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Infrared and EXAFS Study of Compositional Effects in Nanoscale Colloidal Palladium−Copper Alloys

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The reaction between colloidal palladium and cupric acetate in 2-ethoxyethanol leads sequentially to the reduction of Cu(II) to Cu(0) at the surface of the palladium particle and dissolution of the deposited copper in the palladium matrix. The reaction was monitored by infrared spectroscopy using carbon monoxide adsorbed on samples of the colloid during the reaction and by X-ray absorption spectroscopy (NEXAFS and EXAFS) on the colloidal metal after completion was reached. The Cu K near-edge X-ray absorption spectrum shows reduction of Cu(II) to Cu(0). After deposition on the palladium surface the copper is zerovalent, and subsequently it migrates into the palladium particle but only to within a few atomic layers of the surface.

Introduction

The importance of alloying in catalysis by metals is well known, and the structural and surface chemistry of alloys has received much attention in this context.[1−9] Since surface composition and structure are factors of central importance in any investigation of alloy surface chemistry, alloy surfaces have been studied extensively, as single crystals, as polycrystalline foils, or, in their common catalytic form, as supported metal particles. Highly dispersed metals are especially amenable to study in the colloidal state,[10] since they can often be prepared at quite high concentrations and high dispersions, thus providing particularly useful samples for structural and spectroscopic analysis. For example, a sample of colloidal metal, prepared and isolated in a solid polymer matrix by simple sol preparative methods,[10] can be conveniently studied by any of the methods normally used for supported metal catalysts (X-ray diffraction, TEM, solid state NMR, X-ray absorption spectroscopy). Alternatively, after dispersion of the polymer−metal composite in a suitable liquid, the colloidal metal particles may be studied by methods usually applied for molecular species in solution, such as solution infrared spectroscopy and liquid-phase NMR.

We have been investigating the preparative, structural, and surface chemistry of colloidal transition metals and their alloys, applying the techniques of solution phase molecular chemistry and of solid state chemistry to their synthesis and characterization.[11−17] We recently reported[11,12,18] the preparation of poly(vinylpyrrolidone) (PVP) stabilized colloidal bimetallic copper−palladium alloys from the acetates of the divalent metals in refluxing alcoholic solvents. The colloidal alloy particle sizes were approximately 45 Å and compositions were in the range Pd_xCu_{1-x} ($1 \geq x \geq 0.37$). We observed by infrared spectroscopy of adsorbed CO on these colloidal alloys a surprising surface enrichment in palladium,[18] in contrast to the more commonly reported, if slight, preference of copper for surface sites in bulk palladium−copper alloys,[19] and a further enhancement of surface palladium concentration under the prolonged influence of adsorbed CO. A similar enrichment of palladium has been suggested on the basis of X-ray diffraction data for PdCu/PVP sols prepared by ethylene glycol reduction of the colloidal mixed hydroxides.[20]

The preparative method we used throughout this investigation was chosen as one likely to result in the exclusive formation of bimetallic particles, since under the conditions of synthesis only palladium(II) was reducible by the alcoholic solvent, and so copper would be deposited only in a redox reaction at the surface of a preformed palladium particle. Similar PdCu/PVP col-

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loids, but with smaller particle sizes, have been reported by Toshima et al.[20,21] by coreduction of the mixed hydroxides of the metals in refluxing ethylene glycol, a modification of the polyol process[22] for the preparation of small metal particles. It has been suggested by these authors[23] that the relative redox potentials of Pd^0/Pd^{2+} and Cu^0/Cu^{2+} made it unlikely that Cu^{2+} would be reduced to the zerovalent state by Pd(0) in the reaction system we reported, with the implication that Cu(I) was the likely form of copper produced. While the study we report here was essentially complete when these questions were raised, the results contained here are presented in such a way as to address the important questions raised by Toshima et al., and we believe that they establish clearly the mechanism of the deposition of copper onto palladium by reduction of Cu(II) by surface palladium atoms.

The important issue is how Cu(II) reacts with colloidal palladium. The redox chemistry of Cu^{2+}/ Pd^0, the deposition of Cu(0) at the surface and the chemistry of alloy formation (the dissolution of copper) are all involved in the growth of the colloidal alloy particles. To elucidate these steps in the process of alloy formation, we have separated the initial formation of Pd(0) from Pd(II) from the subsequent copper deposition step by allowing Cu(II) to react with preformed palladium colloid particles in a reducing alcoholic solvent at temperatures between 70 and 135 °C. In this way, by a combination of infrared and X-ray spectroscopic analysis, we have monitored the reduction of cupric ions and observed the progressive coverage of the palladium particles by Cu(0) with the formation of a bimetallic surface and then a wholly copper plated particle in which the deposited copper slowly dissolves in the subsurface layers of the colloidal alloy. We draw from these results on the plating reaction conclusions about the formation of colloidal PdCu in the original reaction between palladium acetate and copper acetate in a reducing solvent.

Throughout this paper we use the term “suspension” in referring to polymer solutions containing colloidal metal particles.

Experimental Section

The stabilizing polymer used throughout this study was poly(vinylpyrrolidone) (PVP, Aldrich, MW 40 000). Palladium acetate was purchased from Aldrich, and cupric acetate monohydrate from MCB. Colloidal palladium (ca. 60 Å) was prepared by refluxing palladium acetate in the presence of PVP in 2-ethoxyethanol under nitrogen for 2 h, followed by filtration through a 0.2 μm Teflon millipore filter.

Colloidal PdCu/PVP Prepared from Homogeneous Solutions of the Acetates: $Pd_{90}Cu_{10}$−H and $Pd_{80}Cu_{20}$−H. Palladium−copper particles with nominal composition $Pd_{90}Cu_{10}$, stabilized with PVP, were prepared in colloidal suspension from palladium acetate (0.45 mmol) and copper acetate monohydrate (0.05 mmol) by reduction in warm (90 °C) 2-ethoxyethanol (35 mL) for 2 h, under nitrogen. The temperature of the solution should be kept below the boiling point of the solvent, at which temperature occasional precipitation of solids can occur. Concentrations of the metal salts were adjusted appropriately in the preparation of sols with the composition $Pd_{80}Cu_{20}$.[24] Particle sizes of the resulting colloidal alloys were determined by TEM to be ca. 50 Å.

