Effect of pH on the Spontaneous Synthesis of Palladium Nanoparticles on Reduced Graphene Oxide

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ABSTRACT

Palladium (Pd) nanoparticles were spontaneously deposited on reduced graphene oxide (rGO) without any external reducing agents. The prepared Pd/rGO composites were then characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Spontaneous deposition occurred because of a redox reaction between the Pd precursor and rGO, which involved reduction of bivalent Pd to metallic Pd⁰ and oxidation of the sp² carbon of rGO to oxygen-containing functional groups. The amount of Pd deposited on rGO varied with pH, and this was attributed to electrostatic interactions between the Pd precursor and rGO based on the results of zeta potential measurements. The importance of the redox reaction in the spontaneous deposition was demonstrated in the experiment with Zn, Ni, Cu, Ag, Pt, Pd, and Au.

Keywords

Reduced Graphene Oxide; Palladium Nanoparticle; Precursor; Redox Potential; Spontaneous Redox Deposition; Zeta Potential

1. Introduction

Graphene, composed of regular sp^2 -bonded hexagonal carbon atoms, has high theoretical surface area ($2630 \text{ m}^2 \cdot \text{g}^{-1}$) and exceptional electrical conductivity ($2000 \text{ S} \cdot \text{cm}^{-1}$) [1–6].

Graphene thus is a promising support for high loading of ultrafine catalyst particles, which may influence the catalytic properties of the metal particles. Recent research on metal/graphene catalysts has focused on a wide range of applications, including fuel cells [6–9], organic catalyst reactions [10–12], and environmental protection [13].

Reductants such as NaBH_4 [14,15] and N_2H_4 [16], or surfactants such as polyvinylpyrrolidone [17,18], are normally required for synthesis of metal/graphene catalysts. The use of these additives often requires multiple steps and makes the synthetic and purification protocols complex. In addition, the reductants pose environmental and health risks, while the surfactants can block the active catalytic sites of the metal. Recently, a facile and environmentally friendly synthesis that required no additional reductants or surfactants was introduced for depositing metals on carbon nanotubes [19]. A similar method has been applied to preparation of carbon-based support materials, including reduced graphene oxide (rGO), and graphene oxide (GO), decorated with metal nanoparticles (NPs) such as Pd, Pt, Ag, and Au [11, 20–28], and this method is referred to as spontaneous redox deposition.

Redox potential is believed to be the driving force behind spontaneous redox deposition of metals on carbon-based support materials [19]. However, most studies have focused on the formation of metal NPs, and transformation of the carbon-based support materials has not been investigated in detail. The transformation of carbon-based support materials, especially rGO, after spontaneous deposition of metals should be carefully examined because changes in the amount of the oxygen-containing functional groups could greatly affect the catalytic activity. In

addition, electrostatic interactions between the metal precursor and rGO are affected by pH, and this could affect the amount of metal deposited. Therefore, the effect of pH on spontaneous redox deposition should also be investigated.

In the present research, spontaneous redox deposition of Pd NPs on rGO in H₂O was investigated systematically with changes in the pH of the Pd precursor solution. Possible oxidation reactions of rGO accompanying reduction of the Pd precursor are discussed.

2. Experimental

2.1 Materials

All chemicals were from commercial sources and used without further purification, including graphite powder (purity >98%; Wako Pure Chemical Industries, Osaka, Japan), sodium nitrate (purity >99%; Wako Pure Chemical Industries), sulfuric acid (purity >95.1%; Wako Pure Chemical Industries), potassium permanganate (purity >99.3%; Kanto Chemical Co., Tokyo, Japan) hydrogen peroxide (purity 30.0–35.5%; Wako Pure Chemical Industries), hydrazine monohydrate, (purity >98.0%; Wako Pure Chemical Industries), and palladium(II) chloride (special grade; Wako Pure Chemical Industries).

2.2 Preparation of rGO

Graphite oxide was prepared from graphite powder by a modified Hummers' method [6,8], briefly, the graphite powder was chemically oxidized to graphite oxide by NaNO₃, KMnO₄ and H₂SO₄. The obtained graphite oxide was dispersed in distilled water at a concentration of 2.0 mg/mL and ultrasonicated for 5 h to form GO sheets. The GO sheets were reduced to rGO using hydrazine hydrate (1 mL for every 100 mL of GO solution). The obtained rGO was washed repeatedly with distilled water to remove any free reagents. Finally, the rGO was dried at 80 °C. The characterization results of rGO are shown in Fig. S1.

