Preparation of Polycrystalline Pt Nanosheets Using Graphene Oxide Template and Evaluation of Their Catalytic Performance for PEFC

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Abstract: Nanosheets composed of polycrystalline Pt metal could be prepared using graphene oxide (GO) as templates. Furthermore, the particle size of Pt species stabilized on the GO could be reduced by addition of oleylamine as a capping agent, which resulted in the preparation of thinner polycrystalline Pt nanosheets. Electrochemically active surface area of Pt nanosheets prepared in the presence of oleylamine was twice as large as that of Pt nanosheets. Additionally, Pt nanosheets prepared in the presence of oleylamine had a higher ECSA than Pt black commercially available.

Keywords: Pt nanosheets, Graphene Oxide, Template

1. Introduction

Pt has been utilized as an active component of the catalysts in chemical industry since Pt metal shows high activity for various reactions, for example, the purification of exhaust gas from automobiles and the oxygen reduction reaction (ORR) at cathode in polymer electrolyte fuel cells (PEFCs). However, Pt metal is expensive. Thus, the amount of Pt metal in the catalysts should be reduced as much as possible. One method for the reduction of Pt amount in the catalysts is to develop catalysts with nanoscaled structures. The preparation of nanoscaled Pt catalysts contributes not only to a high activity due to high specific surface areas but also to unique catalytic performance based on the nano-scaled structures such as nanosheets. The nanosheets have high surface areas and the diffusion of reactant molecules on the Pt nanosheets is easier than that on Pt metal particles supported in porous supports. However, few preparation methods for the Pt nanosheets have been reported so far [1].

We have prepared metal oxide nanosheets such as TiO_2 and ZrO_2 using graphene oxide (GO) as templates [2]. In this study, we tried to prepared Pt metal nanosheets using GO as templates. The structure of Pt nanosheets and their electrochemical activity and durability were examined.

2. Experimental

Pt species were densely deposited on GO surface by impregnation of GO into ethanol containing Pt(II) acetylacetonate ($Pt(acac)_2$) during UV irradiation at room temperature. The sample thus obtained was calcined in air for the removal of GO to form Pt nanosheets. The sample thus obtained is denoted as Pt NS. Particle size of Pt species on the GO could be reduced by addition of oleylamine as a capping agent for the preparation of thinner Pt nanosheets. Oleylamine was added to the suspension containing GO and $Pt(acac)_2$ under UV irradiation. The sample thus obtained is denoted as Pt NS(OA).

To clarify the structure of Pt nanosheets, we used atomic force microscopy (AFM) and transmission electron microscopy (TEM). In addition, we measured cyclic voltammetry (CV) in N_2-purged 0.1 M $HClO_4$ in order to clarify the electrocatalytic performance of Pt nanosheets.

3. Results and discussion

Figure 1 shows TEM images of Pt NS and Pt NS(OA). TEM images for the samples before the removal of GO template were shown in Fig. 1a, b, d and e. Materials with a sheet structure could be observed in the TEM images for both the samples. Many particles of Pt(II) with ca. 1 nm in diameter were densely stabilized in the Pt NS before the calcination. In contrast, any particles could not be found in the TEM images for Pt NS(OA) before calcination, although Pt of 30 wt % was supported on GO. This means that very small Pt(II) particles are densely deposited on GO in the Pt NS (OA) before calcination. As shown in Figure 1c and f, a sheet structure was maintained for both the samples, in spite of the removal of GO. In addition, electron diffraction patterns for these sheet materials showed the formation of polycrystalline Pt metal. Thus, polycrystalline Pt metal nanosheets could be prepared by the removal of GO from the samples shown in Fig. 1b and e. In this preparation method, Pt(II) particles can be stabilized with high density on GO, and Pt metal nanosheets are formed after the removal of GO by combustion. The thickness of Pt NS and Pt NS(OA) was evaluated with AFM. The AFM images also showed the formation of two-dimensional materials for both the samples. The thickness for Pt NS and Pt NS(OA) was evaluated to 5 and 2 nm, respectively. Thus, the thickness of Pt nanosheets could be controlled by the size of Pt(II) particles deposited on GO.

