

Arrangement and Dispersion of Rh and Pt Atoms on Graphene Oxide Sheets

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Hybrid materials of ultimately minimized metal particles, namely, isolated atoms or subnano-sized particles, on thermally exfoliated graphene oxide sheets were produced using cation-exchanged highly oxidized graphite as a precursor. Rh atoms on graphene sheets arrange with a regular spacing of 0.50 or 0.45 nm and form square or rectangular grid patterns, whereas isolated Pt atoms disperse on graphene sheets randomly.

Carbon materials supporting metal nanoparticles or metal oxide nanoparticles have been widely used as highly efficient catalysts such as electrocatalysts for fuel cells, catalysts of organic syntheses, and photocatalysts for the degradation of molecules.¹ Recently, graphene materials^{2,3} and graphene-derived materials such as graphene oxide^{4–7} and exfoliated graphene sheets^{8,9} have attracted much attention as metal catalyst supports due to their high theoretical surface area (2630 m² g^{–1}) and low production cost. They can achieve higher catalyst utility than those using conventional porous carbon materials such as activated carbon, carbon black, etc. To date, several graphene-based materials supporting metal or metal oxide have been reported.^{10,11} Generally, metal or metal oxide is dispersed as nanoparticles on carbon surfaces for use as effective catalysts. Nanoparticle surfaces are more active for catalytic reactions than those of bulk metals. Therefore, dispersing smaller particles is an attractive target.

We have previously reported several graphene–metal or –metal oxide composites.^{12,13} The materials, including Pt, Pd, Ru, Au, Ag, Cu, Co, or Ni nanoparticles on graphene sheets, were produced by the simple heat treatment of precursors, which were graphite oxide (GO) cation-exchanged with cationic metal complexes such as amine complex ([Pt(NH₃)₄]²⁺, [Pd(NH₃)₄]²⁺, etc.). High BET specific surface areas (300–700 m² g^{–1} for each composite) and good dispersion of nanoparticles (1–7 nm of the average particle diameter) were achieved by the heat treatment at 200–400 °C. During the heat treatment, it was found to be significant for good exfoliation that sufficient metal complex is exchanged onto GO, because the thermal decomposition of the intercalated metal complex is one of the strong driving forces for exfoliation. Thus, it was limiting the metal content in the derived products. In this letter, we show that a reduced metal complex content in the precursor can still achieve good exfoliation by using highly oxidized GO.

GO was prepared using Brodie's method.¹⁴ 2.0 g of graphite powder (Nippon Graphite Industries, Ltd.) was oxidized in a solution of fuming nitric acid (40 mL) and potassium chlorate (16 g) for 3 h (GO(3)) or 48 h (GO(48)). After drying, the GO(3) or GO(48) (0.10 g) was dispersed into 50 mL of water and treated under ultrasonic irradiation for 15 min. The pH of the

dispersed solution was adjusted at 10.4 by NH₃ solution. [Rh(en)₃]Cl₃·3H₂O (0.10 g) (en: ethylenediamine) synthesized according to a literature method¹⁵ was added to the mixture of GO(3), and stirred for 24 h. The compound obtained by filtering was heated under nitrogen atmosphere for 30 min at 400 °C (Rh-Gr(1)). Similarly, Rh-Gr(2) sample was produced using the same conditions with 0.10 g of GO(48) and 0.02 g of [Rh(en)₃]Cl₃·3H₂O. Sample including Pt was produced by adding [Pt(NH₃)₄]Cl₂·H₂O (0.02 g, Tanaka Precious Metals) into GO(48) at pH 9.5. After stirring and filtering, the compound of metal complex and GO(48) was heated at 400 °C in nitrogen atmosphere (Pt-Gr(1)).

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained for the samples dispersed on a Cu microgrid, which is covered with a carbon-coated porous thin membrane, using a microscope (JEM-2100F; JEOL) with a CEOS CS-corrector for STEM. The accelerating voltage, the probe current, and the probe size were 200 kV, 35 pA, and ca. 0.1 nm, respectively. Extended X-ray absorption fine structure (EXAFS) spectra were obtained using NW10A beamline (6.5 GeV) for Rh, and BL-9C beamline (2.5 GeV) for Pt at the KEK-PF facility (Tsukuba, Japan). The composition of each sample was inspected using thermogravimetry (TG) analysis (MTS9000; Ulvac, Inc.) in air and CHN elemental analyzer (2400 II, Perkin-Elmer).

