Controlled Deposition of Iridium Oxide Nanoparticles on Graphene

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ABSTRACT

For hydrogen production by water electrolyzers, iridium dioxide (IrO2) works as a catalyst for oxygen evolution reaction (OER) at an anode. In this report, we aim to study the formation mechanism of IrO2 nanoparticles on graphene by inducing nanoscale defects artificially. The defects on graphene grown on a copper foil by chemical vapor deposition were created by UV-ozone treatment, and IrO2 nanoparticles were deposited by hydrothermal synthesis method. We investigated the amount of defects and oxygen-functional groups on graphene by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The size and distribution of defects and IrO2 nanoparticles on graphene were analyzed by atomic force microscopy (AFM). Raman spectroscopy and XPS measurement showed that defects and oxygen-functional groups increased with the UV-ozone treatment time. The size of IrO2 nanoparticles was reduced to ca. 4.5 nm on defective graphene, whereas the nanoparticles deposited on pristine graphene is ca. 8.8 nm in diameter. It is found that the IrO2 nanoparticles were deposited and anchored on the edge of hole-like defects on graphene. In addition, the size of deposited nanoparticles can be controlled by the extent of modification in graphene.

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Keywords : Water Electrolysis, Iridium Oxide Nanoparticles, Defect Induced Graphene, Atomic Force Microscope

1. Introduction

Recently, renewable energy sources has been introduced into society to handle environmental issues, especially global warming. However, in regard to renewable energy sources such as solar cells and wind-powered electricity, the regulation of energy supply is not enough to meet commercial high demand. To overcome the issue, improving technology of energy conversion is necessary to store and transport the energy effectively.1,2 A possible candidate of the energy storage techniques is hydrogen production by water electrolysis, including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).3,4 Water electrolysis is one of the processes for generating hydrogen molecules, where water splitting takes place by application of a potential, and oxygen is generated at anode while hydrogen is produced at cathode. IrO2 and Pt are commonly used as anode and cathode catalysts, respectively.5,6 To improve performance and cost of a commercially available water electrolyzer, high over-potential of OER and high cost of catalysts, in particular, for IrO2 anode, are critical issues in a cell with acidic electrolyte or proton exchange membrane.7–10 A great amount of efforts have been invested to develop catalysts for further improvement of water electrolysis efficiency.5,7–10

Recently, nanocarbon materials such as reduced graphene oxide (RGO) and carbon nanotubes (CNTs) have been focused as supporting materials to increase catalytic activity of IrO2 by the formation of nanoparticles.11–13 Nanocarbon materials are common support materials for electrocatalysts, especially in fuel cells,14,15 because of their significant properties, such as high electric conductivity, high surface area, high chemical stability, and facileeness of structural modification on a nanoscale.16 The most popular preparation method to obtain RGO is thermal, hydrothermal, or chemical reduction of graphene oxide (GO), which is prepared from graphite by chemical exfoliation, for example Hummers’ method.17–20 RGO possesses a lot of oxygen-functional groups, such as C-O, C=O, COOH, and C-OH.20 The oxygen-functional groups are expected to work as nucleation and anchoring sites for nanoparticles,21 resulting in homogeneous dispersion of deposited catalyst nanoparticles. As is well known for fuel cell catalysts, high activity can be achieved by adjusting the catalyst particle size and loading amount of the homogeneously dispersed catalysts.22–24 Inhomogeneous dispersion of catalysts accelerates agglomeration of catalyst particles and suppresses efficient diffusion of reactant. A previous report on density functional theory (DFT) study claimed that the size of metal nanoparticles, related to its specific surface area, depends on the type or density of defects in carbon-based supporting materials.25 The behavior of metal (Pt and Pd) nanoparticle deposition was also reported on an atomic scale on highly oriented pyrolytic graphite or glassy carbon supports as a model substrate.26–28 However, effect of nanocarbon or practical carbonaceous supporting materials on the formation of nanoparticles is still unclear, because carbon supports contain a large amount of defects, and to identify the type of defects on a nanoscale is difficult from the point of view of controlling carbonaceous material characteristics and limited observation methods with atomic resolution. In addition, effect of functional groups of carbons on the deposition process of metal oxide such as IrO2 is not fully understood.

