CHEMISTRY LETTERS, pp. 1925-1928, 1992.

Preparation of Organosol of Noble Metal Clusters with Novel Method

Naoki TOSHIMA* and Hanfan LIU*†
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

The organosols of noble metal clusters such as monometallic Pt, Pd, and Rh clusters, and bimetallic Au/Pd, Pd/Pt, and Pt/Rh clusters in organic media like butanol were prepared by reversible transfer of the cluster particles from an aqueous phase to the organic phase by using a coordination capture technique with triphenylphosphosphine. The electronic spectra and transmission electron micrographs of the dispersed clusters before and after the transfer indicate that no change occurs in size and size distribution during the transfer.

Metal colloids or metal clusters are interested in academia and industries from a viewpoint of the bridge between the atom and the bulk metal.[1-3] Not only interest in the physicochemical properties of metal colloids has been ongoing since the time of Faraday, but also current efforts focus on a number of different area and applications. One is the area of catalysis, in which the special activity of the metal colloids or clusters is emphasized.[4,5] Additional studies have been also examined for applications as biological stains and ferrofluids.[6] On the fundamental level, the issue of "quantum size effect" is an actively debated topics, with a number of experimental approaches currently being utilized.[7]

Metal colloids or clusters can be usually prepared in an aqueous phase. We have been prepared colloidal dispersions of a lot kinds of noble metal clusters by reduction of the corresponding metal ions under mild conditions in the presence of water-soluble polymers or surfactants in water or alcohol/water.[4,5] They have advantages in high dispersity, small particle size, and narrow size distribution. However, it is not so easy to prepare pure organosols, dispersions of the metal clusters in pure organic

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†JSPS Fellow, 1991-1992. Present address: Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

solvents. The successful method to prepare the organosols involves the deposition of metal atoms into organic solvents at low temperature,[8] the decomposition of the soluble metal complexes in organic solvents,[9] and the reduction of metal ions solubilized in organic solvents by using reverse micelle.[10]

Recently a large metal complex cluster has been extensively prepared. Some of them, such as $Au_{55}(PPh_3)_{12}Cl_6$, were reported to be solubilized into water by ligand exchange with water-soluble ligands such as sodium diphenylphosphinobenzenesulfonate (DPPS).[11] We have also succeeded to immobilize noble metal colloids or metal clusters onto inorganic supports by ligand exchange using phosphine and/or sulfur ligands.[12,13] These successes encourage us to prepare the metal colloids or clusters in organic phase by the ligand exchange. Here we would like to report the preparation of organosols by the transfer of the metal clusters from an aqueous phase to an organic phase by the ligand exchange technique.

An aqueous dispersion of platinum clusters protected by poly(N-vinyl-2-pyrrolidone) (PVP) was prepared by dispersing the dry solid of the PVP-protected clusters into water after reduction of hexachloroplatinic acid in refluxing ethanol/water by the previously reported method.[14] The concentrations of the platinum and PVP in monomer unit were 1.0 and 4.0 mmol dm^{-3}, respectively. The same volume (20 cm^3) of a toluene solution of triphenylphosphine (15.3 mmol dm^{-3}) was added to the brown black aqueous dispersion of the platinum clusters, and the mixtures were shaken vigorously for 5 min by hand. Centrifuging the mixtures for a while made both upper toluene and lower aqueous phases clear, giving the black platinum cluster flocculate in the interface between the toluene and the aqueous phase. Both clear phases were carefully removed from the vessel by small pipette, leaving the flocculated platinum clusters, which were then washed with 5 cm^3 of dry acetone several times. After removal of the acetone, the clusters were examined to be dispersed into various organic solvents.

When butanol was used as the dispersion medium, the dry clusters were dispersed in butanol by using an ultrasonic generator. The dispersion can be easily achieved even by shaking by hand. Similar phenomenon was observed in octanol and decanol. In contrast, the dispersion cannot be achieved in pure toluene. However, addition of 10 %(v/v) of butanol to the toluene made the dispersion possible. The colloidal dispersion of the platinum clusters in the organic solvent prepared by the present method is quite stable and no change was observed when the dispersion was kept at room temperature under air for months.