All samples showed surface areas above 340 m² g^{–1}, which indicates good exfoliation of carbon layers. In previous reports,^{12,13} 0.1 g of metal complex for 0.1 g of GO oxidized for 3 h (GO(3)) was required for each sample to achieve good exfoliation because the thermal decomposition of the complex provides the required driving force for exfoliation. In our present study, only 0.02 g of metal complex was found to be sufficient for good exfoliation when highly oxidized GO (GO(48)) is used. The oxidation for surfaces of each carbon layer results in weaker interlayer interactions and made the exfoliation easier. The amount of metal for each sample was estimated respectively at 15.2, 11.9, and 9.4% for Rh-Gr(1), Rh-Gr(2), and Pt-Gr(1) samples, using TG analysis. The wt% of nitrogen in each sample was 3.2, 2.8, and 1.2% for Rh-Gr(1), Rh-Gr(2), and Pt-Gr(1), respectively, which was much smaller than the estimated content of oxygen.

Figures 1a and 1b display HAADF-STEM images of Rh-Gr(1) and Rh-Gr(2) samples. They clearly show that the sample consists of thin carbon layers, metal nanoparticles (white spheres), and isolated metal atoms (white dots). The sizes and the number of nanoparticles of Rh-Gr(2) (Figure 1b), which was produced using a smaller quantity of Rh and highly oxidized GO (GO(48)) than Rh-Gr(1), is clearly smaller than that of Rh-Gr(1) in Figure 1a. Surprisingly, regularly arrayed Rh atoms in a grid

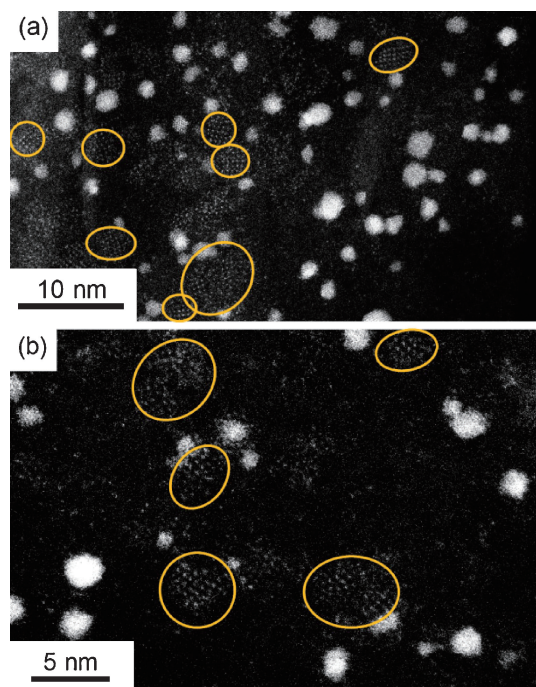


Figure 1. HAADF-STEM images of Rh-Gr(1) (a), and Rh-Gr(2) (b). Rh atoms arrayed regularly in a grid pattern were indicated by yellow circles.

pattern (yellow circles in the Figures) were clearly observed on large areas of the graphene sheets. The structure was stable not only at ambient temperature in air but even after heating at 400 °C in nitrogen gas. The isolated Rh atoms still did not aggregate by the heat treatment at 800 °C, although the structure became disordered (Figure S2a¹⁷). Reduction using hydrogen gas at 400 °C made the Rh atoms aggregate and created Rh nanoparticles on graphene sheets (Figure S2b¹⁷); however, the grid structure of Rh atoms partially remained. Noise-filtered inverse Fourier transform (FT) images for two parts in STEM images of Rh-Gr(2) (Figures 2a and 2b) show clear images of Rh arrangement. The interatomic distances between Rh atoms were estimated along the blue and green lines shown in Figures 2a and 2b, using calibration with a SrTiO₃ crystal. Interestingly, two different arrangements were observed, i.e., a grid of squares with 0.50 ± 0.01 nm distances to nearest neighbor (Figure 2c) and rectangles with 0.50 ± 0.01 and 0.45 ± 0.01 nm distances to neighbor (Figure 2d). The area covered by the former arrangement was much greater than that for the latter.

