Preparation of Photoreduced Precise Platinum Nanoparticle

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1. Introduction

Platinum is used as the catalyst for many important reactions, for example, fuel cells [1]. However, the supply of platinum on earth is limited, so it is very important that we use platinum very effectively. On the other hand, metal nanoparticles have higher catalytic activity than bulk metals. The reason is that metal nanoparticles have much larger surface areas than bulk materials. In addition, some metal nanoparticles show “size effect,” meaning a special function depending on their sizes. Based on these factors, the establishment of a synthesis method for precise platinum nanoparticles has been desired for a long time.

Recently, it was reported that the dendrimer is a good template for the synthesis of metal nanoparticles [2]. This synthesis method is as follows. First, the dendrimers complex with metal salts. Second, the dendrimer-metal complexes are reduced. (Metal ions are reduced to metal(0).) By using this method, the size of the metal nanoparticle depends on the amount of metal ions which complexed with the dendrimer. In addition, the “shell effect” of the dendrimer prevents aggregation among the metal nanoparticles. Therefore, precise metal nanoparticles were synthesized. In a general way, the reduction method is a chemical reduction, for example, using NaBH₄. However, the method has some demerits, i.e., the need for elimination of any by-product (salt) and being able to be carried out only in the liquid phase. In this respect, photoreduction is very useful method. By using photoreduction, no by-product is produced and it is carried out in the solid phase in addition to the liquid phase.

In this report, we describe preparation of photoreduced precise platinum nanoparticles by using the tetraphenylmethane core fourth generation phenylazomethine dendrimer (Fig.1), which can precisely assemble many kinds of metal salts [3-7], as a template in the solid phase.

Fig. 1 Structure of the phenylazomethine dendrimer.

2. Experimental

The tetraphenylmethane core phenylazomethine dendrimer was synthesized by a convergent method following a literature procedure [8]. PtCl₄, dehydrated solvents (acetonitrile and chloroform), and other compounds were purchased from Kanto Kagaku Co., Ltd., and used as received.

The XPS spectra were obtained using a JEOL JPS-9000MC with MgKα radiation. The binding energy of electrons in the spectra was referenced to the Au 4f⁷/₂ (83.8 eV) peak of the substrate. TEM images were taken using a TECNAI F20 (200keV). Cu grids with carbon substrata were purchased from Oken Shoji, Inc. The photoirradiation was carried out using a Hg-Xe lamp (3000W).
3. Results and Discussion

The UV irradiation of platinum chloride(\(\text{PtCl}_2\)) in the solid phase was carried out. However, the product was not Pt(0) particles, but Pt(\(\text{Pt}^{+}\)) compounds. This was confirmed by XPS measurement. (It is shown in Fig. 2(b).) Therefore, the next UV irradiation was carried out in a methanol atmosphere. As a result, the Pt 4f peak shifted to the value of Pt(0) and no chlorine peak was found. (This is shown in Fig. 2(c)). It showed that the Pt salt was reduced to Pt metal and chlorine evaporated as a gas. It was confirmed by XPS measurement that not only platinum chloride(\(\text{PtCl}_2\)), but also the phenylazomethine dendrimer-platinum chloride(\(\text{PtCl}_2\)) complex was reduced to Pt(0) under the same conditions.

Fig. 2 XPS spectra change of PtCl\(_4\) (a) before and after photoirradiation (b) without methanol and (c) with methanol

TEM observations were then carried out. The size of the platinum particles, which were synthesized by using the phenylazomethine dendrimer template, was 1.17 ± 0.28 nm. The size was very small and the size distribution is nearly monodisperse. On the other hand, the size of the platinum particles and the size distribution are larger. Therefore, we concluded that the phenylazomethine dendrimer is a useful template for the preparation of platinum nanoparticles by photoreduction.

To confirm the catalytic activity for oxygen reduction, cyclic voltammetry measurements were carried out. The working electrode (GCE) was modified with the dendrimer-PtCl\(_4\) complex and then photoirradiation was carried out. Cyclic voltammograms of the modified electrode in H\(_2\)SO\(_4\) solution showed a distinct cathodic current increase around 0.45 V vs Ag/AgCl under an O\(_2\) atmosphere, whereas it disappeared under N\(_2\) atmosphere. With a bare GCE, no current increase appeared in the O\(_2\) atmosphere. These results indicated that the very small platinum nanoparticles synthesized by photoreduction with the dendrimer template have a catalytic activity for the oxygen reduction reaction.

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References