Preparation of PdCu/PVP Sols by Reaction of Cu(II) Acetate with Preformed Pd/PVP Sols: Pd_xCu_{100-x}−P. Plating experiments were performed by heating a 2-ethoxyethanol suspension of ca. 60 Å PVP stabilized colloidal palladium (ca. 2 wt % Pd) containing appropriate concentrations of copper(II) acetate. Temperatures were between 70 and 135 °C, as described below. TEM analysis of the resulting colloidal alloys showed no significant size change or aggregation during copper deposition experiments.

Metal particles were characterized by transmission electron microscopy (Phillips CM 12). Samples were prepared by addition of a drop of sol onto a carbon coated copper grid, removal of most of the sol onto a filter paper by capilliary action and air drying. PVP protected metal sols are sufficiently air stable to be prepared in this manner. In the case of the bimetallic colloids single particle electron microprobe analysis (EMA, Phillips EM 420 ST STEM 200 keV) was performed on similarly prepared samples but on a carbon coated nickel grid.

Infrared and X-ray spectroscopy experiments were performed on a series of samples which were shown by TEM to be of similar particle size (ca. 50 Å for PdCu−H sols and ca. 60 Å for PdCu−P sols) and not aggregated.

Infrared spectra of adsorbed CO were obtained on samples prepared by evaporation of a colloid suspension to the dry polymer, dissolution in dichloromethane, and then passing a stream of CO saturated with the solvent into the redispersed sol. The spectrum of the sol before CO addition was used as a reference. A saturated solution of CO in CH_2Cl_2 is ca. 10^{-2} M, greatly in excess of the surface metal atom concentration, and so it can be assumed that all available CO binding sites on the colloidal metal are occupied. Concentrations were adjusted so as to give infrared bands with intensities of ca. 5%. Infrared analysis was performed on a Perkin-Elmer 787 grating spectrophotometer or a Mattson Galaxy 5000 FTIR in dichloromethane solutions typically containing 4−20 mg/mL metal using 0.1−0.5 mm sealed solution cells with CaF_2 windows. X-ray absorption experiments were performed at the National Synchrotron Light Source, beamline X10C, Brookhaven National Laboratory. The absorption edges of Pd and Cu were measured at 10 K using an Oxford Instruments cryostat equipped with beryllium windows. The samples were in the form of powdered PVP encapsulated colloids, mounted in aluminum cells, and sealed with Kapton polyimide tape. Sample preparation was carried out in an inert atmosphere box, although the encapsulation of the colloidal metals in an organic polymer seemed to prevent oxidation even during exposure to air for the duration of the experiment, as judged by the energy of the X-ray absorption edge of the metals compared to that of a metal foil after several hours. The fluorescence and absorption signals from the colloid sample, and the absorption signal from a metal foil taken as a reference were recorded simultaneously, thus giving a reliable comparison of energies of the Cu and Pd K edges in colloidal alloys with those of the elemental metals. Precise determination of the X-ray absorption edge shift was carried out by measuring the energy of the maximum in the derivative of the absorption coefficient with respect to energy.

Results and Discussion

Preparation of the Colloidal Alloys. Two types of colloidal PdCu were investigated, both stabilized by PVP. In the first, colloidal alloys with the composition $Pd_{90}Cu_{10}$ or $Pd_{80}Cu_{20}$ were prepared from homogeneous solutions of the divalent acetates of the metals, at appropriate concentrations, by reduction in warm 2-ethoxyethanol.[11] The sols prepared by homogeneous nucleation and growth are designated $Pd_{90}Cu_{10}$−H and $Pd_{80}Cu_{20}$−H and contained well formed apparently crystalline colloidal alloy particles[25] ca. 50 Å in diam-

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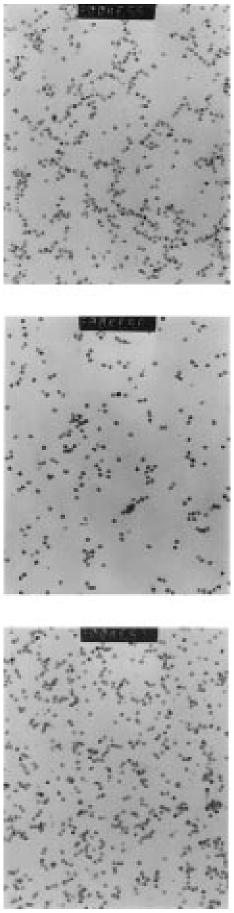

Figure 1. Transmission electron micrographs of (a, top) PVP-stabilized colloidal palladium, (b, middle) as in (a) after treatment at 70 °C for 5 h, in the presence of 10 atom % copper(II) acetate, 2-ethoxyethanol solvent, and (c, bottom) as in (b) after heating to 135 °C for 2 h. The scale bar represents 125 nm.

eter, consistent with our previous reports.[11,18] In the second preparation, a preformed 60 Å PVP stabilized palladium colloid, prepared from palladium(II) acetate by reduction in refluxing 2-ethoxyethanol,[13,16] was treated with cupric acetate monohydrate in 2-ethoxyethanol. The plated samples prepared in this manner, with the composition Pd_xCu_{100-x} and designated Pd_xCu_{100-x}−P, showed a particle size and morphology similar to the starting Pd sol. Transmission electron micrographs of the sol during one such plating experiment are shown in Figure 1.