In this study, in order to clarify the behavior of nano-sized IrO2 particle deposition on nanocarbon materials, we employed a large size single crystal graphene prepared by chemical vapor deposition (CVD) as a model carbon substrate. The surface of the CVD graphene was modified with defects or vacancies introduced by UV-
precursor solution was dropped on the graphene transferred on the SiO2/Si substrate, and then the sample was dried on a hot plate at 80 °C. The Ir precursor-deposited graphene on the SiO2/Si substrate was moved into a Teflon lined autoclave with a mixture of ethanol and water (9:1) and heated at 150 °C for 4 h (hydrothermal method). During these processes, IrO2 nanoparticles were deposited on graphene.12,13 The obtained sample was washed and dried overnight at room temperature. The deposited amount of Ir was controlled by adjusting the drop amount of precursor solution.

2.3 Characterization of samples

Crystallinity of graphene was confirmed by Raman spectroscopy (InVia Raman Microscope, Renishaw plc.) equipped with a 532 nm excitation laser. A 50× magnification objective, a Peltier-cooled CCD camera, and an 1800-line mm⁻¹ grating were utilized for Raman spectroscopy. Graphene surface morphology and the size of IrO2 nanoparticles were observed by atomic force microscopy (AFM, Multi-Mode 8, Bruker Co.) in a peak force tapping mode. The size of the nanoparticles is measured by AFM software. Elemental and chemical properties of the prepared samples were analyzed by scanning electron microscopy (SEM, SU3500, Hitachi High Technologies Co.) with energy dispersive X-ray spectroscopy (EDX, EMAX Evolution X-Max, Horiba) and X-ray photoelectron spectroscopy (XPS, PHIS000 Versa Probe II, ULVAC-PHI) with Al Kα radiation (1486.6 eV).

3. Results and Discussion

Figure 2(a) shows Raman spectra of the prepared graphene on the SiO2/Si substrate (Fig. S3 of the SI) with various periods of UV-ozone treatment. After the UV-ozone treatment, three peaks of D, G, and G’ were observed on the Raman spectra of graphene, whereas only G and G’ peaks were obtained on the pristine graphene. G peak derived from Eg₂ vibration of sp² C–C bond appears at 1585 cm⁻¹, and D-peak due to A₁g breathing of sp² C–C activated by defects is observed at 1343 cm⁻¹. G’ peak at 2685 cm⁻¹ is characteristic of second-order Raman process involving two iTO phonon scattering.27,28 The Raman spectra show increasing D peak intensity with time of the UV-ozone treatment, indicating that defects were introduced in graphene by oxidation with ozone. Figure 2(b) shows the plot of the relationship between UV-ozone treatment time (ozone exposure time) and the intensity ratio of G and D bands (I_G/I_D ratio), which was calculated from the Raman spectra shown in Fig. 2(a). I_G/I_D ratio is used to represent the density of defects on graphene to know the crystallinity of graphene. The value of the I_G/I_D ratio decreased with the extending UV-ozone treatment period. The result indicates that crystallinity of graphene was degraded by UV-ozone treatment. The degradation could occur by reaction of carbon atoms with ozone molecules. Theoretically, ozone molecules produced in the UV-ozone generator react with graphene to generate vacancies and oxygen-containing functional groups, which break weaker sp² bond in graphene, whereas Ar ion bombardment forms vacancies without formation of additional oxygen-function groups around defects.35 Our results confirm that the amount of defects in the CVD graphene can be controlled by the time of UV-ozone treatment.

