The synthesis and characterization of PdCu bimetallic nanoparticles and Pd and Cu monometallic nanoparticles, consisting of an average of ~64 atoms, is described. The bimetallic nanoparticles were prepared by cocomplexation of Pd$^{2+}$ and Cu$^{2+}$ to interior functional groups of a sixth-generation poly(amidoamine) dendrimer template, followed by chemical reduction to yield dendrimer-encapsulated nanoparticles (DENs). Extended X-ray absorption fine structure (EXAFS) spectroscopy indicates that the particles have an alloy structure. TEM studies indicate particle diameters of 1.2–1.3 nm. This is a rare example of a stable nanoparticle in this size range that consists of one reactive metal and one substantially more noble metal. Such materials are predicted by first-principles theory to have interesting catalytic properties.

### Conclusion

The synthesis of metallic nanoparticles via dendrimer templating has previously been used by our group and others to prepare well-defined monometallic and bimetallic DENs consisting of Pt$^{6–14}$ Cu,$^5$ Au$^{16–20}$ Pd,$^{12,14,21–27}$ synthesizing and characterizing very well-defined nanoparticles whose electrocatalytic properties can be directly compared to theory.

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### References


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X-ray Absorption Study of PdCu Bimetallic Alloy Nanoparticles Containing an Average of ~64 Atoms

Sue V. Myers, † Anatoly I. Frenkel,*‡ and Richard M. Crooks*⁺

The nanoparticles discussed here were prepared by cocomplexation of Pd$^{2+}$ and Cu$^{2+}$ to interior functional groups of a dendrimer template, followed by chemical reduction to yield dendrimer-encapsulated nanoparticles (DENs). Extended X-ray absorption fine structure (EXAFS) spectroscopy indicates that the particles have an alloy structure. TEM studies indicate particle diameters of 1.2–1.3 nm. This is a rare example of a stable nanoparticle in this size range that consists of one reactive metal and one substantially more noble metal. Such materials are predicted by first-principles theory to have interesting catalytic properties.

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PtPd,28,29 PdRh,30 PdAu,5,31 PtCu,32 and AuAg.5 This technique has proven to be a powerful means for synthesizing nanoparticles containing less than 250 atoms and that are tailored to specific sizes and compositions not accessible by standard methods. Bimetallic particles can be engineered to have either a core—shell or alloy structure depending on the synthesis method used and the types of metals.

There has been one previous study of unsupported PdCu nanoparticles in the size range relevant to the present report. Specifically, Asakura and co-workers used EXAFS to characterize the structure of polymer-stabilized PdCu alloy nanoparticles dispersed in a glycol solution.33 A preference for heterobond formation between the two metals was observed. There has also been one EXAFS study of supported PdCu bimetallic nanoparticles having diameters in the 2–6 nm range.34 These materials were prepared by either an atomic layer epitaxy technique or by coimpregnation of the metals onto SiO2 and γ-Al2O3 supports. The results indicated that the structure of the particles was dependent on the properties of the support: nanoparticles prepared on silica substrates had an alloyed structure whereas particles on alumina exhibited surface segregation of the Cu.

In the present study, Pd2+ and Cu2+ salts were added to a dilute solution of sixth-generation, hydroxyl-terminated poly(amidoamine)(PAMAM) dendrimers (G6-OH) at five different ratios of Pd2+/Cu2+. The total metal-ion-to-dendrimer content was fixed at 64:1, because this ratio represents the maximum loading of Cu2+ ions into the interior of G6-OH PAMAM dendrimers.15 UV—vis absorption spectra indicate complete complexation of the metal salts to the dendrimer. The metal-ion/dendrimer precursor complex was reduced with NaBH4, which yielded DENs having diameters in the range of 1.2–1.3 nm as measured by TEM. The coordination environments of the two metals were measured by EXAFS and fit those of an alloy structure. The particle size was also estimated from the EXAFS data and was found to be in good agreement with the TEM results.

**Experimental Section**

**Chemicals.** G6-OH dendrimers in methanol were purchased from Dendritech, Inc. (Midland, MI). The methanol was removed by vacuum evaporation at 23 ± 3°C prior to use, and either a 100 or a 500 μM aqueous stock solution was prepared. K2PdCl4 and NaBH4 were purchased from Sigma-Aldrich. CuSO4 was purchased from Fisher Scientific. All chemicals were used without further purification; 18 MΩ·cm Milli-Q deionized water was used to make all solutions.