Figure 2 showed CVs for Pt NS, Pt NS(OA) and Pt black commercially available in N_2-purged 0.1 M $HClO_4$. CVs for all the samples are very similar one another, indicating that Pt metal surface is exposed for all the samples. However, the peak current is strongly dependent on the types of the samples. Peak current in the range of 0.05 to 0.4 V, which is due to the adsorption and desorption of hydrogen on Pt, is higher for the Pt NS(OA) than that for Pt NS. This suggests that Pt NS(OA) is thinner than Pt NS. Based on these CVs, we evaluated the electrochemically active surface area (ECSA) of these samples. ECSA was evaluated to be 11, 19 and 9 m^2/g-Pt and Pt NS, Pt NS(OA) and Pt black, respectively. Therefore, the Pt NS(OA) should show the highest activity for the catalytic reaction such as oxygen reduction reaction among all the samples tested in the present study.

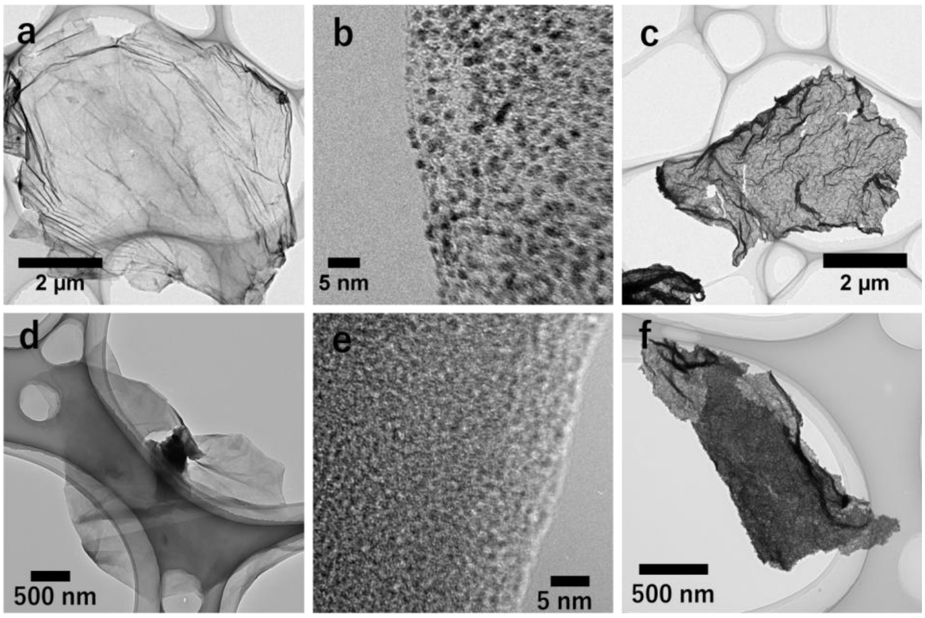

Figure 1. TEM images of Pt NS and Pt NS(OA).

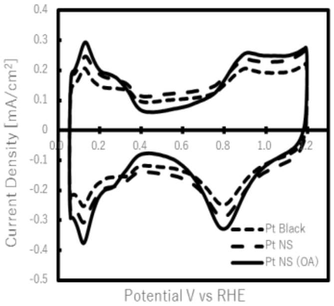

Figure 2. CV for Pt black, Pt NS and Pt NS(OA).

4. Conclusions

In conclusion, polycrystalline Pt nanosheets were prepared using graphene oxide as templates. Additionally, the thickness of polycrystalline Pt nanosheets could be controlled by the addition of oleylamine as a capping agent for Pt(II) particles deposited on GO. The Pt nanosheets showed high activity for the electro-catalytic reactions.

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References

1. F. Sallem, B. Xu, B. Ni, H. Liu, F. Nosheen, H. Li, X. Wang, Adv. Mater. 27 (2015) 2013.
2. S. Takenaka, S. Miyake, S. Uwai, H. Matsune, M. Kishida, J. Phys. Chem. C 119 (2015) 12445.