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Novel Preparation, Characterization and Catalytic Properties of Polymer-Protected Cu/Pd Bimetallic Colloid

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

Polymer-protected Cu/Pd bimetallic colloids with different atomic ratio of Cu to Pd were successfully prepared by refluxing a glycol solution of hydroxide of copper and palladium in the presence of poly(N-vinyl-2-pyrrolidone). The TEM, XRD, AAS and UV-vis spectrum measurements indicate the formation of bimetallic alloy phase in the bimetallic colloids. High catalytic activity and selectivity for the hydration of acrylonitrile to acrylamide was achieved by using the Cu/Pd(Cu/Pd = 2) bimetallic colloid as a catalyst.

Intensive efforts have been made to prepare new kinds of metal clusters or colloids by new strategies in order to get materials with superious properties.1) Since bimetallic catalyst has become the subject of increasingly intensive efforts both in industries and academia,2) of which the activity, selectivity and stability are greatly influenced by the electronic and conformational properties of its components as well as its composition and geometric factors involved at the metal surface, it is reasonable to expect that polymer-protected bimetallic colloids should have some novel catalytic properties in view of their high dispersity and properties derived from the combinations of different components. Several examples have been published on the synthesis, characterization and catalytic properties of polymer-protected bimetallic colloids composed of two kinds of noble metal elements.3) However, reports on the preparation of polymer-protected bimetallic colloid composed of noble metal and light transition metal, which may have much greater potential to be tailored with respect to not only catalytic properties but also other properties, have so far been scarce.4) For the preparation of such kind of bimetallic colloids, the most serious difficulties are caused by the difference in the redox potential of the noble metal and light transition metal elements and in the protective abilities of the polymer to the different kinds of metal species. In this letter, a novel method is proposed for the preparation of polymer protected bimetallic colloids composed of noble metal and light transition metal, i.e. refluxing a polyol solution of corresponding polymer-protected bimetallic hydroxide or oxide colloid or polynuclear complexes, which is different from the usually adopted co-reduction and aggregation method and is expected to be of universal significance. The reduction method by using polyol had been adopted to prepare ultrafine powders of Cu, Ni and Co with micron size by Fievet's group,5) while studies on the synthesis and characterization of polymer-protected Cu and Fe hydroxide colloids or polynuclear complexes have been reported.6) The original idea of the present method is to prevent the noble metal atoms from aggregating before the reduction of light transition metal ions so as to obtain real bimetallic colloids. Here we would like to report the preparation of a poly(N-vinyl-2-pyrrolidone)(PVP)-

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†On leave from Institute of Chemistry , Chinese Academy of Sciences, Beijing, China.