**Synthesis of DENs.** Bimetallic DENs having different ratios of Pd/Cu are denoted as G6-OH(Pd/Cu)64–x complexes. (a) UV—vis absorbance spectra were obtained using a Hewlett-Packard HP8453 spectrometer and a 1.00 cm optical path length quartz cuvette. A solution of G6-OH in water was used as the background. (b) Spectra of the G6-OH(Pd/Cu)64–x complexes after reduction with NaBH4. (c) Optical path length of the cuvette was 1.00 cm. 2.0 μM G6-OH was used as the background.

The synthesis method used for background correction. TEM images were collected using a JEOL-2010F TEM operating at 200 kV. Images were collected in transmission, as
as well as high-angle annular dark field (HAADF) mode. TEM grids were prepared by dropping several microliters of a 2 μM DEN solution onto a carbon-coated 400-mesh Cu grid (EM Sciences) and drying in air.

EXAFS data were collected on beamline X18b at the National Synchrotron Light Source at the Brookhaven National Laboratory in New York; 100 μM solutions of freshly reduced DENs were placed in 1 cm thick solution cells having Kapton tape windows. The K absorption edges of Pd and Cu were measured simultaneously in transmission and fluorescence modes, by orienting the sample 45 degrees relative to the beam. A five-grid Lytle detector filled with Ar gas was used for fluorescence detection, and in the case of the Cu K-edge, Soller slits and a Ni filter were used. At least two and as many as eight, energy scans were averaged to improve the signal-to-noise ratio. Pd and Cu foil reference spectra were collected concurrently with the DENs spectra at the Pd and Cu K-edge, respectively, and were used for energy calibration. The data were analyzed using the IFEFFIT software package and FEFF6 program.35,36 The details of our data modeling procedure for monometallic and bimetallic systems are presented below.

Results and Discussion

UV-vis Analysis of Cu, Pd, and PdCu DENs. Figure 1a shows UV-vis absorption spectra of 2.0 μM aqueous solutions of G6-OH(Pd2⁺)₆₄(Cu2⁺)₆₄₋ₓ (x = 64, 48, 32, 16, 0) before reduction with BH₄⁻. The DEN precursor solutions exhibit strong absorption bands at ~230 and 290 nm and an isosbestic point at 261 nm. These peaks arise from ligand-to-metal charge-transfer (LMCT) bands associated with the dendrimer/metal-ion complexes.15,26 Pd²⁺ salts not associated with the dendrimer absorb in this region, and therefore, the presence of an isosbestic point implies that all of the Pd²⁺ salts have complexed to the dendrimer interior. The absorbance data for G6-OH(Cu²⁺)₆₄ and G6-OH(Pd²⁺)₆₄ are comparable to previously published results.15,26

The optimal pH range for complexation of the metal salts to the dendrimer was found to be between 7 and 8. Complexation of Cu²⁺ is pH dependent due to competition of H⁺ for binding sites at low pH.37,38 At high pH

Figure 2. (a) Bright-field TEM micrograph and (b) HAADF STEM micrograph for G6-OH(Pd₃₂Cu₃₂). Particle size distribution for (c) Pd monometallic and (d–f) PdCu bimetallic DENs.

values, loss of Pd from the complex is observed. In the pH range used for this study, the absorbances of the LMCT bands of the bimetallic precursors are proportional to the mole ratios of Pd\(^{2+}\) and Cu\(^{2+}\) present in the dendrimers (Figure 1b). This finding provides additional evidence that the metal ions completely bind to the dendrimer.

Following chemical reduction of the G6-OH(Pd\(^{2+}\))\(_x\)-(Cu\(^{2+}\))\(_{64-x}\) complexes, the LMCT bands are replaced by broad, monotonically decreasing bands (Figure 1c) characteristic of interband transitions of spherical metal nanoparticles.\(^{39}\) The irregular behavior below 230 nm is caused by the high absorbance of the dendrimer in this region. The absence of a plasmon at 570 nm in the monometallic copper sample indicates a particle diameter below the uncertainty of the fit, and therefore, they were constrained to be the same as measured from each DEN.

EXAFS Fitting Procedure. The fits were constrained to include only the first coordination shells. This eliminates all multiple scattering effects and significantly reduces the number of independent variables. S\(^0\) values were taken from fits to Pd and Cu reference foil data collected under similar conditions on beamline X18b. A k-weight of 2 was used for all fits.