The particle size and the size distribution of the platinum clusters

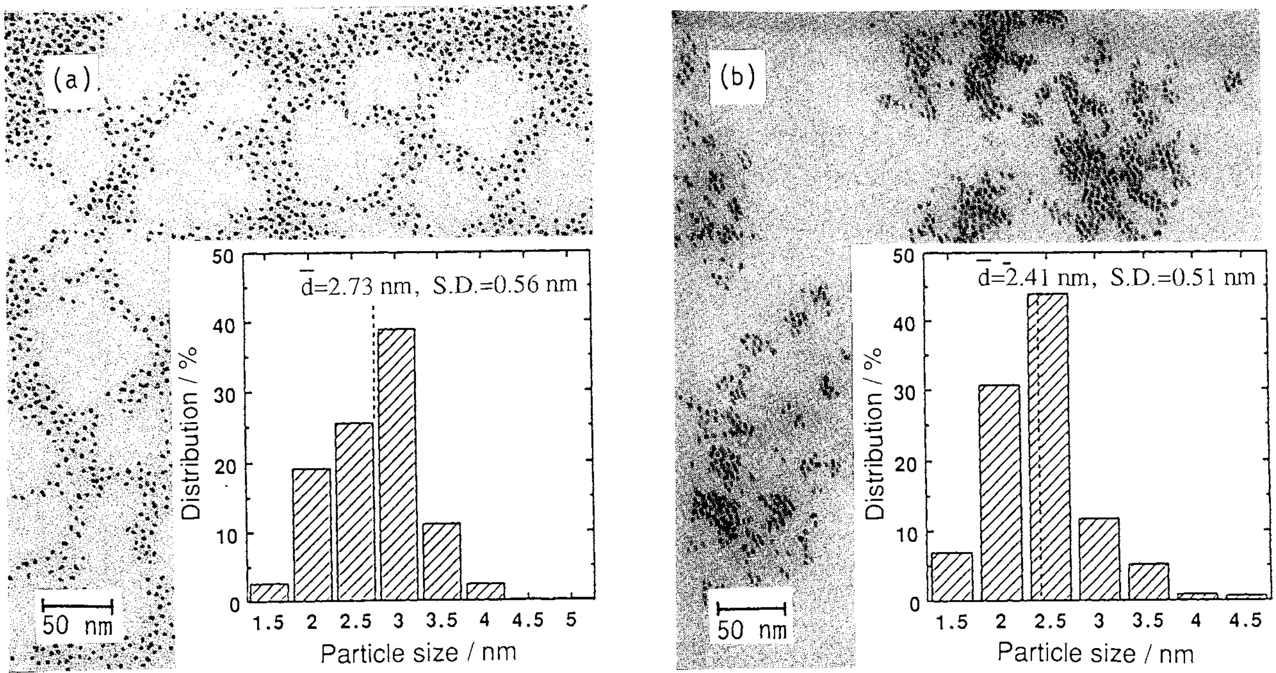

Fig. 1. TEM photographs of (a) original Pt clusters in water and (b) the clusters transfered into butanol.

Table 1. Comparison of the dispersions of Pt clusters by absorbance at 600 nm and their particle size before and after the transfer from an aqueous phase to organic phases

Solvent	Absorbance at 600 nm[a]	Particle size	
		Average diameter/nm	Standard deviation/nm
Water(Original)	0.904	2.73	0.56
Butanol	0.900	2.41	0.51
Water(Original)	0.900	2.08	0.28
Butanol	0.908	2.05	0.32
Toluene-butanol(9/1 v/v)	0.950	2.03	0.32
MIBK[b]-butanol(9/1 v/v)	0.930	2.04	0.32

a) [Pt] = 1.0 mmol dm^{-3}. b) Methyl iso-butyl ketone.

were measured by transmission electron microscopy (TEM). Figure 1 shows the TEM photographs of the dispersed clusters before and after the transfer from the water to the butanol as well as the histograms of the size distribution, which indicate that essentially no change occurs during the transfer.

The similar absorbance in electronic spectra of the dispersions before and after the transfer suggests the quantitative transfer of the clusters from the aqueous phase to the organic phase by the present method. Table 1 shows the absorbance at 600 nm as well as average diameter and standard deviation, obtained from the TEM photograph, before and after the transfer from the water to various organic media starting from two different lots of aqueous dispersions of platinum clusters. The quantitative transfer was confirmed by comparing the absorbance of the original aqueous dispersion with the aqueous dispersion which was obtained by reverse transfer from the organic phase to a fresh water by using PVP instead of TPP in the initial transfer.

The organosols of other noble metal clusters, such as monometallic Pd, Rh and Au clusters as well as bimetallic Pt/Pd, Pt/Rh and Au/Pd clusters, were prepared by the transfer of the corresponding PVP-protected metal clusters dispersed in water to the organic phase by the present method.

The Pt clusters dispersed in the organic medium seem to be stabilized by coordination of the ligands. In order to clarify this coordination, an estimation was carried out for mole ratio of the platinum to the ligand molecule coordinating to the cluster particle in the stabilized dispersion. Then, Pt : TPP was 1.0 : 0.6 from the calculation based on the ^{31}P NMR measurement of the free TPP in benzene-d_6 from which the Pt clusters were removed by the ligand exchange treatment.

Further mechanistic studies as well as investigations on their application to catalysis are in progress.

The authors express their sincere thanks to Dr. Tokiji Kawamura and Mr. Masafumi Harada for measurements of NMR and TEM, respectively, and to Japan Society for the Promotion of Sciences (JSPS) for granting a Fellowship to H. L. This work was supported by a special grant from the Asahi Glass Foundation.

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(Received July 2, 1992)