2.3 Preparation of Pd NPs on rGO

The rGO (30 mg) was dispersed in 50 mL of H₂O by ultrasonication for 1 h. Separate solutions of PdCl₂ at different concentrations (the prescribed amounts of 5, 10, and 20 wt% compared with rGO) were also prepared in 50 mL of H₂O and strongly agitated for 1 h. The pH values of the PdCl₂ solutions were adjusted to between 1 and 13 using 1 mol/L (or 0.1 mol/L) HCl or 1 mol/L NaOH aqueous solutions. Then, each PdCl₂ precursor solution was mixed with the rGO solution, ultrasonicated 10 min, and agitated on a magnetic stirrer. The prepared Pd/rGO composites were isolated by vacuum filtration using a circulating aspirator (WJ-20, Sibata Scientific Technology, Saitama, Japan) and 0.2- μ m membrane filter papers (Merck Millipore Ltd., Tokyo, Japan), followed by drying at 80 °C in air.

2.4 Characterization

To investigate the surface charge and isoelectric point, the zeta potential of a rGO aqueous colloidal suspension was measured in a capillary cell (750 μ L) using electrophoretic light scattering (Zetasizer Nano ZS, Malvern Instruments, Malvern, UK). An automatic pH titration was performed with 1 mol/L HCl or 1 mol/L NaOH, and the zeta potential, which is related to the mobility of particles in an electric field, was determined using the Smoluchowski equation [29]. Thermogravimetric differential thermal analysis measurements were carried out using a TG/DTA7300 (Seiko Instruments Inc., Chiba, Japan). Measurements were performed with an air flow of 200 mL/min. The temperature range was 25–1000 °C, and the temperature was increased at a rate of 10 °C/min. X-ray diffraction (XRD) measurements were performed on a PANalytical PW 3050 Philips X'pert Pro with Cu K α radiation (1.541 Å). The scan speed was 0.05°/s (at 2θ) up to 90°. A reflection-free Si plate was used as the sample stage. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a JEOL JPS 9010 TR (Japan) with an

Al K α (1486.6 eV) X-ray source and a pass energy of 50 eV. The binding energy was calibrated based on the position of the C1s peak of graphite at 284.6 eV. Transmission electron microscopy (TEM) was carried out using a JEM-2100 at 200 kV. For TEM measurements, each Pd/rGO composite was dispersed in absolute ethanol by ultrasonication and then deposited on a support, which was a carbon film on a copper grid.

3. Results and discussion

TEM images were obtained of rGO and the Pd/rGO prepared at pH 1 with the prescribed amount of 20 wt% (Figs. 1 (a–d)). Curled and folded graphene can be seen in the TEM image of rGO (Fig. 1(a)). After Pd deposition, dark spots emerged on the rGO, and these were attributed to the Pd NPs (Fig. 1 (b–d)). The presence of Pd on the rGO was confirmed by the XPS survey scan of Pd/rGO (Fig. 1 (e) and Fig. S2). The size distribution of Pd NPs on the rGO (Fig. 1(f)) showed that the Pd NPs were on average 3.8 nm in diameter with a narrow size distribution. These results show that Pd NPs were spontaneously deposited on rGO in H₂O.

Fig. 1 (a) TEM image of rGO, (b–d) TEM images and (e) XPS survey scan of Pd/rGO prepared at pH 1 with the prescribed amount of 20 wt%, (f) histogram of the sizes of the Pd particles in the TEM images. $\langle d \rangle$ is the average particle size.

The amounts of Pd deposited on rGO at different pH values were determined by thermogravimetric differential thermal analysis (Fig. S3). Evaluation of the pH dependence of the amount of Pd deposited on rGO (Fig. 2(a)) showed that from pH 2–11 the amounts of Pd deposited on rGO were consistent with the prescribed amounts of Pd (5, 10, and 20 wt%). By contrast, at pH values below 2 and above 11, the amounts of Pd deposited on rGO were lower than the prescribed amounts of Pd. Furthermore, the mean particle size of Pd NPs was calculated using Scherrer equation from XRD patterns for the Pd/rGO composites with the prescribed amount of 20 wt% (Fig.S4). It showed that the mean particle size of Pd NPs is in the range of 33–53 nm from pH 2–11, which it is 27 nm at pH 12.

Fig. 2 (a) pH dependence of the amount of Pd deposited on rGO. The symbols show the amounts of Pd deposited, and the dashed lines show the prescribed amounts of Pd. (b) Changes in the zeta potential (ZP) of rGO with pH.