Before deposition of IrO2 nanoparticles, we evaluated the morphology of the defects formed on graphene by AFM on a nano scale. Figure 3 shows AFM images of graphene surface before and after UV-ozone treatment with various exposure time, 1 to 5 min. In Fig. 3(a), a curved step line of 0.97 nm in height, corresponding to monoatomic height of flat-laid graphene layer on SiO2 surface,36 was observed in the upper part of the AFM image. We conclude that the step line is the edge of the CVD graphene. The bright terrace area is CVD graphene, and the dark area in the upper part of the image is SiO2 surface. The bright line-shaped structure on graphene are wrinkles of graphene caused during the transfer process.

Figure 1. Schematic images of processes for preparing IrO2 nanoparticles deposited on defective CVD graphene on SiO2/Si substrate. (a) Single layer graphene prepared on Cu foil by CVD. (b) CVD graphene transferred on SiO2/Si substrate. (c) Defects-introduced graphene by UV-ozone treatment. (d) IrO2 nanoparticles deposition on graphene prepared by hydrothermal reaction.

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small spots observed on an AFM image, which are 4 to 8 nm in height, are impurities adsorbed on the surface during the transfer of the graphene from Cu foil to SiO2/Si substrate, such as the residues of PMMA or small carbon particles. Figures 3(b)–(e) are enlarged images of the white dot frame in Fig. 3(a) and were obtained at almost the same area. After UV-ozone treatment, small holes were formed on graphene as dark spots. During UV-ozone treatment, ozone molecules oxidize carbon atoms in the graphene lattice and remove them as a CO or CO2 gas molecules, creating holes in graphene. An average depth of the holes estimated from cross-section analysis (Fig. S4 of the SI) of the AFM images is ca. 1.0 nm, similar to the height of graphene edge, and the value of holes depth was unchanged even after UV-ozone treatment time, implying that the present CVD graphene is monolayer and the SiO2 substrate is exposed in the hole regions. Figure 4 shows the size and density of the holes as a function of UV-ozone treatment time. The hole size became larger up to 800 nm2 with increasing UV-ozone treatment time, whereas the density decreases after 1 min of the UV-ozone treatment because of merging neighboring holes. In comparison with Raman spectroscopy shown in Fig. 2, the defects were clearly observed on the graphene, whereas the intensity of D band peak is small for the graphene with 1 min UV-ozone treatment. Although the condition of UV-ozone treatment is same, it is difficult to correlate them directly, because the sample for AFM measurement are not identical to those for Raman spectroscopy. However, overall tendency is correct and reproducible. Although the D peak intensity is small after 1 min treatment, D band intensity increases as compared with the pristine graphene (Fig. 3(b)). In Fig. 3(c), it is clear that the number of bright particles (PMMA residues) are

**Figure 2.** (a) Raman spectra of graphene exposed to ozone with various time. (b) I_G/I_D ratio as a function of exposure time estimated from Raman spectra in Fig. 2(a).

**Figure 3.** (a) A large-scale AFM image of pristine graphene and magnified AFM images of the synthesized CVD graphene (dotted box) exposed to ozone with various time, (b) 0, (c) 1, (d) 3, and (e) 5 min, obtained at the same area.

**Figure 4.** Plots of average area size of holes (blue circle) and density of defects on graphene formed by ozone treatment (red triangle) as a function of exposure time.
Comparison. However, we did not obtain \( \text{IrO}_2 \) nanoparticles on \( \text{SiO}_2 \) without graphene by the same procedure as described above, as a result of defective graphene surfaces. We also confirm that the nanoparticles are \( \text{IrO}_2 \) because the size of the particles on the graphene are \( \text{IrO}_2 \) because the size of the particles on the graphene lattice and form defective graphene.