Metal–metal (M–M) and metal–low Z (M–E, E = C, O, N) interactions were included in the preliminary simulations. Cu–E interactions were found to be well below the uncertainty of the fit, and therefore, they were not included in the final models for the Cu edge of the monometallic and bimetallic DENs. The CNs for Pd–E (n\(_{\text{PdE}}\)) are close to the uncertainty level of the fits for all DENs studied, but better fit values consistently resulted when Pd–E interactions were included. Further studies would be required to meaningfully quantify low-Z coordination to Pd.

The data from both metal edges of the bimetallic materials were fit simultaneously. The Pd–Cu (n\(_{\text{PdCu}}\)) and the Cu–Pd CNs (n\(_{\text{CuPd}}\)) were fixed according to eq 1.\(^{41}\)

\[
n_{\text{PdCu}} = \frac{z_{\text{Cu}}}{z_{\text{Pd}}} n_{\text{CuPd}}
\]

The heterometallic bond lengths and Debye–Waller factors were also constrained to be the same as measured from each edge (Pd or Cu).

Table 1. Fitting Parameters for PdCu DENs

<table>
<thead>
<tr>
<th>G6-OH</th>
<th>n(_{\text{CuCu}})^a</th>
<th>n(_{\text{CuPd}})^b</th>
<th>n(_{\text{PdCu}})^b</th>
<th>n(_{\text{PdPd}})^b</th>
<th>r-range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(_{64})</td>
<td>7.1 ± 0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(<em>{16})Cu(</em>{48})</td>
<td>4.2 ± 0.8</td>
<td>1.3 ± 0.4</td>
<td>3.5 ± 2.0</td>
<td>1.9 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>Pd(<em>{32})Cu(</em>{32})</td>
<td>3.0 ± 1.1</td>
<td>3.1 ± 0.5</td>
<td>4.1 ± 1.3</td>
<td>0.8 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Pd(<em>{48})Cu(</em>{16})</td>
<td>0.9 ± 0.7</td>
<td>4.8 ± 1.9</td>
<td>4.0 ± 1.4</td>
<td>1.4 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>Pd(_{64})</td>
<td>6.5 ± 0.4</td>
<td>6.5 ± 0.4</td>
<td>0.2 ± 0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Number of independent data points. \(^{b}\)Number of fit variables.

Table 2. First-Shell Coordination Numbers for PdCu DENs

<table>
<thead>
<tr>
<th>G6-OH</th>
<th>n(_{\text{CuCu}})</th>
<th>n(_{\text{CuPd}})</th>
<th>n(_{\text{PdCu}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(_{64})</td>
<td>7.1 ± 0.4</td>
<td>7.1 ± 0.4</td>
<td>7.1 ± 0.4</td>
</tr>
<tr>
<td>Pd(<em>{16})Cu(</em>{48})</td>
<td>4.2 ± 0.8</td>
<td>1.3 ± 0.4</td>
<td>3.5 ± 2.0</td>
</tr>
<tr>
<td>Pd(<em>{32})Cu(</em>{32})</td>
<td>3.0 ± 1.1</td>
<td>3.1 ± 0.5</td>
<td>4.1 ± 1.3</td>
</tr>
<tr>
<td>Pd(<em>{48})Cu(</em>{16})</td>
<td>0.9 ± 0.7</td>
<td>4.8 ± 1.9</td>
<td>4.0 ± 1.4</td>
</tr>
<tr>
<td>Pd(_{64})</td>
<td>6.5 ± 0.4</td>
<td>6.5 ± 0.4</td>
<td>0.2 ± 0.2</td>
</tr>
</tbody>
</table>

The small size of these ∼64-atom PdCu DENs, in conjunction with the low mass of Cu, make it difficult to obtain high-quality, bright-field TEM images. Therefore, particle diameters were estimated from HAADF-STEM micrographs. Due to their instability in air, it was not possible to obtain TEM images of monometallic DENs. Figure 2a and b shows representative TEM images of the G6-OH(Pd\(_{32}\)Cu\(_{32}\)) particles. Theoretical particle sizes are estimated to be 1.4 and 1.3 nm for monometallic Pd and Cu particles, respectively, assuming a spherical geometry. Histograms of the measured particle diameters are provided in Figure 2c–f, and they indicate that the measured particle diameters are just slightly smaller (1.2–1.3 nm).

If the DENs are stored in a reducing atmosphere, such as a H\(_2\)-saturated aqueous solution, they are stable and their absorbance spectra do not change as a function of time. However, on nonreducing environments, like air-saturated water, result in partial DEN oxidation and gradual regrowth of the LMCT bands. This observation is consistent with previous studies, although the exact mechanism of oxidation is not fully understood. Dry Pd DENs are stable in the presence of air, but Cu DENs oxidize in air even when dry.

