The use of graphite oxide to produce mesoporous carbon supporting Pt, Ru, or Pd nanoparticles

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Abstract

Mesoporous carbon having platinum, ruthenium or palladium nanoparticles on exfoliated graphene sheets were produced from graphite oxide (GO) and metal complexes. The Pt included carbon was made by heating of the intercalation compound including tetraammineplatinum (II) chloride monohydrate. Samples having Ru or Pd are producible by heating in nitrogen gas atmosphere using hexaammineruthenium (III) chloride or

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tetraamminepalladium (II) chloride monohydrate instead of Pt complex. The particle sizes of platinum, ruthenium, and palladium were, respectively, 1–3, 1–2, and 3–7 nm. The platinum- or palladium- containing sample showed catalytic activity for oxygen reduction.

Article

Graphite oxide (GO), a derivative produced from graphite by oxidation in solution, can form various intercalation compounds with cationic molecules because of its functional groups on the surface such as carboxylic acid and hydroxyl group [1]. In recent years, some new porous graphite materials produced from intercalated graphite oxide (GO) by calcination (heating) have been reported: iron oxide pillared graphite having selectivity of gas adsorption [2], a pillared porous carbon produced through pyrolysis of silylated graphite oxide [3], exfoliated graphite oxides with colloidal titania [4], and so on.

On the other hand, nano-size particles of noble metals such as platinum, ruthenium or palladium, which are supported on carbon materials, have attracted much attention for applications such as catalysts and hydrogen storage materials. One known method of metal dispersion consists of the following steps: (i) oxidation of the carbon surface, (ii) adsorption or intercalation of the metal complex by cation exchange, and (iii) deposition of metal through pyrolysis of the complex. For example, some reported catalysts consist of activated carbons or high surface area graphites (HSAGs) supporting Pt [5] or Ru [6] nanoparticles, which were produced using the method above. Recently, Mastalir et al. reported a graphite oxide having Pd nanoparticles, which was not calcined [7]. The material is made by intercalation of palladium complex between GO layers and subsequent reduction by hydrogen gas at 300 K. They reported that Pd nanoparticles supported on the GO sheets have 1–6 nm diameter and that the content of Pd was estimated as 0.18 wt%.

In this letter, we report mesoporous carbon containing ca. 20 wt % of platinum, ruthenium or palladium nanoparticles by pyrolysis of intercalation compound of graphite oxide and metal complexes. Catalytic activity for oxygen reduction reaction (ORR) for the Pt- or Pd-containing samples is also examined.

Graphite oxide (GO) was prepared by oxidation of graphite powder (Wako Pure Chemical Industries, Ltd.) according to Brodie's method [1] using nitric acid and potassium chlorate. The composition of the GO was estimated to $C_8O_{3.6}H_{3.1}$ by elemental analysis. Then, the GO was dispersed into water of pH = 9.5 adjusted using NaOH solution, and treated with ultrasonic irradiation for 15 min. Tetraammineplatinum (II) chloride monohydrate was then added to the solution. The mixture was stirred for 24 h to enable ion exchange. After the reaction, the compounds of Pt complex and GO were heated to temperatures of 473–773 K in air or in nitrogen gas (Pt-GO). Similarly, samples having Ru or Pd were produced by adding hexaammineruthenium (III) chloride or tetraamminepalladium (II) chloride monohydrate into the GO dispersed solution instead of Pt complex (Ru-GO and Pd-GO). These specimens were heated to temperatures of 473–773 K in nitrogen gas because samples heated in air readily combusted. The amount of included metal in each sample was estimated as 18–25% using thermogravimetric (TG) examination in air. The metal loads could be decreased to some extent by changing the degree of oxidation for graphite.

Table 1 portrays BET surface area (P/P_0 =0.3) and average pore width (2V/A, where V is the total pore volume, and A is the surface area) estimated from the following nitrogen adsorption-desorption isotherm measurement of each sample. After heating, the surface area of samples increased remarkably from 5.4 to 349– 515 m^2g^{-1}. For the Pt-GO sample heated in air, the expanded surface area of the sample heated at 473 K had 349 m^2 g^{-1}. Then it decreased with further increasing temperature by combustion of carbon, whereas all samples heated in nitrogen gas showed over 360 m^2 g^{-1}. Nitrogen gas adsorption-desorption isotherms of some Pt-GO, Ru-GO, and Pd-GO samples are shown in Fig. 1. Not only demonstrated samples, but all samples showed little micropore volume and a large hysteresis loop, which is attributable to mesopores in each sample. The samples' average pore widths of 8–15 nm shown in Table 1 were consistent with the hysteresis loops.