Figure 5 shows AFM images of graphene surface after \( \text{IrO}_2 \) deposition by the hydrothermal synthesis method. No hole or defect structure was observed on the pristine graphene, which is placed inside the dashed frame in Fig. 5(a). The result means that graphene was not damaged physically during the hydrothermal treatment process for \( \text{IrO}_2 \) deposition. The white dots in the AFM image are \( \text{IrO}_2 \) nanoparticles formed on graphene, and the size of the nanoparticles is \( \sim 8.8 \) nm. Furthermore, we cannot observe the residue of impurities on the graphene surface, because the impurities were removed during hydrothermal reaction of \( \text{IrO}_2 \) deposition. The composition and formation of \( \text{IrO}_2 \) nanoparticles was also confirmed by SEM-EDX (Fig. S5 of the SI), where Ir elements were dispersed sparsely on the graphene surface, while \( \text{IrO}_2 \) nanoparticles cannot be observed clearly because of low resolution of SEM. Only a few \( \text{IrO}_2 \) nanoparticles were observed on the pristine graphene, and the number of the \( \text{IrO}_2 \) nanoparticles on pristine graphene is less than that on the UV-ozone treated graphene. The low density of the \( \text{IrO}_2 \) nanoparticles is consistent with low defects on the pristine graphene.

On the other hand, a large number of holes and nanoparticles were distributed on the UV-treated graphene surface, as shown in Figs. 5(b)–(d), in which a whole area shows graphene surface. The average size of deposited \( \text{IrO}_2 \) nanoparticles was \( \sim 4.5 \) nm on all defective graphene surfaces. We also confirm that the nanoparticles on the graphene are \( \text{IrO}_2 \) because the size of the particles on the AFM images is smaller than that observed on defective graphene, 4 to 8 nm in height, before \( \text{IrO}_2 \) deposition. Furthermore, it is noted that \( \text{IrO}_2 \) nanoparticles were located along holes on the defective graphene, indicating that the edge of holes can anchor the particles as well as a nucleation site for the \( \text{IrO}_2 \) nanoparticles. It is noteworthy that we attempted to deposit \( \text{IrO}_2 \) on \( \text{SiO}_2/\text{Si} \) substrate without graphene by the same procedure as described above, as a comparison. However, we did not obtain \( \text{IrO}_2 \) nanoparticles on \( \text{SiO}_2 \) surface because iridium precursor or iridium oxide diffused into or migrated onto \( \text{SiO}_2 \) surface, resulting in formation of agglomerates. Then, the agglomerated \( \text{IrO}_2 \) particles were removed during washing the \( \text{SiO}_2/\text{Si} \) substrate with ultrapure water to remove residues.

Table 1 summarizes the size of defects, the density of defects, and deposited nanoparticles on graphene with various periods of UV-ozone treatment. The values in Table 1 reveal that the density of the deposited \( \text{IrO}_2 \) nanoparticles increases with the density of defects. The AFM observation suggests that the edge of the holes serves a critical role to form and distribute the \( \text{IrO}_2 \) nanoparticles. A comparison among the three graphene with the UV-ozone treatment specifies that the distribution of \( \text{IrO}_2 \) nanoparticles became worse with increasing the UV-ozone treatment time, because the size of the holes increased and the number of holes decreased with the UV-ozone treatment period. In other words, the distribution of holes decreased with the UV-ozone treatment period. Comparing \( \text{IrO}_2 \) nanoparticles deposited on the graphene with and without the UV-ozone treatment, that size of the \( \text{IrO}_2 \) nanoparticles became half after the UV-ozone treatment, and as a tendency, the size decreased with increasing the time of UV-ozone treatment. However, after 1 min of UV-ozone treatment, the size of the \( \text{IrO}_2 \) nanoparticle did not change significantly.