Infrared Spectroscopy of Adsorbed Carbon Monoxide. *(a) Sols Prepared from Mixed Homogeneous Solutions of the Metal Acetates.* We have previously shown that CO will bind to both Cu and Pd surface atoms in this colloidal alloy system.[11,18] Infrared absorptions due to [PdCO] are observed near 1940 and 2050 cm^{-1} in both monometallic palladium colloids and in the PdCu colloidal alloys, and a higher frequency band near 2090 cm^{-1} is observed due to [CuCO] in the case of the bimetallic particles. The assignment of the [CuCO] band is consistent with previous assignments for the vibrational bands of CO on zerovalent copper surfaces. The frequencies reported are crystal face dependent, with bands at 2077 (Cu(111)), 2088 (Cu(110)), and 2089 cm^{-1} (Cu(100)), but all lie below 2100 cm^{-1}, whereas the corresponding frequency for CO on Cu^+ is found above 2100 cm^{-1}.[26−28] However, at copper concentrations below 50 atom % the intensity of the [CuCO] band for CO on the PdCu colloidal alloys under study is greatly reduced, and for the 10 atom % Cu and 20 atom % Cu particles prepared here as $Pd_{90}Cu_{10}$−H and $Pd_{80}Cu_{20}$−H no infrared absorption due to [CuCO] was observed.[29]

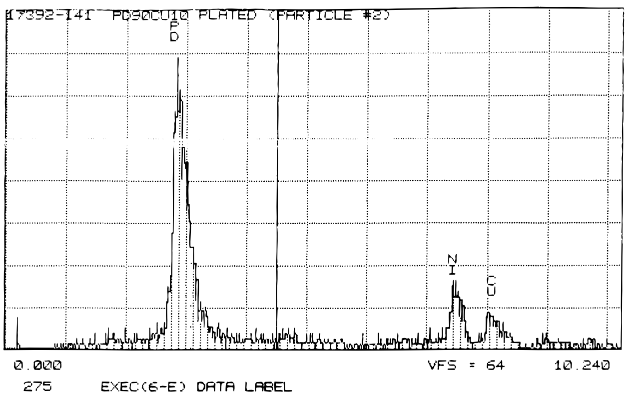

Figure 2. Electron probe microanalysis of a single $Pd_{90}Cu_{10}$ particle prepared by reaction between PVP stabilized colloidal palladium (60 Å) and copper(II) acetate in 2-ethoxyethanol.

(b) Sols Prepared by Reduction of Copper(II) at the Surface of Preformed Colloidal Palladium. The bimetallic sol prepared by treatment of a pure palladium colloid (ca. 60 Å mean diameter, <10% dispersed) with cupric acetate was prepared using sufficient Cu(II) so that the total reduction of the cupric ions would give approximately one monolayer of copper at the colloid surface by redox substitution of surface palladium atoms. Such a material would provide a suitable sustrate for adsorbed CO in experiments to measure the relative extinction coefficients for [CuCO] and [PdCO] infrared absorptions on a PdCu surface,[18] since in this plating procedure the surface concentration of copper would be known.

Although single particle EDAX (Figure 2) showed that the copper had indeed added to the colloidal palladium, the infrared spectrum of adsorbed CO, shown in Figure 3a, showed no trace of an absorption band at ca. 2090 cm^{-1} characteristic of CO adsorbed on surface copper atoms. The spectrum was essentially indistinguishable from that of CO on a colloidal alloy of identical composition prepared from a homogeneous solution of the mixed acetates, as shown in Figure 3(b), in which material the surface is composed entirely of palladium atoms. While the infrared spectrum of CO on the "homogeneous" PdCu alloy particles shown in Figure 3a is in accord with that reported previously by us and is diagnostic of a surface layer of palladium,[11,18] in the case of the copper-plated particles under discussion we had expected the deposited copper atoms to remain on the

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(25) Palladium-rich colloidal PdCu particles which are prepared by this method, giving XRD patterns consistent with an fcc lattice, but as copper content increases significant changes occur consistent with considerable disorder.

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(29) All of the infrared spectra of adsorbed CO reported here were recorded immediately after addition of the gas to a solution of the colloid. We have previously shown that although CO adsorption induces an enrichment in palladium at the colloid surface, the enrichment process is relatively slow (of the order of days), and so the relative intensities of the infrared absorptions due to [CuCO] and [PdCO] in spectra taken just after CO addition are a measure of the relative concentrations of the two metals in the as-prepared colloid.

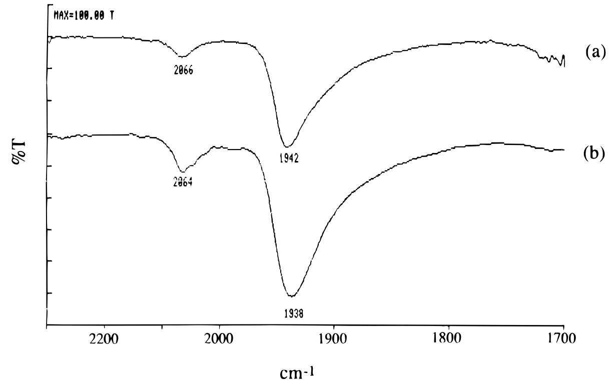

Figure 3. Infrared spectra (CH_2Cl_2 solution) of CO adsorbed on (a) PVP stabilized colloidal palladium (60 Å) after treatment with copper(II) acetate in 2-ethoxyethanol, 135 °C, 4 h ($Pd_{90}Cu_{10}-P$); (b) PVP-stabilized $Pd_{90}Cu_{10}$ prepared by coreduction of palladium acetate and copper acetate in 2-ethoxyethanol, 130 °C, 4 h ($Pd_{90}Cu_{10}-H$).