Table 1
BET surface areas and average pore widths of calcined samples, graphite and GO.

sample	heating temperature (K)	atmosphere	surface area ($m^2 g^{-1}$)	average pore width (nm)
Graphite	-	-	5.2	-
GO	-	-	5.4	-
Pt-GO	473	air	349	12
Pt-GO	673	air	121	11
Pt-GO	573	N_2	408	12
Pt-GO	673	N_2	405	12
Pt-GO	773	N_2	363	13
Ru-GO	673	N_2	515	15
Pd-GO	673	N_2	508	8

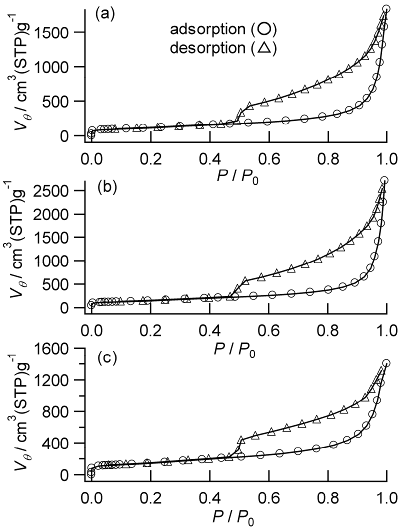

Fig. 1
Nitrogen gas adsorption–desorption isotherms of Pt-GO (a), Ru-GO (b) and Pd-GO (c) samples. The heating temperature and atmosphere of all samples are, respectively, 673 K and nitrogen gas.

Figure 2 shows X-ray diffraction (XRD) patterns of the raw materials and Pt-GO, Ru-GO, and Pd-GO samples. The interlayer distances of 0.66 nm for GO were expanded, respectively, to 0.83, 0.70, and 0.79 nm through intercalation of the Pt, Ru, and Pd complex cations. After heating, the layer structure disappeared and a broad carbon (002) reflection was observed. Strong (111) and (200) reflections of platinum metal were observed for the sample of Pt-GO heated in air. The peaks became stronger with increasing calcination temperature, although samples heated in nitrogen gas showed no reflections of metal. The samples of Ru-GO also showed no reflection of metal. However, the sample of Pd-GO showed broad reflections of Pd metal. The crystallite size of Pd calculated from the peaks using Scherrer's equation was ca. 4 nm. Actually, ca. 40 nm of the estimated crystallite size for the reflections of Pt in Fig. 2a(ii) can be explained by crystal growth of platinum particles through gradual combustion. The peak of Pd metal in Fig. 2c is assignable to larger Pd nanoclusters than to those of either Pt or Ru. The size of metal clusters in each sample observed by TEM is discussed in the following paragraphs.

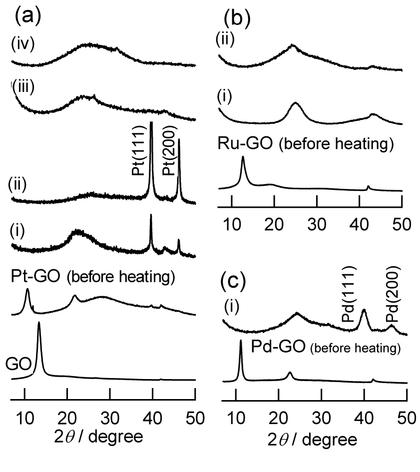

Fig. 2
X-ray diffraction (XRD) patterns of raw materials and heated samples: (a) GO and Pt-GO (before heat treatment), and the latter Pt-GO heated at 573 K (i), 673 K (ii) in air, 573 K (iii), 673 K (iv) in N_2; (b) Ru-GO (before heat treatment) and Ru-GO heated at 573 K (i), 673 K (ii) in N_2; (c) Pd-GO (before heat treatment) and Pd-GO heated at 673 K (i).

Some TEM images of Pt-GO, Ru-GO, and Pd-GO samples are shown in Figs. 3(a)–3(d). All specimens apparently consist of exfoliated graphene sheets; no micropore or mesopore was observed on the carbon surface. Therefore, a mesoporous structure estimated by isotherm measurement is attributable to the nitrogen adsorption in the space between exfoliated graphene sheets. The average pore widths of samples (8–15 nm) are consistent with the interpretation.

Both Pt-GO samples heated in air and in nitrogen gas (Figs. 3(a) and 3(b)) have homogeneous particles of 1–3 nm diameter on the exfoliated graphene sheets and voids of graphene sheets. The particles were produced certainly at the heat temperature greater than 673 K. On the other hand, the Ru-GO sample showed 1–2 nm diameter particles; the particles were deposited clearly, even at 573 K, and the diameters were almost independent of the heating temperature. The Pd-GO sample produced at 673 K had particles of 3–7 nm, which is in good agreement with XRD data. Using Energy-Dispersive X-ray spectroscopy (EDX) analysis, these particles were confirmed to be platinum, ruthenium, and palladium.

