expected mechanism that the photo-excited electrons efficiently transfer from TiO₂ to Pt and promote the reduction of O₂ to O₂⁻.

Keywords: Decomposing organic-platinum colloid/ Epitaxial growth/ Analytical electron microscopy

A photocatalytic reaction is induced at surfaces of semiconductors being related with the generation of electrons and holes photo-excited by light irradiation. Their high chemical activities cause reduction or oxidation of reaction system. In the photocatalytic effect of the semiconductor, the activity usually increases with increasing surface area, and also it is possible to improve the reaction rate and the selectivity of reaction by changing metal species [1].

The effect of embedding of metal particles is considered to depend on the exchange of the electron or the positive hole at the boundary between the semiconductor surface and metal particle. Recently Komatsu *et al.* have proposed a new method to embed fine metal particles on TiO₂ by decomposing colloidal organic-metal complexes [2]. The enhancement in photocatalytic activity was considered to be due to the increase in numbers of surface

reaction sites, and also the photo-excited electrons transfer mainly from TiO₂ to metal at the surface of ultra-fine particles. However, the boundary structure has not been made clear. Therefore, in the present study, the Pt ultra-fine particles embedded on TiO₂ were studied by transmission electron microscopy (TEM) including high resolution imaging (HR-imaging), elemental mapping by energy-dispersive X-ray spectroscopy and electron energy-loss spectroscopy analyses.

The TiO₂ embedded with ultra-fine particles of Pt was prepared following the decomposing method already reported [2]. HR-images were taken with a high resolution high voltage TEM (HRHVTEM, JEOL ARM-1000) and elemental mapping with characteristic X-ray was carried out with a JEM-2010F scanning transmission electron microscope (STEM) equipped with a field emission gun at 200kV. Electron energy-loss spectroscopy (EELS) and

STATES AND STRUCTURES — Crystal Information Analysis —

Scope of research

Structures of materials and their structural transition associated with chemical reactions are studied through the direct observation of atomic or molecular imaging by high resolution spectro-microscopy. It aims to explore new methods for imaging with high resolution and for obtaining more detailed chemical information. The following subjects are studied: direct structure analysis of ultrafine crystallites and ultrathin films, crystal growth and adsorption states of organic materials, and development on high resolution energy filtered imaging as well as electron energy-loss spectroscopy.



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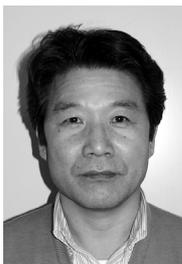
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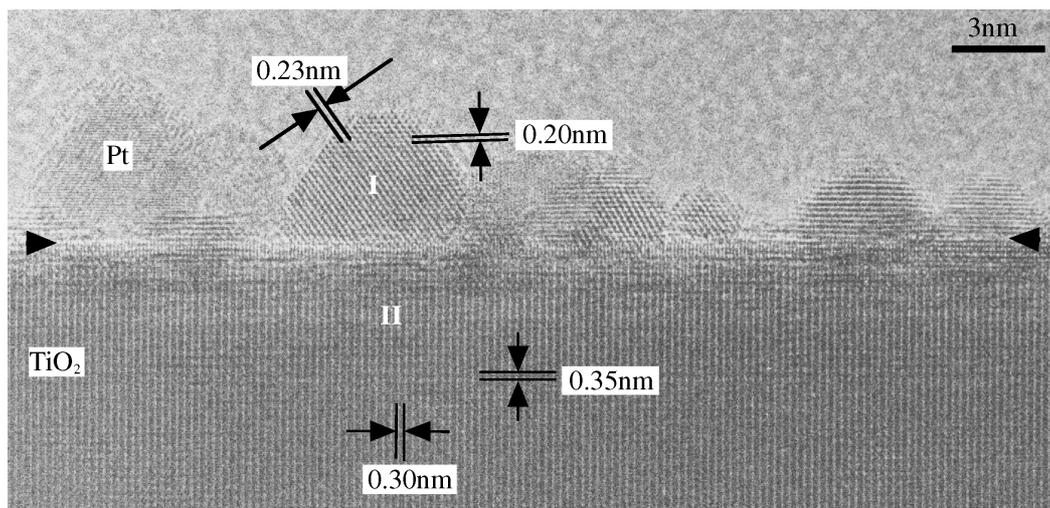