To clarify the origin of the pH dependence of the amount of Pd deposited on rGO, the zeta potential (net electrokinetic surface charge) of rGO was measured at different pH values. The zeta potential was positive below pH 1.8 and negative above pH 1.8 (Fig. 2(b)). From pH 1.8 to pH 5, the zeta potential decreased rapidly and then became stable above pH 5. The isoelectric point of rGO was 1.8. The zeta potential of rGO is affected by the gain or loss of protons (H^+) by its oxygen-containing functional groups, such as C–O–C or C–OH. When rGO is dispersed in H_2O , its oxygen-containing functional groups will be ionized or hydrolyzed, for example,

In addition, the species present in the aqueous Pd precursor solution will also be affected by pH, and this can be evaluated using equilibrium constants (Table S1 and Fig. S5). In the present study, positively charged species, such as Pd^{2+} and $Pd(OH)^+$, or soluble neutral species, such as $Pd(OH)_2^0$, were dominant below pH 11. Above pH 11, negatively charged $Pd(OH)_3^-$ was

dominant. Therefore, the pH dependence of the amount of Pd deposited on rGO is a combination of the effects on the zeta potential of rGO and the charge of the Pd ion. From pH 2–11, rGO and Pd ion have opposing charges, which results in electrostatic attraction. In this situation, negatively charged oxygen-containing functional groups serve as anchor sites for positively charged Pd ions, such as Pd^{2+} or $\text{Pd}(\text{OH})^+$, which leads to efficient adsorption of Pd ions onto rGO. However, when the pH is below 2 or above 11, rGO and Pd ions in the precursor carry charges of the same sign; that is, positive charges below pH 2 and negative charges above pH 11. This leads to electrostatic repulsion and means Pd ions cannot be efficiently adsorbed on rGO. It should be noted that small quantities of Pd (5 wt%) were deposited on the rGO at pH values below 2 and above 11. This probably occurred because a small number of species with opposite charges will be present on the rGO surface even when the net charge is positive ($\text{pH} < 2$) or negative ($\text{pH} > 11$). In any case, these results clearly show that the initial step of the spontaneous deposition is adsorption of Pd ions onto the charged oxygen-containing functional groups of rGO.

The XRD patterns of the Pd/rGOs prepared at different pH values with the prescribed amounts of 20 wt% are shown in Fig. 3(a). Formation of metallic Pd NPs on the rGO from pH 2–11 was shown by the presence of the following XRD peaks: Pd(111) at 40.1° , Pd(200) at 46.7° , Pd(220) at 68.1° , and Pd(311) at 82.1° (PDF # 00-005-0681). The lack of metallic Pd peaks for Pd/rGO at pH 1, and the weak peaks observed at pH 12 and 13 were attributed to the small amounts of Pd deposited on rGO (Fig. 2(a)). Although Pd peaks were not detected in the XRD pattern for Pd/rGO at pH 1, the deposition of Pd was observed in TEM images and the XPS survey scan (Fig. 1). The formation of metallic Pd NPs on rGO indicates that the bivalent Pd species were reduced to metallic Pd^0 even without any external reducing agent in H_2O .

Fig. 3 (a) XRD patterns and (b) C1s XPS spectra for the Pd/rGOs prepared at different pH values with the prescribed amount of 20 wt%, and rGO. Positions of metallic Pd peaks are marked with inverted triangles in the XRD patterns.

The results of our experiments suggested that rGO itself was the reducing agent for bivalent Pd. To verify this, the chemical state of Pd/rGO was examined by XPS. Figure. 3(b) shows C1s spectra of Pd/rGO prepared at different pH values. The C1s peaks were assigned as graphitic carbon (sp^2 , 284.6 eV), C–O (286.2 eV), epoxy carbon (C–O–C, 287.9 eV), and carbonyl carbon (C=O, 289.8 eV) [30–36]. Compared with the C1s spectrum of rGO, all of the prepared Pd/rGOs

showed less intense graphitic carbon peaks and more intense C1s peaks at binding energies above 286 eV. This implies that rGO was oxidized during the spontaneous deposition of Pd NPs. Deconvolution of the C1s XPS spectra (Fig. S6) showed that the increase for C–O was much larger than that for C–O–C or C=O. Therefore, the spontaneous deposition of Pd on rGO is suggested to occur through a redox reaction that involves reduction of the bivalent Pd precursor and oxidation of the rGO.

To confirm that the deposition occurred via a redox reaction, the amounts of oxygen and Pd were estimated (Fig. 4(a)) based on the XPS peak areas and taking into consideration atomic sensitivity. The amounts of oxygen and Pd increased with increasing pH up to pH 7, and then decreased above pH 7. This indicates that the concentration of oxygen species in rGO corresponds to the amount of Pd deposited.