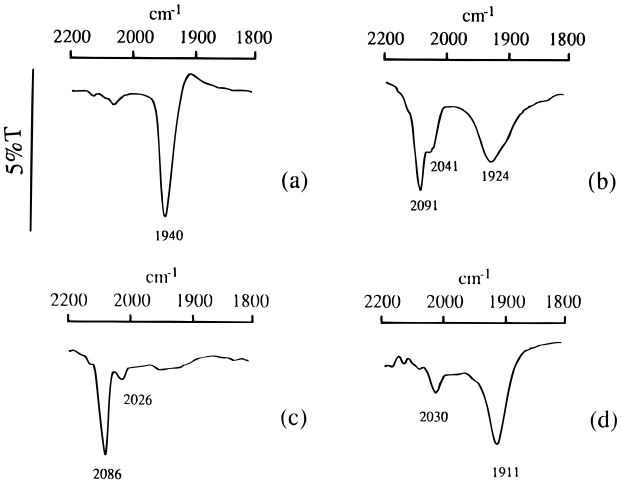

Figure 4. Infrared spectra (CH_2Cl_2 solution) of CO adsorbed on (a) PVP-stabilized palladium (60 Å); (b) as (a) after warming to 70 °C in the presence of 30 atom % copper(II) acetate in 2-ethoxyethanol for 6 h; (c) as (b) after warming to 125 °C for 1 h; (d) as (c) after heating to 135 °C, for 3 h.

surface of the alloy particles under the relatively mild conditions employed in their preparation. The fate of the deposited copper atoms was thus in question, and a more careful analysis was performed by carrying out the deposition of copper at an initially lower temperature, but at a higher concentration of Cu(II), in an attempt to observe the formation of a bimetallic PdCu surface, and then, on raising the temperature to that of the 10% copper deposition (see above) to observe any subsequent change in the composition of the alloy particle surface. As a substrate for this reaction, a PVP stabilized palladium sol of particle size ca. 60 Å, prepared from palladium acetate in refluxing methanol, was dispersed in 2-ethoxyethanol. Figure 4a shows the infrared spectrum of CO adsorbed on a sample of the PVP-stabilized palladium as prepared. The spectrum comprises one principal absorption at 1940 cm^{-1} with a low intensity absorption at 2040 cm^{-1} and is characteristic of a palladium surface for colloid particles of this size.[13] After warming the sol to 70 °C for 6 h in the presence of 30 atom % Cu(II) acetate, a sample of the solution, evaporated and redispersed in dichloromethane, gave the spectrum shown in Figure 4b on addition of CO. The absorption below 2000 cm^{-1} now comprises only ca. 50% of the total intensity, and there are two absorptions above 2000 cm^{-1}, which together make up the remaining ca. 50% intensity. In addition to the band at 2041 cm^{-1} there is an additional band at 2091 cm^{-1}, and the spectrum is characteristic of a bimetallic PdCu surface, similar in fact to that we observed previously for a PdCu sol with a composition of $Pd_{37}Cu_{63}$.[11,18] On warming the sol to 125 °C for 1 h the spectrum of added CO now shows a single absorption at 2086 cm^{-1} as shown in Figure 4c, characteristic of a surface comprising only copper atoms. When the temperature is raised to 135 °C for 3 h the spectrum has reverted to that characteristic of a palladium surface as shown in Figure 4d.

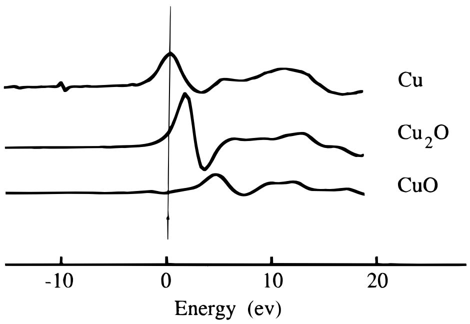

Figure 5. Derivatives with respect to energy of the copper K-edge X-ray absorption spectra of standard Cu(0), Cu(I), and Cu(II) materials. The zero of energy is the copper K edge at 8979 eV.

These results demonstrate the deposition of zerovalent copper on the colloidal palladium particles, but followed by a slower dissolution of the copper atoms in the palladium lattice, similar to the process which we proposed to be occurring in the growth of colloidal PdCu from homogeneous solutions of the acetates.

X-ray Absorption Spectroscopy. (*a*) *Near-Edge Spectra.* It was important to determine the oxidation state of the copper in both the homogeneous and plated colloidal alloys, in view of the uncertainties associated with the assignment of oxidation states of surface metal atoms on the basis of infrared frequencies of adsorbed CO and especially in view of the suggestion[20] that Cu(II) might not in fact be reduced to Cu(0) at a Pd(0) surface. The near edge regions of X-ray absorption spectra are indicative of the electron configurations of the absorbing atoms, and these data have in fact been used in analyzing mixtures of copper compounds of different oxidation states.[30] As standards in the determination of the copper oxidation state in the PdCu system, we used Cu metal, Cu_2O, CuO and cupric acetate. The shift in absorption edge energy in going from Cu(0) to Cu(II) is shown in Figure 5, in which derivatives of the absorption vs energy curve at the Cu K edges for Cu metal, Cu_2O, and CuO are shown. In the measurement of the Cu K edge for the colloid samples, shifts from the energy for the elemental metal were precisely determined by comparison with the absorption energy for the copper foil standard which was recorded simultaneously with that of the colloid sample. The reduction of Cu(II) to Cu(0) is apparent from the ca. 5 eV shift in the K-edge energy between Cu(II) as the acetate and in the final plated form in $Pd_{90}Cu_{10}-H$ and $Pd_{80}Cu_{20}-H$, and a similar result was found for $Pd_{90}Cu_{10}-P$, as shown in Figure 6. (We have measured this shift in a separate

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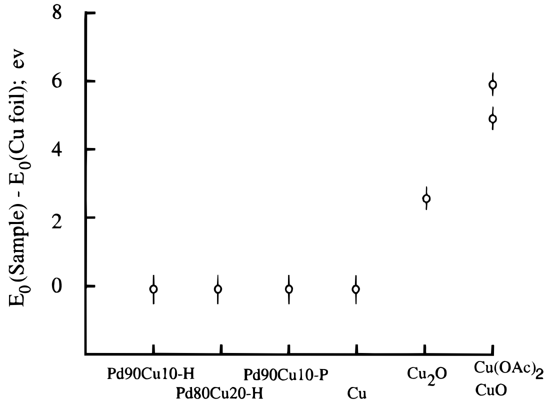

Figure 6. Comparison of Cu K-edge energy shifts (from copper foil) for PdCu colloids with Cu(0), Cu(I), and Cu(II) standards.

real-time experiment in which the copper K edge of Cu(II) acetate is monitored during the reduction process. These results will be reported separately.) It being thus established that the cupric ion had been reduced to the zerovalent state in both the homogeneous co-reduction sols and in the plated sol, it remained to identify the environment of the copper atoms in the two types of sample.