To discuss an essential factor deciding the size of the \( \text{IrO}_2 \) nanoparticles, we calculated the total circumference of holes on graphene from size and density of holes. Figure 6(a) shows the relationship between the size of the \( \text{IrO}_2 \) nanoparticle and the circumference of holes. Figure 6(b) also shows the relationship between the size of the \( \text{IrO}_2 \) nanoparticles and the concentration of oxygen-functional groups such as ketone (C=O) and carboxyl (COOH) groups on graphene, estimated by XPS analysis of the graphene surface (Fig. S6 of the SI) before the \( \text{IrO}_2 \) particles deposition. Figure 6(a) indicates that the total edge length of holes on graphene has almost same value as on the defective graphene. The result implies that the ability to anchor nanoparticles along holes is the same on all the defective graphene, resulting in similar average size of the \( \text{IrO}_2 \) nanoparticles. On the other hand, the concentration of oxygen-functional groups on graphene was increased with the increasing time of UV-ozone treatment, as shown in Fig. 6(b). In spite of the fact that oxygen-functional groups are counted on anchoring and sticking the nanoparticles on carbon supports, the additional effect on the \( \text{IrO}_2 \) nanoparticles could not be determined in this research. We assume that the oxygen-functional groups on graphene were reduced under hydrothermal reaction condition, and the amount of functional groups became similar under \( \text{IrO}_2 \) deposition process despite different UV-ozone treatment period. In future, in situ analysis of reaction materials during hydrothermal reaction is required to understand the effect of oxygen-functional groups on metal nanoparticle deposition.

**Table 1.** The area size and density of defects on CVD graphene introduced by various period of UV-ozone treatment, and the density of deposited \( \text{IrO}_2 \) nanoparticles on the defective graphene.

| UV-ozone treatment (min) | Average defect size (nm²) | Density of defects (µm⁻²) | Density of nanoparticles (µm⁻²) |
|------------------------|--------------------------|----------------------------|-------------------------------|
| 1                      | 1.8 × 10²                | 1.1 × 10⁴                  | 5.9 × 10²                     |
| 3                      | 7.9 × 10²                | 5.3 × 10³                  | 2.1 × 10²                     |
| 5                      | 8.0 × 10²                | 4.7 × 10³                  | 2.3 × 10²                     |
found that as the amount of defects increased, the size of the IrO$_2$ nanoparticles decreased. In addition, the number of IrO$_2$ nanoparticles was proportional to the density of vacancy holes. The irradiation of UV light and photochemically-induced ozone treatment results suggest that the vacancies created by UV-ozone treatment molecules oxidized the graphene surface and formed holy structures. This work was supported by Strategic Research Foundation of Private Universities and JSPS KAKENHI Grant Number 17K05969 from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT). This work was also supported by JST-CREST Grant Number JPMMCR1875, Japan.

References

4. Conclusion

In this study, we demonstrate CVD graphene as a model support material for IrO$_2$ nanoparticles, and succeed to investigate the effect of defects in graphene sheets on formation of the IrO$_2$ nanoparticles. The irradiation of UV light and photochemically-induced oxygen molecules oxidized the graphene surface and formed holy structures on graphene. The diligent AFM analysis reveals the morphology change of graphene and deposited IrO$_2$ particles on a nanoscale. It is found that as the amount of defects increases, the size of the IrO$_2$ nanoparticles decreased. In addition, the number of IrO$_2$ nanoparticles was proportional to the density of vacancy holes. The results suggest that the vacancies created by UV-ozone treatment work as nucleation sites for IrO$_2$ nanoparticles. Here, we propose controlling the density and concentration, properly on nano-carbon supports such as graphene, by UV-ozone treatment to improve the catalytic activity of metal nanoparticles deposited on the nanocarbons. Though some phenomena such as the role of oxygen-functional groups still remain obscure, appropriate modification of support carbons on a nano level will encourage development of supported catalysts with exceptional activity.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-64075.

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Figure 6. Average particle size of IrO$_2$ nanoparticles and (a) estimated total edge length of defect holes calculated from AFM images of defective graphene, and (b) ratio of oxygen-functional groups formed on graphene obtained by XPS analysis.

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