

# Synthesis of Monodispersed Bimetallic Palladium-Copper Nanoscale Colloids

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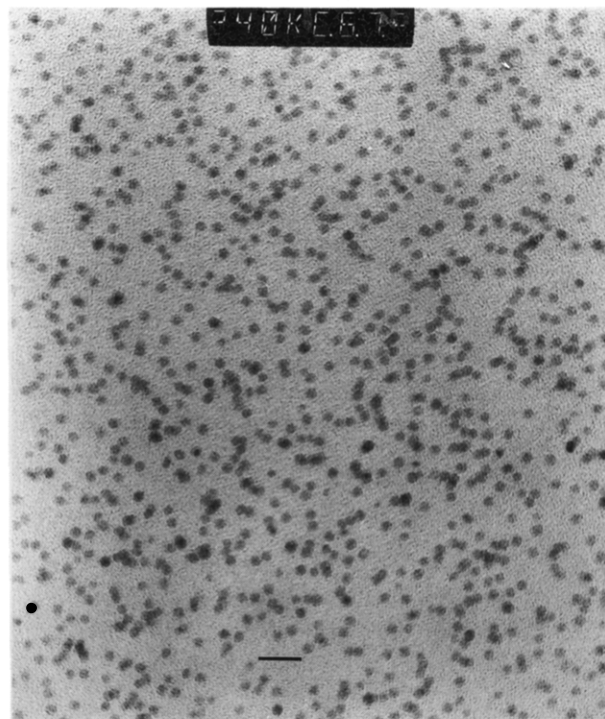
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Bimetallic clusters have been the subject of many studies of the surface chemistry and catalytic properties of metal crystallites on solid supports.<sup>1</sup> As an extension of our research on the surface chemistry of nanoscale transition-metal clusters in liquid media,<sup>2</sup> we have prepared a series of poly(vinylpyrrolidone)-stabilized palladium-copper bimetallic colloids, thus introducing a potentially instructive complexity to the palladium nanocluster surfaces which were the subject of our previous reports.<sup>2d,3</sup> Copper was chosen as the diluting metal since copper and palladium are miscible over their entire composition range.

Bimetallic PdCu colloids were recently reported by Esumi et al.,<sup>4</sup> who prepared them by the thermal decomposition of mixtures of copper acetate and palladium acetate in high boiling organic solvents such as bromobenzene, xylenes, and methyl isobutyl ketone. The bimetallic particles produced by that method often contained CuO in addition to Cu, depending on the solvent used, and particle size also was solvent dependent. The smallest bimetallic colloid particles produced, in bromobenzene, were in the range 90–160 Å, the smaller size being ascribed to the rapid nucleation rate at the boiling point of the solvent (156 °C). In approaching the preparation of more highly dispersed bimetallic CuPd colloids, we have used modifications of Esumi's method<sup>4</sup>, by reducing the acetates of palladium and copper in a reducing alcohol solvent (2-ethoxyethanol) which, at its boiling point (135 °C), rapidly reduces Pd(II) to the metal. The zerovalent Pd produced would be expected to reduce Cu(II) at the surface of the growing Pd particle, thus providing a chemical means of assuring the formation of bimetallic particles. As a further modification of Esumi's



**Figure 1.** Transmission electron micrograph of Pd<sub>70</sub>Cu<sub>30</sub>/PVP prepared from palladium acetate and copper acetate in refluxing 2-ethoxyethanol. (Scale bar = 17 nm.)

method we used poly(vinylpyrrolidone), PVP, as a stabilizing polymer, with the expectation of preparing small particles with a narrow size distribution.

Palladium-copper particles were prepared by heating mixtures of palladium acetate (Alfa) and copper acetate hydrate (Alfa) in 2-ethoxyethanol to reflux (135 °C) in the presence of poly(vinylpyrrolidone) (MW 40 000, Aldrich) for 2 h. In a typical preparation of a Pd<sub>50</sub>Cu<sub>50</sub> colloid, 30 mL of 2-ethoxyethanol containing 75 mmol each of copper and palladium acetates and 1.66 g of PVP was refluxed for 2 h. The resulting dark brown solution was filtered through a 0.2 μm Teflon filter and stored under nitrogen. Metal particles were characterized by transmission electron microscopy, selected area diffraction, and single-particle EDAX analysis on a Phillips CM12 TEM and a Phillips EM 420 ST STEM, at 200 keV.

