Formation of Palladium(0) Nanoparticles from a Microemulsion System Composed of Bis (*N*-octylethylenediamine)palladium(II) Chloride Complex

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Palladium(0) nanoparticles were obtained in high densities from a novel type reverse micelle (or W/O microemulsion) of bis(*N*-octylethylenediamine)palladium(II) chloride (=[Pd(oct-en)$_2$]Cl$_2$)/water/chloroform (=CHCl$_3$). The shape of the nanoparticles was largely affected by the phase of the additive, sodium boron hydride (=NaBH$_4$) reductant, and by the replacement of a small amount of water with methanol.

Noble metal nanoparticles are very useful as catalysts, electronic devices, and so on because of their large surface areas and of the characteristic conductivities; thus it is an important subject to relate their shapes and size-distributions with the conditions of the formation reaction. One of the popular method to prepare uniform-sized noble metal nanoparticles is a reduction of metal ions being dissolved as simple salts in reverse micelles composed of conventional surfactants, such as aerosol OT (=AOT),[1,2] trioctylphosphine oxide,[3] and tetraalkylammonium ion.[3,4] An amount of simple metal salts dissolved in water pools of such surfactants is, however, severely limited (mmol kg^{-1} order concentration in organic solvent) and the yield of the metal nanoparticles is very low for the amount of organic solvent used. The alkanethiolate-protected palladium nanoparticles have also been studied and the mean size and its deviation have been related to the changes in the reaction conditions.[5] In these studies hitherto reported, the change in the morphologies of the original micellar solutions by the water content has not been related with the shapes and the sizes of the metal nanoparticles.

One (M.I.) of the present authors with coworkers has, on the other hand, studied extensive formation of reverse micelles and microemulsions composed of bis(oct-en)metal(II) complexes. These systems have characteristic features that the metal ions are highly condensed in the mesoscopic water pools and a variety of the morphologies of the aggregation systems are dependent on the water content and the complex concentrations.[6–9]

In the present study, we have attempted to prepare palladium(0) nanoparticles from the aggregation systems of [Pd(oct-en)$_2$]Cl$_2$ and to relate the shapes of the palladium(0) nanoparticles with the structures of the original solutions.

The synthesis of the complex and the purification of the solvents were performed as previous reported.[8] A specimen for the transmission electron microscopy (TEM) was prepared by spreading a small drop of around 100 times dilute sol onto a standard copper grid (coated with a thin silicate glass) and letting the drop dry completely in air. The particle size and shape were observed at room temperature on a Hitachi H-7000 electron microscope operating at 100 kV. The size distribution for the relatively spherical systems was derived from histograms for about 200 particles. The structure of the microemulsion has also been observed on a Hitachi H-800 electron microscope using a freeze-fracture method replica. Details of the procedure have been previously reported.[9] NaBH$_4$ was added as a solid state or as a 1 mol kg^{-1} aqueous solution.

The palladium nanoparticles were formed by the following procedures. Relatively uniform-sized particles were obtained from 0.025 or 0.05 mol kg^{-1} [Pd(oct-en)$_2$]Cl$_2$ in CHCl$_3$ solution at [H$_2$O]/[[Pd(oct-en)$_2$]Cl$_2$] (=W_0) =7.6. Under this condition, twice moles of free oct-en ligands for the Pd complex were added to stabilize the reverse micelles. At $W_0 > 20$, we have prepared the microemulsion systems composed of [Pd(oct-en)$_2$]Cl$_2$/water/CHCl$_3$ without cosurfactant according to the phase diagram previously reported.[8] For these solutions, NaBH$_4$ crystal was added 5 times mole of the palladium complex, and then the solution was rigorously shaken for 30 min. After the excess amount of NaBH$_4$ crystal was filtered off, dark yellowish sol was obtained. The sols were diluted with about 50 and 100 times volume CHCl$_3$ for the original solutions below and above 0.1 mol kg^{-1}, respectively.

The structures of the original aggregation system of 0.5 mol kg^{-1} [Pd(oct-en)$_2$]Cl$_2$ in CHCl$_3$ at $W_0 = 50$ were at first measured on the basis of a freeze-fracture method of TEM. (Figure 1) This picture shows an onset of the bicontinuous structure. At $W_0 < 10$, the structure of the aggregates is surely a droplet-type reverse micelle as previously reported in the Zn(oct-en)$_2$Cl$_2$/water/benzene system.[9]

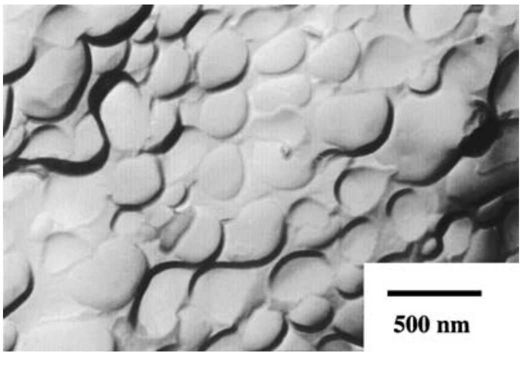

Figure 1. Cryo-TEM photograph for the microemulsions of [Pd(oct-en)$_2$]Cl$_2$/water/CHCl$_3$. [[Pd(oct-en)$_2$]Cl$_2$] = 0.50 mol kg^{-1} in CHCl$_3$, $W_0 = 50$.

As [Pd(oct-en)$_2$]Cl$_2$ in CHCl$_3$ can absorb large amounts of water, if we added aqueous NaBH$_4$ solutions and shake the water/CHCl$_3$ phase, the W_0 value of the solution should be significantly increased in the lower W_0 range and the exact water content in the aggregation system could not de determined. Therefore, it was appropriate to synthesize the uniform-sized Pd(0) nanoparticles with an addition of $NaBH_4$ as a solid state in the lower W_0 range.