EXAFS spectrum of Rh-Gr(1) sample is shown in Figure 3a, together with Rh metal and the oxide for comparison. XANES spectrum is also shown in Figure S3a.¹⁷ The EXAFS spectrum (solid line) has two peaks at 0.25 and 0.17 nm, which correspond to Rh metal and Rh₂O₃, respectively. Each state of Rh is attributable to Rh metal nanoparticles and Rh(III) cation or oxide, respectively. Since an isolated Rh(0) atom is unstable in air, the Rh(III) probably correspond to the isolated Rh atoms arranged on graphene sheets that were observed by HAADF-STEM. Estimated coordination numbers (*N*) and interatomic distances (*r*) from the EXAFS spectrum of Rh-Gr(1) are shown

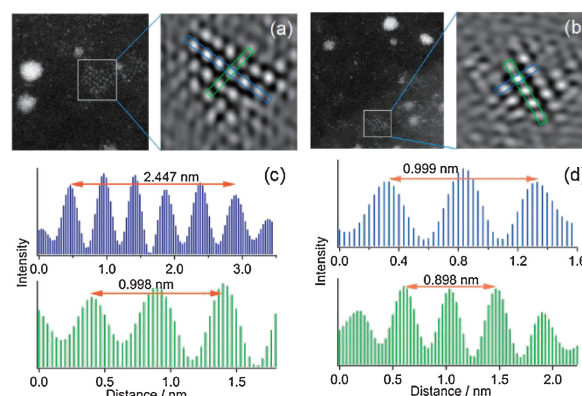


Figure 2. Noise-filtered inverse FT images for two kind of grid patterns of Rh-Gr(2) (a), (b), and intensity along the grid patterns (blue and green) in each image (c), (d).

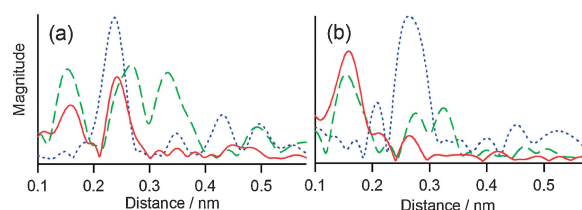


Figure 3. EXAFS spectra of Rh-Gr(1) (red solid line), Rh metal (blue dotted line), Rh₂O₃ (green broken line) (a), and Pt-Gr(1) (red solid line), Pt black (blue dotted line), PtO₂ (green broken line) (b). The scales of distance are in no phase correction.

Table 1. Estimated coordination numbers (*N*), interatomic distances (*r*), and errors (*R*) from EXAFS spectra in Figure 3

	Sample		<i>N</i>	<i>r</i> /nm	<i>R</i> /%
(a)	Rh-Gr(1)	Rh–O	3.0	0.209	1.0
		Rh–Rh	4.3	0.272	1.0
	Rh ₂ O ₃	Rh–O	5.9	0.207	9.5
	Rh-metal	Rh–Rh	11.9	0.271	3.8
(b)	Pt-Gr(1)	Pt–O	2.3	0.195	10.1
		Pt–Pt	1.2	0.264	4.8
	PtO ₂	Pt–O	5.8	0.199	5.7
	Pt-black	Pt–Pt	11.9	0.277	11.0

in Table 1a. The peak at 0.25 nm in EXAFS spectrum is assigned to Rh–Rh bonds because of the coincidence of Rh metal. The *N* of Rh–Rh (4.3), which is much smaller than that of Rh metal (11.9), indicates that the most of rhodium metal atoms are located on the surface of metal particles. On the other hand, the peak for Rh(III) in EXAFS spectrum can be assigned as Rh–O. The *N* of 3.0 for Rh–O is a half of the theoretical coordination number of rhodium(III) oxide. The small *N* number can be explained by coordination of a few oxygen atoms which are on graphene, hydroxy group, and/or water of hydration.