(b) EXAFS Spectroscopy. Analysis of the fine structure associated with the X-ray absorption edges of individual elements in complex nonmolecular systems provides structural information which is difficult if not impossible to obtain by other means. This is particularly the case for small particle alloy systems, and EXAFS analysis has thus been crucial to the elucidation of the structures of many bimetallic particle systems in heterogeneous catalysis.[31−36] Bimetallic PdPt colloids have also been successfully analyzed by this technique,[37] and in the present investigation we have by this method been able both to determine the structural environment of copper in the "plated" colloid Pd90Cu10-P and to compare this result with the analogous copper environments in the "homogeneous" alloy particles $Pd_{90}Cu_{10}$−H and $Pd_{80}Cu_{20}$−H.

Details of the EXAFS experiments, data analysis, fitting procedure, and determination of structural parameters will be published separately, and only a general summary will be given here. The normalized EXAFS functions associated with the K-absorption edges of palladium and copper were extracted in the usual manner from the observed absorption spectra. Fourier transforms of both the $Pd_{90}Cu_{10}$−P, $Pd_{90}Cu_{10}$−H and the $Pd_{80}Cu_{20}$−H data were taken over the range 2−15 $Å^{-1}$ and the corresponding inverse transforms were taken over the range $1.0\ Å < R < 4.0\ Å$. Analysis of both the palladium and copper Fourier-filtered EXAFS data was performed using the double edge fitting routine described previously.[38] Phase and amplitude parameters were either determined experimentally using foils of the pure metals, or from theoretical phases calculated from the program FEFF for CuPd and PdCu pairs.[39] The fitting technique takes into account the constraints on coordination sphere composition imposed by the relationship (eq 1) between the number of copper atoms in the average palladium coordination sphere, N^{PdCu}, and the number of palladium atoms in the coordination sphere of the average copper atom, N^{CuPd} in a bimetallic PdCu matrix with a stoichiometry defined by the atomic fractions X_{Pd} and X_{Cu}:

$$N^{PdCu} = (X_{Cu}/X_{Pd})N^{CuPd} \tag{1}$$

This relationship[38] is independent of the structural details of the system, but when the EXAFS functions for each component in a bimetallic system are fitted separately, it does not always hold, reducing the level of confidence in the structural parameters derived from the separate fits. The incorporation of this relationship into the fitting procedure thus ensures a more physically valid result, even though the precision of the parameters derived is sometimes lower than that resulting from independent fits.

One important aspect of the analysis should be described here as it is important for understanding the significance of the structural parameters we derived from the EXAFS experiments, and that concerns the consequences of disorder. As described below, there is evidence of disorder in the colloidal PdCu alloys reported here, which becomes significant as copper concentration increases above 20%. The fitting of parameters such as bond lengths, R, coordination numbers, N, and the Debye−Waller terms, $\Delta\sigma^2$ (a measure of disorder) ideally assumes independence among these parameters. This is not strictly true, and in particular there is a varying degree of correlation between $\Delta\sigma^2$ and coordination number, N. In disordered systems this can be severe, and the consequences of disorder can include artificially short bond lengths and high coordination numbers,[40] and errors in N which have been estimated at ±20%.[41] This makes the rigorous treatment of errors complex, and we will report the results of such an analysis separately in the context of a paper devoted to the EXAFS results summarized here. However, in assigning an estimated error to coordination numbers of ±20% for all three colloidal alloys, we feel that we err on the side of caution.

EXAFS Analysis of $Pd_{90}Cu_{10}$−H and $Pd_{80}Cu_{20}$−H. Structural parameters for the bulk PdCu system are well established.[42] Colloidal PdCu alloys have been reported with an identifiable fcc structure, consistent with the bulk phase diagram,[21,23] which is dominated by a continuous fcc solid solution of the two metals, with an ordered bcc phase (LiCl) at PdCu and an ordered fcc phase ($AuCu_3$) at $PdCu_3$ at temperatures below 600 °C. However, we have observed evidence from X-ray dif-