Figures 2(a)–(d) are the TEM photographs for the palladium particles and their size distributions in (a) and (b). In the (a) system, the palladium particles are relatively uniform-sized and the sizes are smaller. The result of Figure 2(b) suggests that the spherical domains of the W/O microemulsions are still present even when the structures of larger domains are close to the bicontinuous phase at $W_0 = 50$ and at larger palladium concentration. The size and its deviation are somewhat larger compared to those at $W_0 = 7.6$, where the water pool is a droplet type. It is coincided with a previous result that the metal particles become smaller at lower original metal concentrations.[10] The significant changes in the particle sizes and deviation were, however, not detected here. On the other hand, when $NaBH_4$ was added as an aqueous solution to the same microemulsion system, the palladium particles tend to link each other to form a network domain as shown in Figure 2(c). In this case, the structure of the bicontinuous phase was more clearly reflected in the shape of the nanoparticles. The effect of the reductant phase on the particle shape was remarkable.

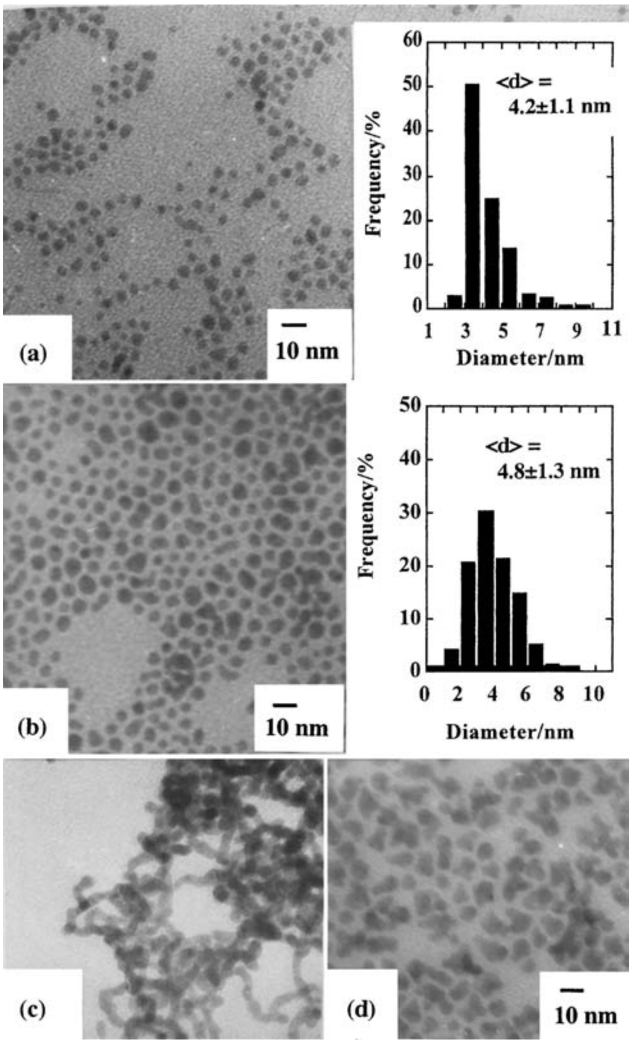

Figure 2. TEM photograph for the Pd(0) nanoparticles of $[Pd(oct\text{-}en)_2]Cl_2/water/CHCl_3$. In the (c) case, $NaBH_4$ was added as the aqueous solution, while in the other cases, it was added as the crystal. The components of the original microemulsions are as follows. (a) $[[Pd(oct\text{-}en)_2]Cl_2]=0.05\,mol\,kg^{-1}$, $[oct\text{-}en]=0.1\,mol\,kg^{-1}$, $W_0 = 7.6$. (b) $[[Pd(oct\text{-}en)_2]Cl_2]=0.50\,mol\,kg^{-1}$, $W_0 = 50$. (c) $[[Pd(oct\text{-}en)_2]Cl_2]=0.50\,mol\,kg^{-1}$, $W_0 = 50$. (d) $[Pd(oct\text{-}en)_2]Cl_2/CH_3OH/CHCl_3$ system. $[[Pd(oct\text{-}en)_2]Cl_2]=0.50\,mol\,kg^{-1}$ in $CHCl_3$, $[CH_3OH]/[[Pd(oct\text{-}en)_2]Cl_2]=10$.

A single phase of $[Pd(oct\text{-}en)_2]Cl_2$ in $CHCl_3$ can also be obtained with an addition of a small amount of methanol. The structure of the reverse micelle is, however, expected to be destroyed with an addition of methanol. Figure 2(d) is the result of the palladium nanoparticles obtained from the $[Pd(oct\text{-}en)_2]Cl_2/methanol/CHCl_3$ system. We can see that the shape of the palladium particles is significantly deformed from the spheres. This photograph indicates that the palladium headgroup irregularly assembles in the original micellar solutions even in the methanol domains and the palladium particles are surely protected by the oct-en ligand.

The present system has the following two characteristic features. Firstly, the highly condensed palladium nanoparticles were obtained by using the novel type double-chain palladium complex. This result is attributed to the high concentrations of the palladium(II) ions in the water domains of the present aggregation systems. Secondly, the structures of the aggregates of the original palladium complex surfactants were directly reflected in the shapes of the palladium nanoparticles because of the palladium being located in the head group of the original metal complex surfactant. In the alkylethylenediamine system, the palladium complex surfactant acts as both a metal ion provider and a metal-particle stabilizer: it is a rare case. As the alkylethylenediamine has a capability to form metal complexes with various transition metals, this method will be universally applicable to obtain metal nanoparticles in high yield.

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