TEM images of samples prepared in 2-ethoxyethanol consistently showed well-formed and monodispersed particles. From preparation to preparation the mean diameter varied in the range 30–50 Å, ±10%. Figure 1 shows a PdCu/PVP sample with particle diameters of 40 ± 4 Å. Energy-dispersive X-ray analysis<sup>5</sup> of the polymer films prepared with various PdCu ratios showed that the metal particles were bimetallic. Analysis of areas of the films between the colloid particles showed that no palladium(II) or copper(II) remained unreduced. Analysis of 10–20 individual particles with a 15-Å electron spot revealed no monometallic particles, and careful analysis of selected

(5) Analysis required placing the electron probe on a particle of interest which was well isolated from nearby particles to avoid risk of contamination. Counting times of several hundred seconds were required with frequent repositioning of the probe to compensate for drift. The absence of emitted X-rays corresponding to palladium or copper during analysis for 600 s of an area of polymer film between metal particles demonstrates that the X-rays emitted during analysis of individual particles were not the result of the excitation of a wide area of the sample by spurious X-rays or by electrons outside the electron probe.

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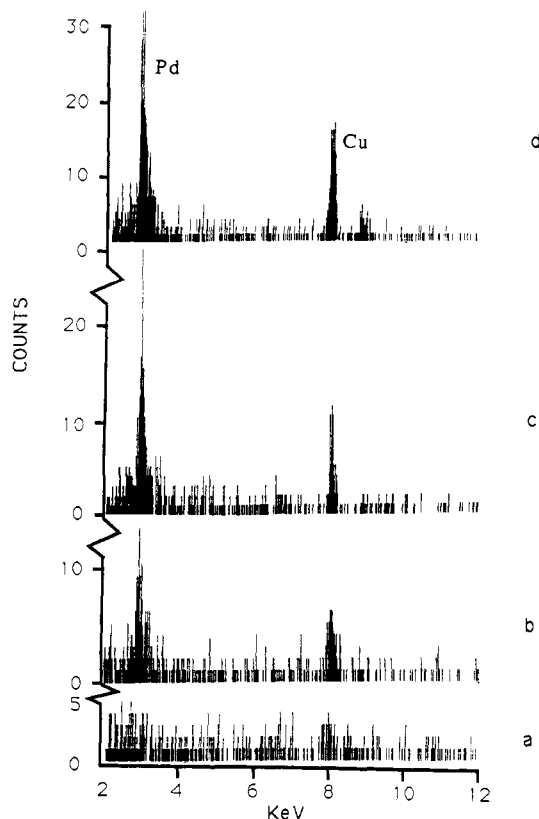
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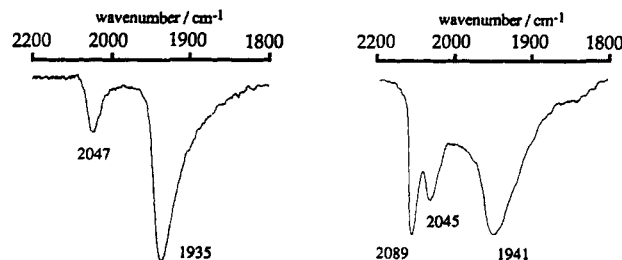


**Figure 2.** EDAX analysis of (a) PVP film and (b–d) three colloid particles in a sample with overall composition  $\text{Pd}_{55}\text{Cu}_{45}$  (see footnotes 5 for details).

particles with differing diameters gave the same composition for each, within the errors associated with the counting statistics for individual particles. Figure 2 shows EDAX analysis of a  $\text{Pd}_{55}\text{Cu}_{45}$  sample. The composition of the colloid particles tracked the composition of the original acetate mixture used. Thus a 50:50 mixture of copper and palladium acetates gave particles with uniform composition  $\text{Pd}_{50}\text{Cu}_{50}$ .

Over a series of preparations we observed electron diffraction rings consistent with crystallinity, although the degree of crystallinity of the particles seemed to vary from preparation to preparation and also with composition. Similar PdCu colloids were prepared from mixtures of the acetates in ethanol under hydrogen at 25 °C. The colloid particles were less geometrically regular but of more reproducible crystallinity, exhibiting strong diffraction rings consistent with an fcc structure. Precise identification of the structures of the nanocrystalline colloid particles we report here is the subject of further detailed study.

