Structural Investigation of Ag−Pd Clusters Synthesized with the Radiolysis Method

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Introduction

Radiolysis of aqueous solutions is an efficient method to reduce metal ions and form homo- and heteronuclear clusters of transition metals.[1−5] In the radiolysis method, aqueous solutions are exposed to γ-rays, eq 1, to create solvated electrons, e_{aq}^-.[2] These solvated electrons, in turn, reduce the metal ions, as shown in eqs 2 and 3. The metal atoms eventually coalesce to form aggregates as shown in eq 4.

$$H_2O \xrightarrow{\gamma\text{-radiation}} e_{aq}^-,\ H_3O^+,\ H^\bullet,\ OH^\bullet,\ H_2O_2 \qquad (1)$$

$$e_{aq}^- + M^{m+} \rightarrow M^{(m-1)+} \qquad (2)$$

$$e_{aq}^- + M^+ \rightarrow M_0 \qquad (3)$$

$$nM_0 \rightarrow M_2 \rightarrow \ldots \rightarrow M_n \qquad (4)$$

In a previous work, we successfully synthesized mono- and bimetallic clusters containing Ag, Au, Pd, and Pt.[6] In our experiments, we developed a variation of the radiolysis method, where a nuclear reactor was employed instead of an intense γ-ray source. In this paper we extended our work and synthesized Ag−Pd alloy clusters for several Ag/Pd ratios. The clusters were characterized with transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). These techniques showed that the synthesized clusters have face-centered cubic (fcc) crystalline structure and are virtually free of contamination. The lattice constant of the Ag−Pd clusters was calculated from selected area diffraction measurements and was found to depend linearly on Ag composition (Vegard's law). This result indicates formation of homogeneous alloys and is in good agreement with previous work by Remita et al.,[4] where Pd−Ag alloy formation was inferred from changes in optical absorption as a function of the Ag/Pd ratio.

Experimental Section

Aqueous solutions[7] were prepared out of chemical grade Ag_2SO_4, $PdSO_4$, 2-propanol, and poly(vinyl alcohol) (PVA, average molecular weight 86 000), all purchased from Alfa Aesar. Solutions had a total metal ion concentration between 10^{-4} and 2×10^{-3} mol·L^{-1} at various Ag−Pd ratios. 2-Propanol was added to scavenge the H$^\bullet$ and OH$^\bullet$ radicals generated during irradiation, eq 1. PVA was added as a surfactant at a (polymer) concentration between 5×10^{-5} and 9×10^{-5} mol·L^{-1}. To prevent formation of palladium hydroxide, the solutions were made acidic (pH $\approx$ 2) by adding H_2SO_4. The solutions were deaerated by bubbling N_2 prior to irradiation. Due to their photosensitivity, the solutions were stored in the dark after preparation.

The samples were irradiated with γ radiation from the fission products of the campus' nuclear reactor.[8] The irradiation procedure was as follows. The reactor was operated at 180 kW for about 1 h, and the samples were placed in front of the core 1 h after reactor shutdown to prevent neutron bombardment and activation of the samples. The samples were exposed to total doses of up to about 2 kGy. This total dose corresponded to a 100% metal ion reduction for the solutions with metal concentration of 10^{-4} mol·L^{-1}, and about 20% metal ion reduction for the solutions with metal concentration of 2×10^{-3} mol·L^{-1}.[1,7] Due to the decay of the fission products, dose rates decreased from an initial value of about 1 kGy h^{-1} to about 0.4 kGy h^{-1} at the end of the irradiation period (typically 2−3 h). After irradiation, the solutions were limpid, and no precipitates were detected.

The synthesized clusters were characterized with TEM. Samples for analysis were prepared by evaporating under N_2 a drop of suspension onto a carbon-coated copper grid. The electron microscope (Philips EM430T) was operated at 300 kV, and the images were magnified about 88 600 times. Electron diffraction was used to characterize cluster structure and determine lattice parameters. Local chemical composition was determined with EDS.

Results and Discussion

The synthesized clusters gave rise to a wide variety of structures, which were found to be dependent on metal and polymer concentration, and the degree of metal ion reduction. Figure 1a shows a typical bright field micrograph obtained for a metal concentration of 2×10^{-3} mol·L^{-1} and a PVA concentration of 9×10^{-5} mol·L^{-1}. The total dose was 2 kGy. In Figure 1 a we notice several isolated particles of diameter between about 2 and 7 nm and a chainlike structure originated by the coagulation of clusters of average size of 26 nm. Formation of large particles is characteristic of suspensions where the metal was not completely reduced during irradiation, as in the case of the sample of Figure 1a. Metal ions remaining in suspension are slowly reduced by the alcohols of the solution and stick preferentially to preformed metal clusters.[2] Figure 1b shows a typical bright field micrograph obtained for a metal concentration of 1×10^{-4} mol·L^{-1}, and a PVA concentration of 5×10^{-5} mol·L^{-1}. The total dose was 2 kGy. The particles are smaller, and less coagulated, than those shown in Figure 1a.