Fig. 4 (a) Amount (at.%) of O1s and Pd3d and (b) $O_{increased (inc.)}/Pd$ relative ratio ($O_{inc.}$ means the increased oxygen amount of rGO by Pd deposition, Supporting Information) of the Pd/rGO composites with the prescribed amount of 20 wt%.

The relative ratio of $O_{inc.}/Pd$ was between one and two at most pH values (Fig. 4(b)). This indicates that when one Pd atom was deposited on the surface of rGO, one or two oxygen atoms

formed in the rGO. In the redox reaction, the oxidation of rGO releases electrons, which are used in the reduction of the Pd precursor as follows: $\text{Pd}^{2+} + 2\text{e}^- \rightarrow \text{Pd}^0$. Possible oxidation reactions of rGO are shown below.

In these reactions, protons (H^+) are released, which decreases the pH. Indeed, when the rGO aqueous colloidal suspension was mixed with the Pd precursor, the pH decreased (Fig. S7).

Generally, a redox reaction involves transfer of electrons from one substance to another, and its spontaneity can be determined from the redox potentials. For a spontaneous redox reaction, the redox potential of the cathodic reaction should be higher than that of the anodic reaction. For Pd/rGO, the standard reduction potential of $\text{Pd}^{2+}/\text{Pd}^0$ (0.92 V vs. the standard hydrogen electrode (SHE) [37]) is higher than that of GO/rGO (0.25 V [25] or 0.38 V [23] vs. the SHE).

Accordingly, the rGO/ Pd^{2+} system undergoes spontaneous oxidation and reduction in H_2O without any external reducing agent, as observed in these experiments.

As described above, the spontaneous redox deposition involved two important steps, which were approach of the metal precursor to rGO, and the redox reaction. The approach of metal precursor to rGO was greatly affected by pH. Thus the amount of Pd deposited on rGO was affected by the pH. The spontaneity of NP formation was governed by the redox potential. Table 1 shows the standard reduction potentials vs the SHE for several metal precursors and rGO. These potentials suggest that Zn, Ni, and Cu could not be spontaneously deposited on rGO, while Au, Pd, Pt, and Ag could be spontaneously deposited on rGO via a redox reaction. To verify this, we conducted a spontaneous redox deposition experiment with Zn, Ni, Cu, Pt, and Pd by mixing

the precursor solution including each metal with the rGO aqueous colloidal suspension without any external reducing agents. The results are summarized in Fig. S8. Compared with the amounts of Pt and Pd deposited on rGO, little Zn, Ni, or Cu was detected on rGO.

Table 1 Standard reduction potentials vs the SHE at 298 K.

Half-reaction	E°/V	Metal deposition ^a
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76 [38]	N
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23 [38]	N
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.34 [38]	N
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80 [38]	Y [22,27]
$\text{PtCl}_4^{2-} + 2\text{e}^- \rightarrow \text{Pt} + 4\text{Cl}^-$	0.76 [37]	Y
$\text{Pd}^{2+} + 2\text{e}^- \rightarrow \text{Pd}$	0.92 [37]	Y
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.40 [38]	Y [23,27]

^a N indicates that no spontaneous redox deposition on rGO occurred, and Y indicates that spontaneous redox deposition on rGO occurred.

4. Conclusions

In summary, metallic Pd NPs were spontaneously deposited on rGO in H₂O without any reducing agents. The amount of Pd deposited on rGO was dependent on the pH. Spontaneous redox deposition involved the following two pivotal processes: first, the approach of Pd ions to rGO, which was electrokinetically controlled by the pH of the aqueous solution; and second, a redox reaction for reducing the bivalent Pd precursor and oxidation of rGO. The amount of Pd NPs deposited on rGO was determined by the electrostatic interaction between the Pd precursor and rGO. The spontaneity was determined by the redox potential difference between the Pd precursor and rGO. The importance of the redox reaction in the spontaneous deposition was demonstrated in the experiment with Zn, Ni, Cu, Ag, Pt, Pd, and Au.

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Supporting Information. Characterization of rGO, XPS survey scan of Pd/rGO, TG curves of Pd/rGO, pH dependence of the mean particle size of Pd NPs, Effect of pH on the species present in the PdCl₂ precursor solution, Deconvolution of the C1s XPS spectra, Calculation of the of $O_{\text{increased (inc.)}}/Pd$ relative ratio, Changes in the pH during spontaneous redox deposition of Pd on rGO, and Investigation of the deposition of multiple metals on rGO.

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