Figure 1. A typical HR-image taken along the $[110]$ of rutile TiO_2 , on which the Pt particles are concluded to grow epitaxially. The (110) -plane surface of TiO_2 is indicated with the horizontal two arrowheads.

energy filtered imaging were carried out with a GIF attached to the HRHVTEM.

From TEM observation, the TiO_2 particles were found to be embedded with smaller Pt particles of about 3nm. The specimen was examined with a STEM, EELS and energy filtered-image with a GIF in HRHVTEM to analyze the elemental distribution in the specimen.

The structure of the boundary between the TiO_2 particle and the embedded Pt particle was observed by HR-imaging (Fig. 1). The image is a projection of rutile TiO_2 along the $[110]$, whose (110) -surface indicated by the two black arrowheads is almost parallel to the incident electron beam. In this case, all observed Pt particles are embedded on the (110) -surface of TiO_2 . In the Pt particles, lattice fringes with the spacings of $d=0.23\text{nm}$ and 0.20nm are observed, which correspond to the (111) - and (002) -spacings of f.c.c. Pt, respectively. Based on the above results, the orientation of the Pt particles in the figure is almost along the $[110]$ -projection of f.c.c. Pt. On the other hand, in the TiO_2 , the lattice fringes of $d=0.30\text{nm}$ and 0.35nm are observed, which correspond to the lattice spacing of (001) - and (110) -planes of rutile TiO_2 , respectively. Consequently, the image of TiO_2 was taken along the $[110]$ -direction of rutile-type structure.

The image of Fig. 1 indicates a specific orientation relation of Pt particles with respect to TiO_2 . In other words, the image was taken as a projection along the $[110]$ of Pt and also along the $[110]$ of TiO_2 . This crystallographic relation is achieved by epitaxial growth of f.c.c. Pt on tetragonal rutile TiO_2 .

Based on the above results, we will discuss here the growth mechanism of Pt on TiO_2 . The epitaxy is usually controlled by lattice misfit at the boundary [3]. The fundamental spacings of $d=0.296\text{nm}$ and $d=0.268\text{nm}$ on TiO_2 (110) are the low-indexed Fourier-components in

the Fourier series of two-dimensional surface potential. Lattice planes of Pt having the similar spacings to 0.296nm and 0.268nm of TiO_2 are the candidates to match with the basic lattice of TiO_2 surface. From the values of misfit, the smallest two cases are selected; (110) of Pt // (001) of TiO_2 and (110) of Pt // $(\bar{1}\bar{1}1)$ of TiO_2 , which may realize the lower interfacial energy due to lower distortion of lattices at the boundary. However, the sign of misfit in the latter case is positive. This designates that the lattice spacing of overlying Pt ultra-fine particle should be compressed at the boundary from that in bulk, but such situation is not favorable. Accordingly, the former case with negative sign of the misfit value may lead to relatively lower interfacial energy than that in the latter case, though the misfit value is slightly larger. Actually observed epitaxial orientation of Pt particles is (110) of Pt // (001) of TiO_2 .

In conclusion, the Pt ultra-fine particles grow epitaxially on TiO_2 surface by decomposing method of colloidal organic Pt complex, which indicates a regular interface between Pt and TiO_2 . Such regular boundary works as a good transfer region for electrons and holes. Consequently the Pt ultra-fine particles contribute to separate distinctly the charges of electrons and holes generated in TiO_2 by light irradiation as well as to enlarge surface area which relates with higher reaction efficiency.

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