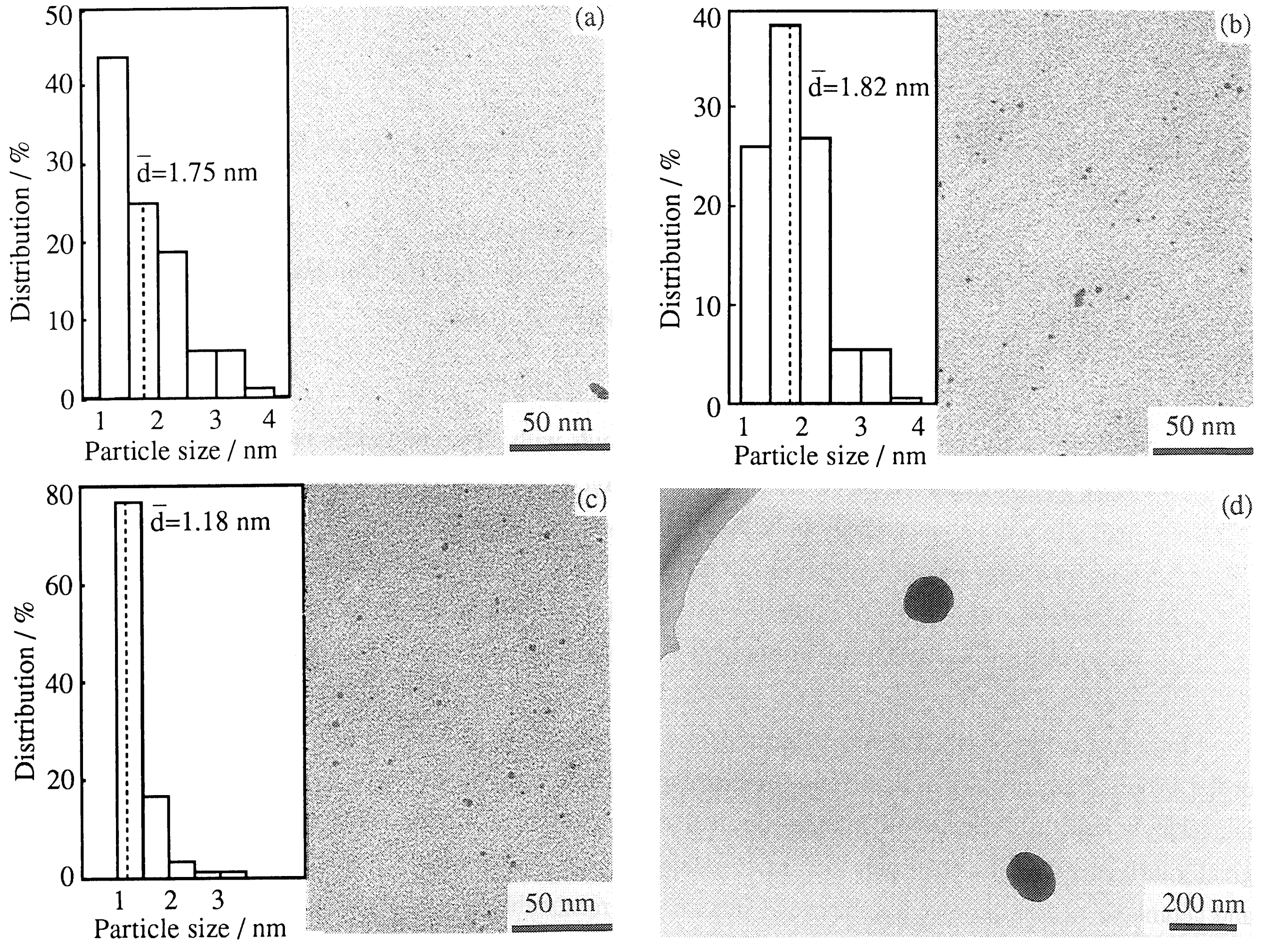

Fig. 1. Transmission electron micrographs of PVP-protected (a) Cu/Pd bimetallic colloid (Cu/Pd = 2); (b) Cu/Pd colloid (Cu/Pd=1); (c) Pd colloid; and (d) Cu dispersion.

protected Cu/Pd bimetallic colloid, which exhibits high catalytic activity and selectivity for the hydration of acrylonitrile to acrylamide, one of important industrial processes.$^{7)}$

The preparative procedure for PVP-protected Cu/Pd bimetallic colloid is as follows: $CuSO_4 \bullet 5H_2O$ (78 mg, 0.312 mmol), palladium acetate (35 mg, 0.156 mmol, dissolved in 2 cm^3 dioxane) and PVP (MW: 40 000, 1 g, 8.9 mmol as monomeric unit) were dissolved in 150 cm^3 glycol, followed by adjusting the pH value to 9.5 -10.5 by adding dropwise NaOH (1 mol dm^{-3}). A color change of the solution from yellow to green occurred during this process. Refluxing this solution at 198 °C with a nitrogen flow passing through the system for 3 h gave a stable homogeneous dark-brown solution of the bimetallic colloid. PVP-protected Pd colloid and Cu turbid dispersion were also obtained by the same method.

Figure 1 shows the transmission electron micrographs of PVP-protected Cu/Pd bimetallic colloids, Pd colloid and Cu dispersion. The bimetallic particles in PVP-protected Cu/Pd colloid mainly distribute within the range from about 1 to 4 nm accompanied with some aggregates which are several times larger in diameter. For example, the bimetallic particles of PVP-protected Cu/Pd (Cu/Pd=2) colloid distribute from 1 to 4 nm in diameter and have an average diameter of 1.75 nm. Palladium particles in PVP-protected Pd colloid are of a narrow size distribution with an average diameter of 1.18 nm, while copper particles in PVP-protected Cu dispersion have a very wide distribution from 3 to 250 nm.

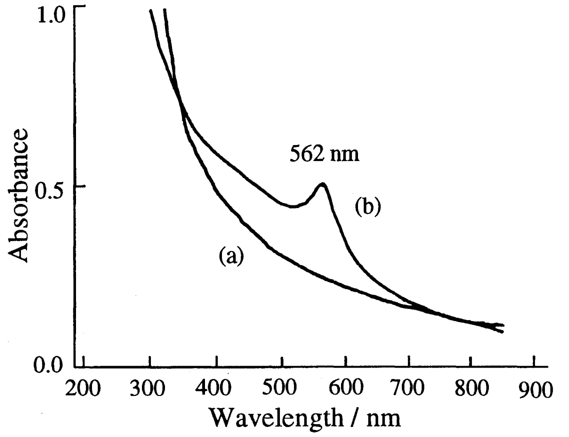

Fig. 2. UV-Vis spectra of (a) PVP-protected Cu/Pd(Cu/Pd = 2) bimetallic colloid and (b) Cu dispersion with the same concentration of copper.