**TEM Analysis of Pd and PdCu DENs.** The small size of these ∼64-atom PdCu DENs, in conjunction with the low...
EXAFS Analysis of Monometallic Pd and Cu DENs. As discussed earlier, G6-OH(Pd$_{48}$Cu$_{16}$) DENs are only stable in reducing environments. Therefore, to prevent oxidation of the DENs during EXAFS experiments, the precursor complexes were reduced with NaBH$_4$ immediately prior to data collection. In addition to reducing the precursor ions to DENs, NaBH$_4$ also slowly reduces water to H$_2$. The presence of H$_2$ in the DEN solutions throughout the period required to obtain EXAFS spectra, as evidenced by continuous bubble formation, ensured the integrity of the DENs. Indeed, UV−vis spectroscopy experiments carried out under nearly identical conditions to those used at the beamline confirmed that no regrowth of the LMCT bands occurred. More significantly, the EXAFS analysis, discussed later, indicates minimal oxide formation under these conditions.

Because the samples are maintained in a reducing environment, Pd hydride formation is possible. The Pd−Pd bond lengths were measured at 2.78 Å, a 1.1% expansion over the bulk value for metallic Pd. This is consistent with the formation of the hydride in particles of this size. However, the bimetallic nanoparticles did not exhibit this behavior (Table S1, Supporting Information).

Figure 3 shows the measured EXAFS data for the monometallic Pd and Cu DENs and theoretical fits of the first nearest neighbor contributions. The selected k-ranges and r-ranges for each edge as well as the number of variables from each fit are given in Table 1. The coordination numbers (CNs) obtained from the fits, together with their 95% confidence limits (error bars) are presented in Table 2.

The total metal−metal CN ($n_{MM}$) can be used to estimate the size of DENs, because as particle size decreases the ratio of low-coordination surface atoms to interior atoms increases and therefore the total metal−metal coordination decreases. Such method can be used only if independent information about the particle shape is available, as in our case, where it is known that the particles are quasi-spherical. The cuboctahedron cluster family was chosen to model CNs, because the values can be easily calculated for different cluster orders.

The Pd and Cu monometallic DENs have $n_{MM}$ values of 6.5 ± 0.4 and 7.1 ± 0.4, respectively. The theoretical fcc cuboctahedron first shell $n_{MM}$ values for 13-, 55-, and 215-, are 6.5, 7.1, and 8.3, respectively. The agreement between the experimental and theoretical $n_{MM}$ values is striking, indicating that the cuboctahedron is a good model for the shape of these DENs.

Figure 4 shows the EXAFS data and fit results for the (a) Pd K edge and (b) Cu K edge of G6-OH(Pd$_{48}$Cu$_{16}$), (c) Pd K edge and (d) Cu K edge of G6-OH(Pd$_{32}$Cu$_{32}$), and (e) Pd K edge and (f) Cu K edge for G6-OH(Pd$_{16}$Cu$_{48}$). The data are plotted in black and the simulated fits are in red.

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palladium ions. As shown in Figure 5a, the palladium ions
are shown in Figure 4. The CNs obtained for all types (AM and
BM) of interactions are different) or the homogeneous
alloy structure (when they are similar, within
the uncertainty of the fits. Accordingly, it is not
possible to distinguish a completely random and homo-
neous alloy from an alloy having either a Pd- or Cu-
rich core.

**Summary and Conclusions**

We have reported on the synthesis and characterization of
Pd and Cu monometallic and PdCu bimetallic nano-
particles prepared within G6-OH dendrimer templates.
Bimetallic nanoparticles, such as those described here, are
predicted by theory to have desirable catalytic proper-
ties. The UV–vis, TEM, and EXAFS data for these
PdCu DENs are consistent with their size corresponding
to an average of ~64 atoms. Moreover, for the bimetallic
DENs, the results indicate at least partial alloying of the
two metals although the degree of alloying cannot be
determined.

The ability to synthesize and characterize nearly mono-
disperse and fully stable particles in this size regime is
important to our larger goal of correlating the size,
composition, and structure of DENs to their catalytic
function. Specifically, we are presently studying the kin-
etics of the electrochemical oxygen reduction reaction
using these bimetallic PdCu DENs as electrocatalysts.
These experimental results will be correlated to first-
principles theory, with a view toward unification of theory
and experiment. The results of that work will be
reported in due course.

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The University of Texas at Austin.

**Supporting Information Available.** Parameters from the fits of the EXAFS data (PDF). This material is available free of charge
via the Internet at http://pubs.acs.org.