Transmission Electron Microscopy Observation of Pt nanoparticles on Graphene Layers at High Temperature

Ayako Hashimoto[1,2,3*], and Masaki Takeguchi[1,2]

[1]Surface Physics and Structure Unit, National Institute for Materials Science, Tsukuba, 305-0003, Japan
[2]Global Research Center for Environment and Energy based on Nanomaterials Science, National Institute for Materials Science, Tsukuba, 305-0047, Japan
[3]Electron Microscopy Station, National Institute for Materials Science, Tsukuba, 305-0003, Japan

Noble-metal catalysts are often used as nanoparticles dispersed on a support material with a high surface area. The size of the catalytic particles is one of the most important factors for efficiencies of catalytic performances and therefore, their downsizing to nanoparticles, clusters and atoms is studied to increase the particle surface area and consequently to improve the catalytic efficiencies. For example, depositions of Pt nanoparticles on graphene layers are investigated for applications to direct methanol fuel cells [1,2]. A graphene layer is one of promising support materials because of its high surface area. In addition, thermal stability is another critical factor for catalytic materials because catalysts are usually reacted at medium and high temperatures. Therefore, the thermal stability of catalytic nanoparticles were investigated by using in-situ and ex-situ transmission electron microscopy (TEM) [3,4]. In this study, we prepared Pt colloidal nanoparticles on graphene layers, and then observed their behavior at high temperature by aberration-corrected TEM, scanning TEM (STEM) and electron energy loss spectroscopy (EELS).

Firstly, we prepared graphene layers by cleaving highly oriented pyrolytic graphite crystals. The graphene layers dispersed in ethanol were dropped onto a thin SiN membrane on a heating specimen holder (Aduro; Protochips, USA). Then, Pt nanocolloids diluted in ethanol were dropped onto the prepared graphene layers. Next, we observed the samples using a TEM/STEM instrument with two aberration correctors (JEM ARM200F; JEOL Ltd., Japan) operating at an accelerating voltage of 200 kV. Recent progress in aberration correction technology made it possible to image a graphene layer with atomic resolution [5,6]. The temperature of the sample was raised to 1000 °C once and then reduced to 800 or 500 °C.

Figure 1 is a TEM image of the Pt nanoparticles dispersed on graphene layers at 800 °C. Before heating, Pt nanoparticles were covered with protective agent and graphene layers were contaminated by solvent and defective carbon. However, heating at high temperature brought removal of carbon compounds. Therefore, clear graphite lattices could be observed by aberration-corrected TEM. The shapes and position of the Pt nanoparticles gradually changed during heating. Furthermore, several single atoms on the terraced graphene layers were observed as dark dots, as shown in Fig. 1. It was expected that the single atoms already existed prior to the TEM observations because the Pt nanoparticles and atoms were considerably stable during the observations, although some of them migrated onto the graphene surfaces. But, it should be noted that the emission of some atoms from the nanoparticles and their subsequent migration onto the graphene surfaces was often observed when an intense electron beam was focused on the nanoparticles.

It was reported from STEM observation that impurity adatoms were detected on graphene layers produced by liquid phase exfoliation of bulk graphite [6]. Therefore, we analyzed such single atoms by STEM and EELS to check whether the atoms are Pt or not. Figure 2 is high angle annular dark field (HAADF) STEM images of atoms on the graphene layers at 500°C. Since it was difficult to detect EELS signals from a single atom, we obtained EELS spectra for Pt M-edge from a nanoparticle emitting atoms. This EELS analysis demonstrated that the nanoparticles emitting such single atoms were Pt. Then, we compared HAADF-STEM images between the atoms emitted from the nanoparticles and the originally existing atoms. The HAADF-STEM contrast of the existing atoms was the same as that of the emitted atoms. It was concluded that the single atoms on the graphene layers were Pt. HAADF-STEM observation showed that single Pt atoms existed stably at

the edges of the terraces of graphene layers. Similar stable Pt atoms were also observed at the edges of graphene holes, as shown in Fig. 1. These results indicated that Pt atoms anchored to the edges of the terraced graphene layers were stationary even at high temperature.

We observed Pt colloidal nanoparticles on heated terraced graphene layers at 500 and 800°C by aberration-corrected TEM. Not only the Pt nanoparticles but also stable single Pt atoms were detected on the graphene layers with atomic resolution. The Pt atoms anchored to the edges of the terraced graphene layers were stationary even at high temperature, while other Pt atoms migrated onto the graphene surfaces. The capability of single atom detection at high temperature with high resolution enables us to understand the interactions between catalytic nanoparticles or atoms, and graphene.

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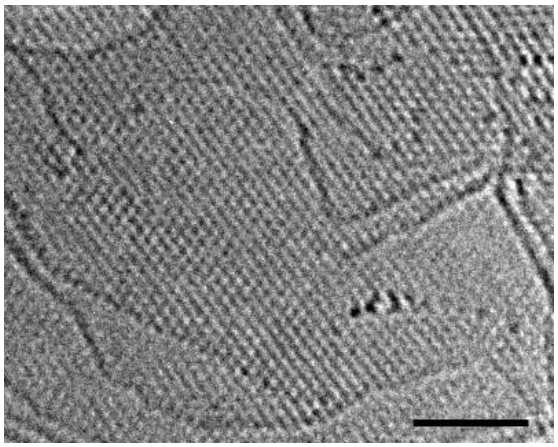

FIG.1 TEM image of Pt-dispersed graphene layers at 800°C. Scale bar is 2 nm.

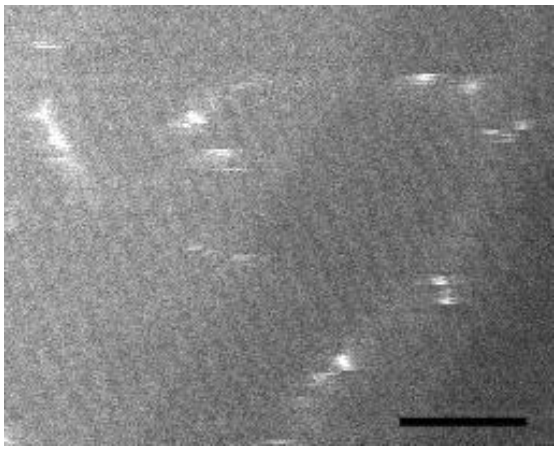

FIG.2 HAADF-STEM image of Pt-dispersed graphene layers at 500°C. Scale bar is 2 nm.