Carbon monoxide adsorbed readily onto the PdCu particles in dichloromethane at 25 °C, as shown by infrared spectroscopy (Perkin-Elmer 787 grating spectrophotometer, dichloromethane solutions typically containing 4–20 mg/mL metal using sealed solution cells with  $\text{CaF}_2$  windows (path length 0.1–0.5 mm)). Figure 3 shows the IR spectra of CO on PVP-stabilized colloids with the compositions  $\text{Pd}_{100}$  (particle size ca. 40 Å<sup>3</sup>) and  $\text{Cu}_{63}\text{Pd}_{37}$  (particle size ca. 45 Å, prepared in refluxing 2-ethoxyethanol). The CO adsorption was performed by passing a stream of CO at 1 atm, saturated with  $\text{CH}_2\text{Cl}_2$ , through the colloid solution until no further increase in infrared intensity was observed. The infrared spectra thus measured were in the presence of a saturation concentration of CO. On the bimetallic



**Figure 3.** Infrared spectra ( $\text{CH}_2\text{Cl}_2$  solution) of carbon monoxide adsorbed on (a) PVP-stabilized colloidal palladium and (b) PVP-stabilized colloidal palladium-copper ( $\text{Pd}_{37}\text{Cu}_{63}$ ) (see text for details).

colloid CO occupied both palladium and copper sites, demonstrating the presence of both metals at the surface of the particles. Although CO is known to bind to pure copper surfaces only at low temperatures (<200 K) under low-pressure conditions, the relative high saturation concentration of CO in the colloid solution (a  $10^{-3}$  M solution of CO would correspond to an effective partial pressure of 17 Torr), well above the pressure at which CO on copper has been observed in supported CuPd alloys.<sup>1e</sup> Comparison with the IR spectrum of CO on copper-containing bimetallic surfaces<sup>1e</sup> allowed the identification of the high-frequency absorption (2089  $\text{cm}^{-1}$ ) as CO on “on-top” copper sites, bound to single copper atoms in a linear fashion, and confirmed that the copper was in the zerovalent state since CO on oxidized Cu would absorb at >2100  $\text{cm}^{-1}$ .<sup>6</sup> The bands at 2045 and 1941  $\text{cm}^{-1}$  are in the regions found for linear and bridged CO on Pd in similarly sized PVP stabilized palladium colloids<sup>2d,3</sup> (see Figure 3a) and similar in frequency to infrared absorptions assigned to on-top and bridged CO on single-crystal palladium<sup>6a</sup> and supported palladium crystallites.<sup>6b</sup>

The relative absorption intensities for the three types of CO on the colloid of this composition seem inconsistent with the bulk composition of the alloy particles and suggest that the surface composition is depleted in copper, in contrast with the surface enrichment of copper found in bulk PdCu alloys.<sup>7,8</sup> For PdCu colloids of less than 50% copper the intensity of the CuCO absorption is very weak, implying very little copper at the surface, and only at compositions with greater than 50% Cu is the intensity of the CuCO absorption band comparable to that of the linear PdCO band. It is not possible to conclude the surface stoichiometry directly from the relative intensities of the CuCO and PdCO bands, since neither extinction coefficients nor site occupancies can be measured independently, and it is known that CO binds less strongly to copper than to palladium. We observe that by passing a stream of nitrogen through the solution, CO is removed preferentially, rapidly, and reversibly at room temperature from copper sites and less rapidly from palladium sites. This raises the possibility that a greater proportion of the surface palladium atoms than copper atoms bind CO. However, it is known that the surface stoichiometry of alloy nanoclusters depends on several factors which include the

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nature of adsorbates,<sup>9</sup> and the polymer-stabilized colloid particles we are studying must be presumed to have considerable amounts of polymer and solvent on their surfaces, albeit weakly adsorbed.

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(9) The IR spectrum of adsorbed CO on a Pd<sub>37</sub>Cu<sub>63</sub> colloid is time dependent and implies a progressive further enrichment of the surface in palladium under the influence of CO. A similar phenomenon was reported by Sachtler et al. in a photoemission study of PdAg surfaces under CO (see: Bouwmann, R., Lippits, G. J. M.; Sachtler, W. M. H. *J. Catal.* 1972, 25, 350).

A detailed analysis of the structural and surface chemistry of monodispersed nanoscale PdCu colloids is underway and will be reported separately.

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