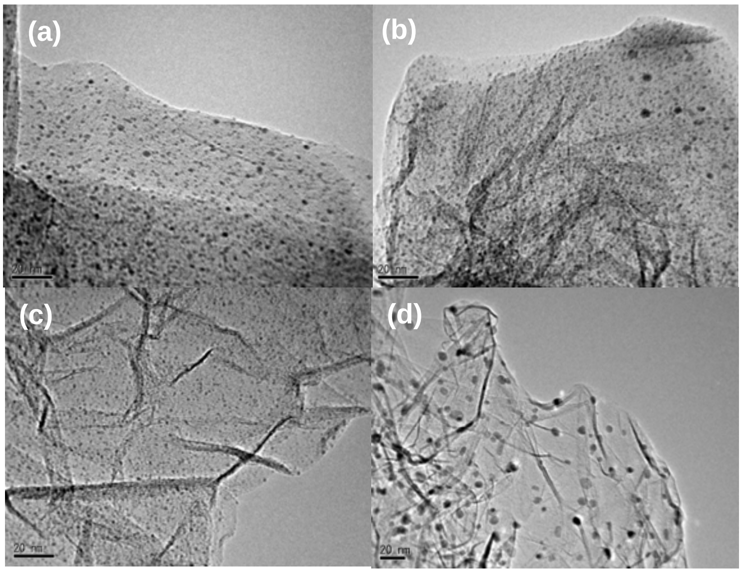

Fig. 3
TEM images of Pt-GO heated at 673 K in air (a), Pt-GO heated at 673 K in N_2 (b), Ru-GO heated at 673 K in N_2 (c), and Pd-GO heated at 673 K in N_2(d). The black scale in each picture shows a length of 20 nm.

Since nanosize of Pt particles supporting on carbon blacks are employed as electrode catalysts in proton exchange membrane fuel cells (PEMFCs) and direct alcohol fuel cells (DAFCs), above GO samples, in particular, Pt-GO and Pd-GO, would possess the catalytic activities for these fuel cell reactions. Then, catalytic activity for ORR of Pt-GO heated at 673 K in air and Pd-GO heated at 673 K in N_2 were investigated using the "rotating disc electrode technique". The sample, highly pure water, and ethanol were mixed at ca. 46.25 mg, 19 dm^3, and 6 dm^3 ,respectively, in a glass vial and then was further mixed ultrasonically in an ice bath. An aliquot of this ink was dropped onto a 5 mm diameter glassy carbon (GC) disc electrode. Here, loading amount of the samples was 17.3 μg cm^{-2} in metal amount per geometric surface area of GC. After evaporation of the solvent, commercially available Nafion® solution diluted with *i*-propanol was dropped onto the electrode surface to fix the Pt-GO or Pd-GO. A glass cell filled with 0.1 mol dm^{-3} $HClO_4$ aqueous solution was used. In addition, Pt mesh and a reversible hydrogen electrode were used, respectively, as a counter electrode and a reference electrode. The disk electrode was dipped carefully into the electrolyte solution and fixed to an electrode rotator. Figure 4 portrays hydrodynamic voltammograms at 900 rpm under an oxygen atmosphere at 298 K. The reduction current attributed to ORR were observed below ca. 0.95 V or 0.84 V vs. RHE, which shows that Pt-GO and Pd-GO are promising electrode catalysts for fuel cells such as proton exchange membrane fuel cells (PEMFCs) and direct alcohol fuel cells (DAFCs). It is well-known that a large part of Pt particles is located inside the carbon supports; therefore, Pt utilization in present fuel cells is low [8]. On the other hand, Pt-GO is anticipated for use to increase Pt utilization because of its unique sheet shape having no micropores. Because we had not measured the amount of hydrogen peroxide produced through ORR, the inherent activity of the Pt-GO was not clarified in this study. Further studies are necessary with regard to its inherent activity as well as its durability.

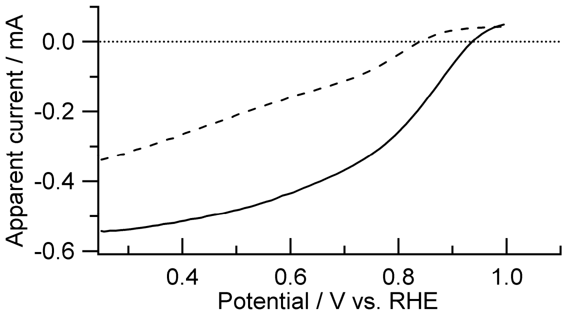

Fig. 4
Hydrodynamic voltammograms at 900 rpm under an oxygen atmosphere of Pt-GO heated at 673 K in air (solid line) and Pd-GO heated at 673 K in N_2 (broken line).

In conclusion, mesoporous carbon having platinum, ruthenium or palladium nanoparticles on the exfoliated graphene sheets was produced from graphite oxide and metal complexes. The mesopores originated from the space between exfoliated graphene sheets. The particle sizes of platinum, ruthenium, and palladium were, respectively, 1–3, 1–2, and 3–7 nm. Although further studies are necessary to clarify the inherent activity and durability, the Pt-GO and Pd-GO show catalytic activity for ORR. Therefore, it is promising for use as a novel electrode catalyst in PEMFCs and DAFCs. Examination of hydrogen adsorption for these samples is now in progress and the results will be reported in the near future.

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