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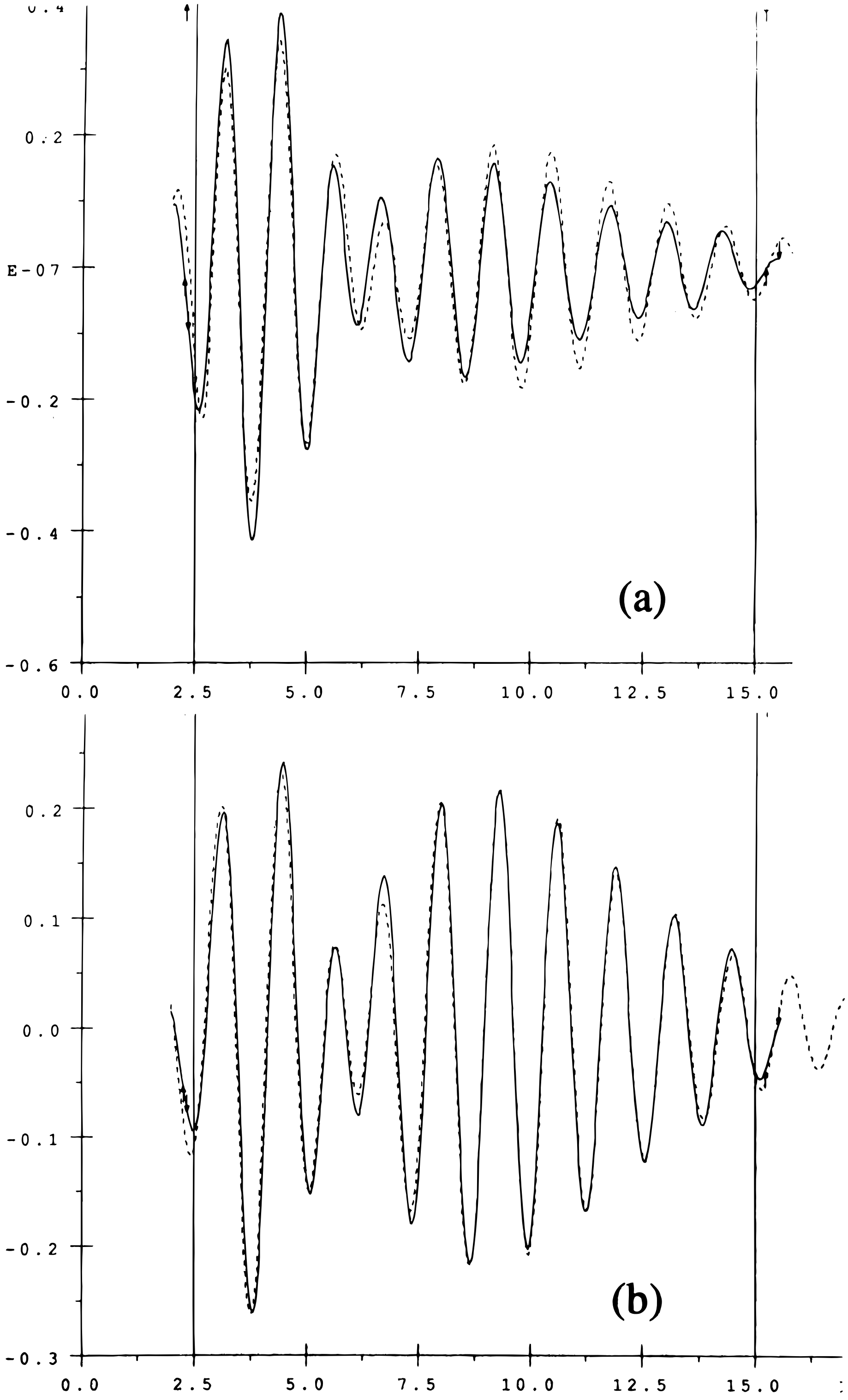

Figure 7. Fourier-filtered EXAFS spectra (solid lines) and best fit (dotted lines) for $Pd_{90}Cu_{10}$–H: (a) Cu EXAFS; (b) Pd EXAFS.

fraction for considerable disorder in the colloidal PdCu alloy particles under study at compositions $Pd_{\leq 80}Cu_{\geq 20}$. X-ray diffraction patterns of these colloidal alloys show general features consistent with an fcc lattice, but with significant changes in the structure factors and broadening of the diffraction lines which are interpreted as due to structural disorder.[43] These sols were prepared from homogeneous solution at lower temperatures than those reported by Toshima, who reported crystalline colloidal alloys. Probably as a result of such a disorder, analysis of the EXAFS spectra for the $Pd_{80}Cu_{20}$–H colloid gave total coordination numbers for the two metals which were physically unreasonably high (i.e., significantly greater than 12) when this parameter was allowed to vary in the fitting procedure. However, it has been pointed out[38] that in such cases poor refinement of N for an *ab* bimetallic, (essentially when a range of total N values give the same quality of fit) that N^{aa} (the coordination number of element *a* in the coordination sphere of *a*), N^{bb}, N^{ab}, and N^{ba} vary less among the several sets which give the same quality of fit. Accordingly total coordination numbers can be arbitrarily fixed

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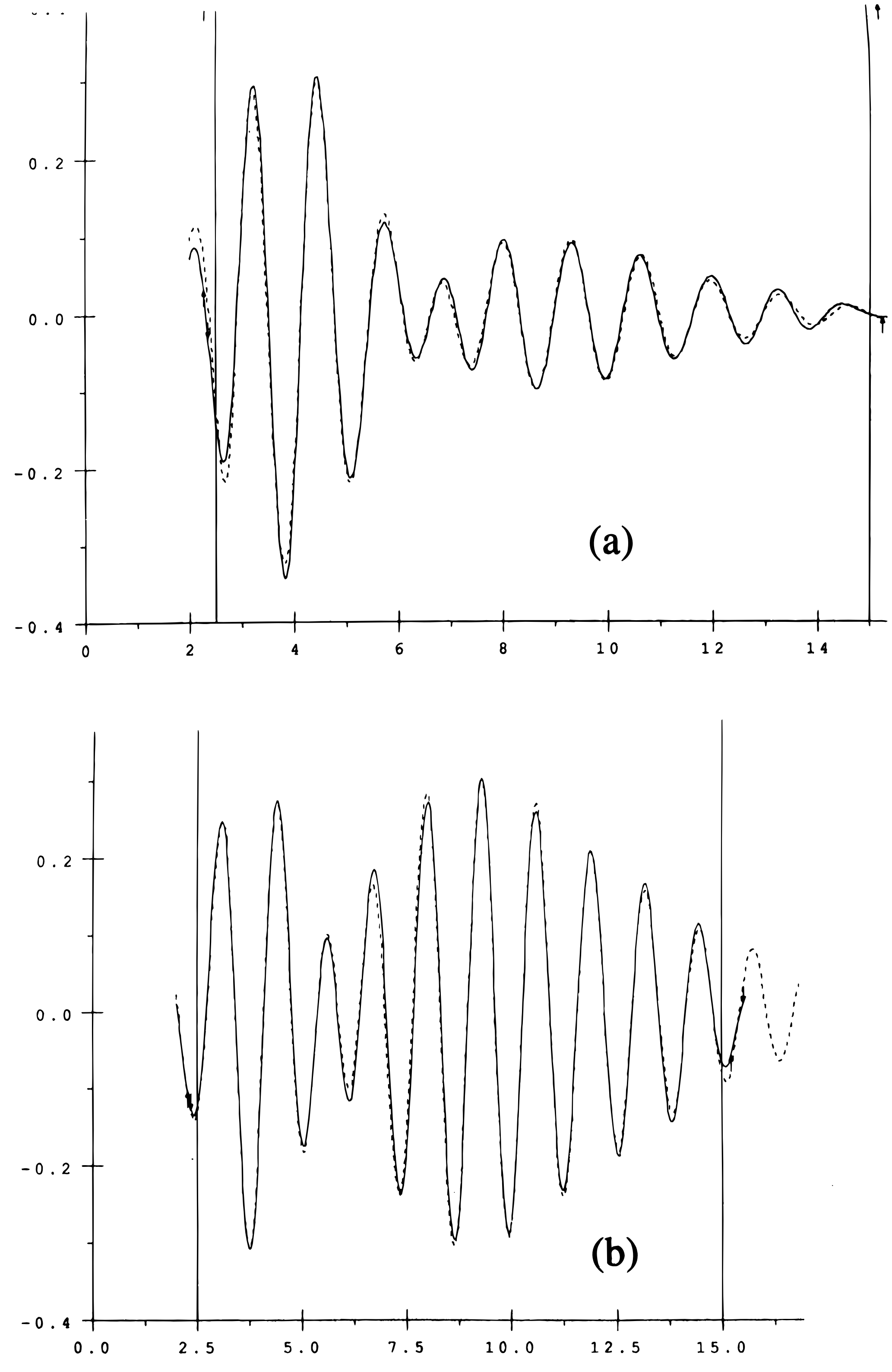