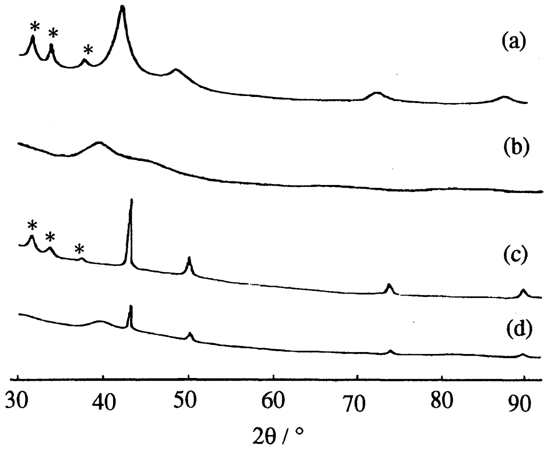

Fig. 3. X-ray diffractograms of PVP-protected metal colloids: a) PVP-protected Cu/Pd (Cu/Pd = 2) bimetallic colloid; b) PVP-protected Pd colloid; c) PVP-protected Cu dispersion; d) Physical mixture of b and c (Cu/Pd =2).

The bimetallic colloid can be easily separated from the glycol by filtration of the precipitates after adding a large amount of acetone. The precipitates can be well resolved in water or alcohol. The atomic ratio of Cu to Pd in the resulting colloidal solution is 2 as verified by atomic absorption spectral analysis, which is the same as the feeding ratio of the original bimetallic colloid.

A UV-vis spectroscopy measurement on PVP-protected Cu/Pd bimetallic colloid and Cu dispersion was carried out (Fig. 2). The absorption peak at ca. 560 nm, due to plasma oscillation characteristic of Cu surface,8) exists in the spectrum of PVP-protected Cu dispersion, but is not detected in the spectrum of PVP-protected Cu/Pd (Cu/Pd = 2) colloids, suggesting the formation of bimetallic colloid particles rather than a mixture of PVP-protected Pd and Cu particles or a palladium core covered by Cu.3c)

It is well known that Cu and Pd are miscible over their entire composition range and the XRD studies of Cu/Pd alloy have been made intensively. The formation of bimetallic alloy phase in PVP-protected Cu/Pd colloid was clearly evident from the X-ray diffraction patterns of the solid samples (Fig. 3). Diffraction lines with star marks are due to sodium sulfate. The following peaks assignable to Cu and Pd are observed in patterns c and b, respectively: 73.8°(73.8°), 50.2°(50.3°) and 43.1°(43.3°) for pattern c, and 39.6°(40.0°) for pattern b, where the numbers in parentheses are cited from a literature.9) The pattern a of PVP-protected Cu/Pd colloid exhibits diffraction lines at $2\theta = 42.0°$, 48.4°, 72.0° and 87.0°, which are located between the corresponding diffraction lines for PVP-protected Cu dispersion (pattern c) and Pd colloid (pattern b). No diffraction line for Cu, Pd, CuO, CuO_2 and PdO can be observed in the pattern of the bimetallic colloid, while the pattern of a physically mixed sample (pattern d) consists of all the corresponding diffraction lines which appear in pattern b and c. From these results it can be concluded that, under our experimental conditions, both palladium and copper ions can be reduced to the state of zero valence, which is further confirmed by the results of far-IR and XPS of the solid samples with and without PVP.

Hydration reaction of acrylonitrile was catalyzed by the PVP-protected Cu/Pd bimetallic colloid in an aqueous solution at 80 °C (acrylonitrile: 0.185 mol dm^{-3}, Cu: 1.1×10^{-2} mol dm^{-3}). Product analyses were made

$$CH_2 = CH - CN + H_2O \xrightarrow{Cu/Pd} CH_2 = CH - CONH_2$$

with gas chromatography (OV-1 column, 50 m × 0.25 mm ϕ, 190 °C). The PVP-protected Pd colloid is inert for this reaction. The average rate of the hydration within 7 h over the PVP-protected Cu dispersion as a catalyst is 0.22 (mol acrylamide/mol Cu•h), while the PVP-protected Cu/Pd (Cu/Pd=2) colloid catalyzes this reaction at an average rate of 1.39 (mol acrylamide/mol Cu•h) within the same period, which is much higher than the Cu dispersion as well as the generally published data for supported Cu-based catalysts. A yield of 93% of acrylamide was obtained within 23 h. No cyanohydrin was detected during the catalytic process, suggesting a nearly 100% selectivity to the amide. Details about this work and the characterization of PVP-protected bimetallic hydroxide will be published elsewhere. Further studies related to this preliminary successful result are in progress.

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4) During our manuscript preparation, a closely related interesting work was published by Bradley et al. (J. S. Bradley, E. W. Hill, C. Klein, B. Chaudret, and A. Duteil, Chem. Mater., 5, 254 (1993)) in which a Cu/Pd bimetallic colloid was prepared by a modified Esumi's method (K. Esumi, T. Tano, K. Torigoe, and K. Meguro, Chem. Mater., 2, 564 (1990)), i.e.by thermal decomposition of mixtures of copper acetate and palladium acetate in 2-ethoxyethanol at 135 °C in the presence of PVP. An absorption peak of CO at 2098 cm^{-1} in the IR spectrum of Cu/Pd bimetallic colloid was thought as the evedence of that the Cu ions were reduced to zero valence.

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