

XAFS Study on the Formation Process of PDDA-protected Pd Nanoparticles by Photo-irradiation

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Introduction

It is well known that metal nanoparticles have the advantages of not only their high surface areas but their unique properties depending on their size, which are different from those of bulk metal solids. Especially, Pd nanoparticles have attracted much attention due to their various catalytic properties. To utilize their catalysis, simple synthesis methods to form mono-dispersed small Pd nanoparticles are required. Usually, colloidal Pd nanoparticles are prepared by reduction of Pd ions in the presence of stabilizing agents. Although chemical reduction and thermal reduction are common and convenient methods, strong reducing agents and high reaction temperature make it difficult to control the reducing rate and the formation of larger particles are inevitable. Some kinds of reducing agents such as amine and ethylene glycol can compose their polymers, which work stabilizing agents as well. By using those kinds of polymers as both reducing and stabilizing agents, the reaction temperature can be lowered. Poly(diallyl dimethylammonium) chloride (PDDA) as shown in figure 1 is a quaternary ammonium polyelectrolyte and it is expected to be both reducing and stabilizing agent. In this study, we tried to develop a simple method to produce Pd nanoparticles at room temperature. Aqueous solution of Pd ions was photo-irradiated in the presence of PDDA. Pd K-edge XAFS spectra were measured before and after photo-irradiation to the Pd solution. The reducing ability and reactivity of PDDA to Pd ions were discussed.

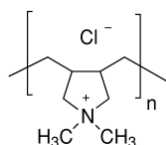


Figure 1. The molecular structure of PDDA.

Experimental

PdCl₂ and PDDA (20 wt% in water, Mw=200000-350000) were dissolved in water under vigorous stirring for 2 h. The mixed solution was irradiated by a high-pressure Hg lamp at room temperature for 12 h.

The Pd solution was placed in a tube of the length of 80 mm with two PMMA windows on both sides of the optical path. PdCl₂ was pressed into a self-supporting disk. Pd K-edge XAFS spectra were measured at NW10A with Si (311) double crystal monochromator in a transmission mode. The XAFS spectra were analyzed by the curve-fitting method with program REX2000 (Rigaku Co.).

Results and discussion

Figure 2 (A) shows the XANES spectra. Profile and edge energy of the spectrum for the Pd solution after photo-irradiation (a) are close to those for the Pd foil (d), while those for the Pd solution before photo-irradiation (b) are close to those for the PdCl₂ (c). The results indicate that the Pd ions are reduced to the Pd particles by photo-irradiation in the presence of PDDA. It corresponds with the results of TEM observations, which are the presence of about 10 nm of Pd nanoparticles. As shown in Figure 2 (B), however only a small peak is obtained at 0.23-0.28 nm, which is the same position of Pd-Pd bond of Pd foil. It is found that a part of Pd ions are reduced. The inverse FT of a main peak at 0.15-0.22 nm for the Pd solution before photo-irradiation (b) was well fitted to PdCl₂. The coordination number and distance of Pd-Cl bonding for the Pd solution before photo-irradiation are 4.0 and 0.23 nm, respectively. It can be said that the reactivity of PDDA to Pd ions is low since PDDA-Pd complexes were not formed.

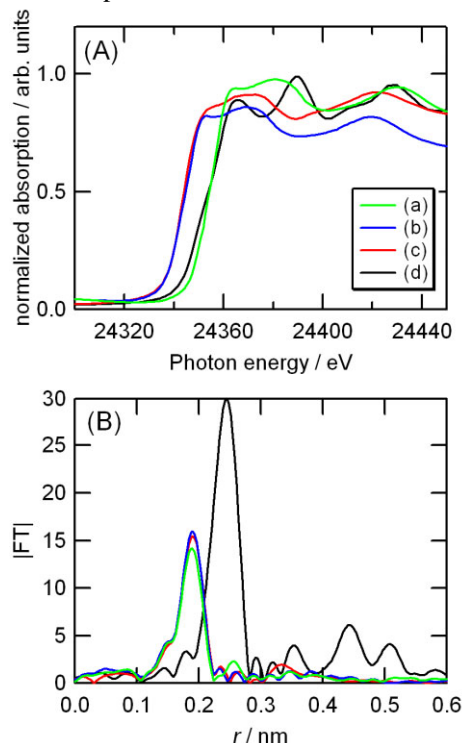


Figure 2. (A) Pd K-edge XANES spectra and (B) FT of Pd K-edge EXAFS spectra for Pd solution (a) after and (b) before photo-irradiation, (c) PdCl₂, and (d) Pd foil.

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