Cluster chemical composition was measured with EDS, and a representative spectrum is reported in Figure 2a. Besides Ag and Pd, we could detect some residual sulfur contamination (<6% for all samples), while oxygen was below detection limit. Other peaks in Figure 2a originate from the support grid (C, Cu), or the EDS detector (Si). In most samples, we detected local variations of the Ag/

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(8) University of Missouri−Rolla's reactor is a pool reactor with a maximum power of 200 kW that employs ^{235}U fuel rods.

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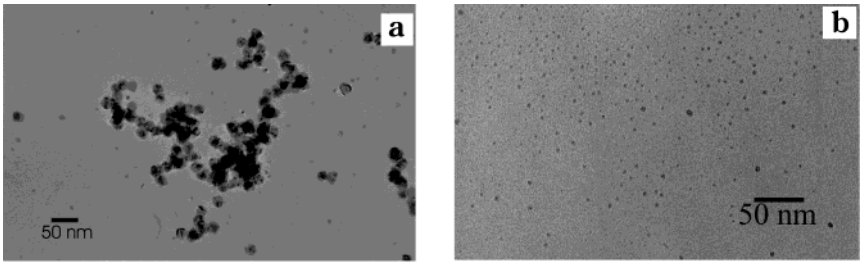

Figure 1. (a) TEM image of 53% Ag, 47% Pd clusters. Metal concentration was 2×10^{-3} mol·L^{-1}; PVA concentration was 9×10^{-5} mol·L^{-1}. (b) TEM image of 76% Ag, 24% Pd. Metal concentration was 1×10^{-4} mol·L^{-1}; PVA concentration was 5×10^{-5} mol·L^{-1}. Total dose was 2 kGy for both samples.

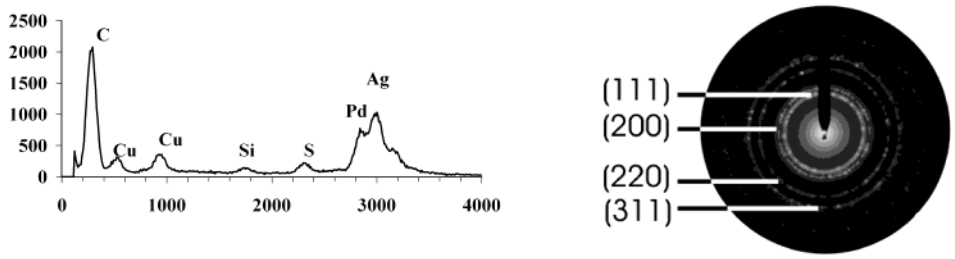

Figure 2. (a) Selected area electron diffraction (SAED) of the clusters in Figure 1a. (b) EDS analysis of Figure 1a. The Cu and C peaks are signatures of the support grid, while Si is from the detector. Sulfur contamination was below 6% in all cases.

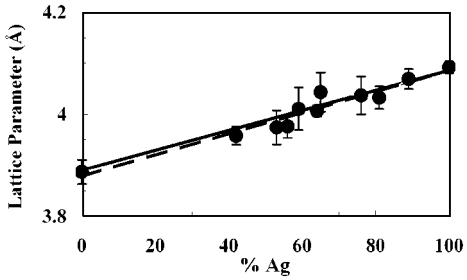

Figure 3. Dependence of lattice parameter of Ag/Pd clusters on Ag concentration. The solid line is the theoretical value (Vegard's law) and the dashed line is a linear fit to the data. Lattice parameters were calculated by measuring the diameters of the innermost four to six diffraction rings. The error bars represent one standard deviation of a calculated lattice constant for a particular concentration.

Pd ratio. For example, the sample in Figure 1a was prepared out of a solution with a nominal Ag 30%−Pd 70% ratio, but EDS yielded 53% Ag (Figure 2a). In other spots on the grid, the Ag/Pd ratio was closer to that of the initial solution. For sample 1b, nominal concentration was 80% Ag, while EDS analysis yielded 76% Ag. Local variations of the composition have been reported for other systems, such as Ag/Au.[2]

Electron diffraction was measured in the same region characterized with EDS. Figure 2b shows electron diffraction patterns taken from the same region of Figure 2a. Debye−Scherrer rings are well evident. These rings can be reconciled with fcc structures,[11] and the indexing is reported in Figure 2b.

Lattice constants were calculated from the diameter of the four to six innermost rings using a diffraction processing program.[9] The calculated lattice constants are reported in Figure 3 as a function of Ag concentration as determined by EDS. The error bars of Figure 3 arise mainly from the low cluster density of several of the samples. This low cluster density originated only a few diffraction spots for each ring and induced large uncertainties in the determination of the diameters. These errors not withstanding, the data points of Figure 3 are in good agreement with Vegard's law (solid line in Figure 3). The best-fit line through the data points (dashed line in Figure 3) also does not deviate from Vegard's law by more than 0.5% for clusters with up to about 40% Ag concentration, which confirms our conclusion.

Conclusions

Radiolysis allows the synthesis of crystalline Ag and Pd bimetallic clusters. At our dose rates, homogeneous alloy clusters are formed, albeit with a pronounced variability in size and concentration. The lattice parameter was measured for several Ag−Pd ratios and was found to closely follow Vegard's law, a strong indication of homogeneous alloy formation.

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