Figure 8. Fourier-filtered EXAFS spectra (solid lines) and best fit (dotted lines) for $Pd_{90}Cu_{10}$−P: (a) Cu EXAFS; (b) Pd EXAFS.

and still give useful and important information about the composition of the coordination spheres, although the actual total N values will not be significant. For this reason it was decided to constrain the total copper and palladium coordination numbers in $Pd_{80}Cu_{20}$ to 12, as described below. In the case of the copper plated material and also $Pd_{90}Cu_{10}$−H the structure is apparently dominated by the well crystalline palladium matrix, which imposes order on the resulting copper-palladium particles, and in this case the coordination number was refined successfully in the fitting procedure.

The constraint of coordination numbers for Pd_{80}-Cu_{20}−H ruled out useful comparison of the total N values of the two metals as a means of identifying which might be predominantly concentrated at the surface in that colloidal alloy. However, as described above, it was possible to determine the distribution of the minor component, Cu, in the particles by comparing the Cu−Cu coordination number with that expected if the copper

Table 1. EXAFS Analysis of Structural Parameters for PVP-Stabilized CuPd Colloidal Alloys[a]

				homogeneously grown PdCu					
	copper-plated palladium $Pd_{90}Cu_{10}$−P			$Pd_{90}Cu_{10}$−H			$Pd_{80}Cu_{20}$−H		
				Copper Coordination Sphere					
	Cu−Cu	Cu−Pd	total	Cu−Cu	Cu−Pd	total	Cu−Cu	Cu−Pd	total
N	2.7	9.7	12.4	1.8	11.0	12.8	3.1	8.9	12 (fixed)
N (stat)	1.2	11.2		1.3	11.5		2.4	9.0	
R (Å)	2.61	2.62		2.62	2.66		2.66	2.64	
$\Delta\sigma^2 \times 10^3$	2.6	5.4		2.9	4.9		2.7	3.5	
				Palladium Coordination Sphere					
	Pd−Cu	Pd−Pd	total	Pd−Cu	Pd−Pd	total	Pd−Cu	Pd−Pd	total
N	1.1	9.8	10.9	1.2	8.3	9.5	2.2	9.8	12 (fixed)
N(stat)	1.1	9.8		1.0	8.5		2.4	9.0	
R (Å)	2.62	2.74		2.66	2.75		2.64	2.72	
$\Delta\sigma^2 \times 10^3$	5.4	0.72		3.3	1.6		3.7	3.3	

[a] N = coordination number; N(stat) = coordination number calculated for a homogeneous solid solution of Cu in Pd; R = bond distance; σ = Debye−Waller factor. Errors in N are estimated at ±20%, and in R at ±1%.

atoms were distributed homogeneously throughout the particles, including a statistical distribution at the surface. Within the constraints imposed by the total coordination number restriction, the Cu−Cu coordination number for $Pd_{80}Cu_{20}$−H samples is still significant. For both $Pd_{80}Cu_{20}$−H and $Pd_{90}Cu_{10}$−H the Cu−Cu contribution to the copper coordination sphere is greater than that predicted from the composition of the colloids. For these two cases it is clear both from the energy of the Cu K edge (Figure 6) and composition of the first coordination sphere around copper (Table 1), which shows a high palladium content (and no light-atom contacts), that the copper atoms are zerovalent and are dispersed throughout the interior of the alloy particles. For $Pd_{90}Cu_{10}$-H a Cu−Cu coordination number of 1.8 was found, compared to a statistical value of 1.3, and for $Pd_{80}Cu_{20}$−H the corresponding coordination numbers were 3.1 vs 2.4. Given the typical imprecision in these coordination numbers, this difference is probably not statistically significant in the former case, but in the latter it is, and is consistent with the copper being confined to the interior of the particles, leaving palladium correspondingly enriched in the surface layer. An alternative explanation involving phase separation of Cu and Pd in the same particle is unlikely on thermodynamic grounds, as the metals form an exothermic alloy. The presence of separate clusters of Pd and Cu is ruled out on the basis of the EDAX analysis. The mean Cu−Cu coordination number thus reflects the higher concentration of copper resulting from its confinement to an effectively smaller volume. These conclusions are consistent with the diagnostic infrared spectroscopy of adsorbed CO on these colloidal alloy compositions described above, which showed the absence of detectable amounts of surface copper.