Derived structures of Rh atoms on graphene sheets from the above results are portrayed as models in Figures 4a and 4b. Rh atoms are placed regularly in the model (a). Rh in both models

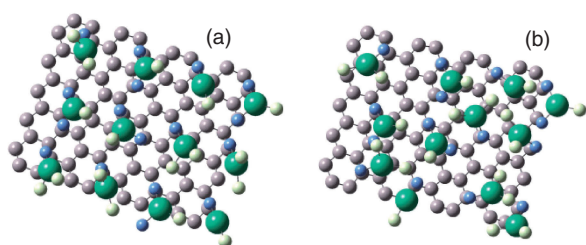


Figure 4. Models of Rh atoms (green sphere) arranged regularly on a partly oxidized graphene sheet (a) and Rh atoms dispersed randomly on a graphene sheet (b). Oxygen atoms on the partly oxidized graphene surface are shown as blue spheres, and oxygen of coordinating water molecules are shown by light green sphere. Hydrogen atoms are not shown in the figure.

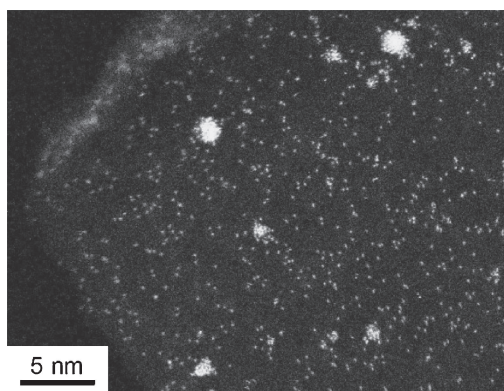


Figure 5. HAADF-STEM image of Pt-Gr(1).

are bonded to one or two oxygen atoms on the partly oxidized graphene surface and coordinated by water molecules. A small part of oxygen atoms can be replaced by nitrogen. The Rh atoms arrange at even intervals to stabilize a surface structure that reflects the underlying graphene structure. These arrangements were disturbed not only by heat treatment at 800 °C but also by an electron beam of HAADF-STEM at high magnification over 10 M (Figure S4¹⁷). Although the arrangement of Rh atoms is basically determined by the surface of graphene oxide, the atoms are not bound strongly, i.e., the structure is flexible. In the model (b) in Figure 4, Rh bonded by one oxygen atom on oxidized graphene easily disperses, and the arranged structure of Rh becomes disordered.

The areas where Rh atoms are observed are unevenly distributed. This can be explained by the distribution of oxidized area of graphene because Rh cation is placed on oxidized graphene surface more easily than on the unoxidized graphene surface. Heat treatment at 800 °C did not reduce Rh cations, but H₂ treatment at 400 °C resulted in Rh atom aggregation into metal nanoparticles (Figure S2b¹⁷). Consequently, the size and distribution of oxidized areas on the graphene sheets affect significantly the dispersion, size, and location of the metal nanoparticles.

Figure 5 shows HAADF-STEM images of Pt-Gr(1) sample. Isolated Pt atoms and small clusters which consist of several Pt atoms by aggregation on graphene sheets are clearly observed.

The average diameter of the clusters is smaller than 1 nm, i.e., the clusters are subnanoscale particles. The diameters of Pt clusters are much smaller than those previously reported for graphene sheets supporting Pt subnanoclusters by Yoo et al.,¹⁶ who also observed both Pt atoms and nanoclusters. EXAFS spectrum of Pt-Gr(1) (solid line in Figure 3b) shows an intense peak at 0.15 nm, which is assignable to Pt bonding to O atoms. A weaker peak at 0.28 nm was also observed, which corresponds well to Pt metal. The coordination number (*N*) of Pt–Pt in Pt-Gr sample estimated from the EXAFS spectrum (Table 1b) is 1.2, which is very much smaller than that for the bulk metal (11.9 for Pt-black). The state of Pt in the clusters is expected to be metal-like; however, the structure is quite different from metal. STEM observation using FT images also displays no lattice structure of Pt metal in small clusters.

Unlike the structure of Rh atoms in Rh-Gr, isolated Pt atoms in each sample do not arrange in a grid pattern or show any regularity. The reason is not clear; however, it may be related to the relative affinities between Pt and graphene or oxidized graphene surface. The minimized Pt or Rh clusters and isolated atoms on graphene are expected to have unique catalyst activities. Further studies to clarify the relation of the Rh-Gr structures to catalytic activities are now in progress.

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