EXAFS Analysis of $Pd_{90}Cu_{10}$−P. As in the case of the “homogeneous” colloidal alloys, the composition of the copper coordination sphere and the value of the Cu K-edge energy show clearly that the copper is zerovalent and is internal to the particle. In this case the total coordination number of each element was again allowed to vary in the fitting procedure, and thus there is significance to the result that the total coordination number for copper is significantly higher than that for palladium, again consistent with the constraining of the copper to the interior of the particles. The location of the copper in the “plated” particles can also be concluded from the fact that the Cu−Cu coordination number of 2.7 is not only higher than that predicted for a statistical distribution in an ideally homogeneous matrix of the same composition (1.2), but is also higher than that found for $Pd_{90}Cu_{10}$−H, the “homogeneous” case, (1.8) in which copper is dispersed throughout the (interior) sites of the alloy particle. Indeed it is closer to that predicted for a uniform $Pd_{80}Cu_{20}$ alloy (2.4), and we interpret the elevated number of Cu−Cu contacts as evidence for the arrested diffusion of the plated copper into the underlying palladium particle, giving a radial copper concentration profile with a maximum in the immediate subsurface layers. This results in the confinement of the copper to an even smaller volume than that occupied in the palladium surface-segregated $Pd_{90}Cu_{10}$−H colloid, and a correspondingly higher Cu−Cu coordination number.

The combined EXAFS and XANES results also confirm that the copper in these dilute palladium−copper alloy colloids is zerovalent and internal to the particle, as previously concluded on the basis of infrared spectroscopy of adsorbed CO.[18] The reactivity of Cu(II) toward Pd(0) surfaces is confirmed, and the pathway from colloidal palladium to the final PdCu alloy particle has been delineated. The fact that Cu(II) is reduced to the zerovalent state by colloidal palladium has significant precedent in the extensive literature on the phenomenon of electroless plating of copper catalyzed by colloidal palladium.[44−50] In these systems Pd(II) is reduced to Pd(0) by Sn(II) and stabilized in colloidal form by adsorbed $[SnCl_3]^-$. Adsorption of the colloidal palladium, which has a particle size of ca. 20 Å, onto a substrate (such as a printed circuit board), exposure to an accelerator to remove adsorbed $[SnCl_3]^-$ and finally immersion in a Cu(II) solution containing a reducing agent results in the catalytic reduction of copper metal

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at the Pd printed sites. The chemistry of the initial stage of this redox reaction, which is now well established, provides a strong analogy to the present system, in which either the solvent alcohol or its corresponding aldehyde (formed during reduction of Pd(II)) act as the reducing agent.

It is possible that the formation of a copper rich interior in these alloy particles might result not only from the dissolution of the surface copper atoms in the underlying palladium matrix but also from the redeposition of oxidized palladium ions back onto the surface of the alloy particles during the plating reaction. However, we have shown previously that a redistribution of copper and palladium atoms in the near-surface region of nanoscale PdCu particles is a facile process, and we therefore prefer the former explanation for the composition profile of the "plated" alloy colloid.

These results confirm the preference of palladium for surface sites in nanoscale PdCu alloys with palladium-rich compositions, even in the absence of a strongly perturbing adsorbate such as CO, a ligand known to cause the segregation of group 10 metals in group 10−11 alloys.[51,52] Given the energetics of copper−palladium alloy formation (the heat of solution of copper in palladium is ca. −0.4 ev),[53] it is reasonable that at low copper compositions there will be a strong driving force for dissolution of copper into palladium to maximize CuPd bond formation by gaining the highest possible coordination number for copper atoms with palladium. However, as the copper concentration increases, copper−copper contacts become more numerous and above a critical concentration copper will take up surface sites to maintain the highest possible CuPd coordination throughout the whole particle. This is in agreement with our previous observation that below $Cu_{50}Pd_{50}$ very little copper is detectable on the surface of the PVP-stabilized colloidal alloy.

Consistent with these results, a theoretical study on very small PdCu particles [54] predicts the segregation of palladium to the surface of nanoscale clusters of the alloy and rationalizes the result on the basis of the preference of copper to maximize CuPd contacts, which it would accomplish by dissolution in the interior of the palladium rich matrix, at least up to a certain critical Cu concentration. There are various other experimental and theoretical reports of varying degrees of segregation of copper to the extended surface of bulk palladium copper alloys,[43,55−58] but in light of the known effect of adsorbates in perturbing the surface composition of alloys, it is not clear what one should predict for the composition of particles surrounded by an (albeit lightly) interacting polymer. Whatever the relative driving forces for segregation of the components in this system, it is obvious that in a small particle they will be especially potent, for the following simple reason. Segregation effects due to proximity to an alloy surface can be found several atomic layers into the bulk,[59,60] and so it is clear that the great majority of atoms in a nanoscale particle will be in the surface influenced region. The dependence of structure on composition in multicomponent systems, as described for the bulk by the phase diagram, means that surface and immediate subsurface structure will be affected by these deviations in composition profile, and therefore that a structural description of the near surface region will be complex. In considering the probable structure of nanoscale alloys, no assumptions can be made about either their structures or the stoichiometry of their surfaces prior to experimental investigation.

The mobility of the copper atoms is worthy of comment. It is clear that even under the mild conditions of copper deposition, copper atoms can readily diffuse into the palladium lattice. Interdiffusion of metal adlayers and substrates has been the subject of much research, as this phenomenon can have a deleterious effect on devices that rely on well-defined multilayer structures.[61] It is known from these studies that a metallic adlayer can diffuse over length scales of the order of 1 μm at temperatures well below the melting point of the metal. For example the mutual interdiffusion of copper and palladium over these considerable distances, which amount to thousands of atomic diameters, has been reported at temperatures as low as 400 °C.[62] The intermixing of gold and silver by the deposition of gold on Ag(110) at submonolayer coverages at room temperature has also been observed.[63] In view of the small size of the colloidal alloy particles in our study, which results in the majority of atoms being within a few atomic layers of the surface, it is not surprising that the positional exchange between surface and subsurface layers can be established under mild conditions, and it suggests that complete equilibration should be possible at relatively low temperatures.

The deposition of one metal at the surface of a second colloidal metal is a potentially fruitful approach to the controlled synthesis of catalyst surfaces with controlled stoichiometries. The careful selection of precursors and deposition conditions is necessary, but by using this approach, a number of potentially interesting colloidal bimetallics should be accessible. For example, the plating of copper on ruthenium should give a much better defined surface stoichiometry than the PdCu case, since copper and ruthenium are immiscible in the bulk. The preparation of this and other colloidal binary alloys are under current investigation using this chemistry.

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