Intradendrimer Exchange of Metal Nanoparticles

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We previously demonstrated that metal nanoclusters ranging in size from 1 to 2 nm can be prepared within dendrimer templates. In this two-step synthesis, metal ions (for example, Cu^{2+}, Pd^{2+}, and Pt^{2+}) first partition into the interior of, for example, a hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimer, and then the resulting nanocomposite is reduced with BH_4^- to yield a dendrimer-encapsulated, zerovalent metal nanocluster. The critical step in this procedure is partitioning of a particular number of metal ions into the dendrimer interior. This process is normally driven by strong association of metal ions with intradendrimer tertiary amine groups. However, for metal ions that do not form either covalent bonds or strong complexes with the interior amine groups (for example, Au^{3+} and Ag^+), an alternative procedure is required. Here we report that dendrimer-encapsulated metal nanoclusters can undergo multiple, in-situ displacement reactions. For example, a 55-Cu-atom-containing sixth-generation PAMAM dendrimer ($G6\text{-}OH(Cu_{55})$) can be prepared by direct BH_4^- reduction of the corresponding Cu^{2+}-containing dendrimer. When $G6\text{-}OH(Cu_{55})$ is exposed to a solution containing ions more noble than Cu, the Cu is displaced and the more noble ions are reduced. Here we show that Ag, Au, Pd, and Pt dendrimer-encapsulated metal particles can be prepared by this sort of primary displacement reaction. Such reactions are fast and go to completion, and the resulting particles are stable (no agglomeration or precipitation) and small (1–3 nm in diameter) and can be relatively monodisperse. Moreover, depending on the pH at which the displacement is carried out, the displaced Cu^{2+} ions may be retained within the dendrimer interior. Au, Pt, and Pd nanoparticles can be also prepared by a secondary displacement reaction between dendrimer-encapsulated Ag nanoclusters (prepared from a primary displacement reaction) and Au^{3+}, Pt^{2+}, or Pd^{2+} ions, respectively. Pd and Pt dendrimer-encapsulated nanoparticles prepared by direct reduction, as well as by primary or secondary displacement reactions, are catalytically active for electrochemical reduction of O_2. The materials resulting from this study are characterized by UV–vis spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscopy, and electrochemical methods.

Introduction

We previously showed that metal nanoclusters ranging in size from 1 to 2 nm could be prepared within dendrimer templates.[1–4] For example, when Cu^{2+} is mixed with a fourth-generation, hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimer (G4-OH), up to 16 Cu^{2+} ions may partition into the dendrimer interior. Upon chemical reduction of such nanocomposites with BH_4^-, the intradendrimer ions are reduced to a zerovalent metal cluster.[1] Very similar chemistry leads to Pt and Pd nanoclusters.[2,3] In this approach to nanocluster synthesis the dendrimer acts as a template to hold a particular number of ions in close proximity prior to reduction and subsequently as a nanoporous stabilizer to prevent particle agglomeration. We have taken advantage of these findings to prepare nearly monodisperse dendrimer-encapsulated Pt and Pd nanoclusters that act as homogeneous[2] and heterogeneous[3] catalysts. Moreover, we recently discovered that dendrimer-encapsulated nanoparticles can be solubilized in virtually any solvent by controlling the end-group chemistry of the dendritic host.[4]

In the examples cited above, metal ions partition into the dendrimer because of a strong ionic or covalent interaction with interior amines. Accordingly, this approach is successful for those metal ions that have a high affinity for amine coordination. To implement this same direct-reduction approach for ions that only weakly coordinate with amines would require the use of dendrimer families having different interior functional groups. However, at the present time only the PAMAM and poly(propyleneimine) dendrimer families are commercially available, and thus for routine use of these interesting new materials an alternative strategy is required.

Here, we demonstrate a new means for preparing dendrimer-encapsulated nanoclusters, which involves in-situ exchange of a dendrimer-encapsulated metal

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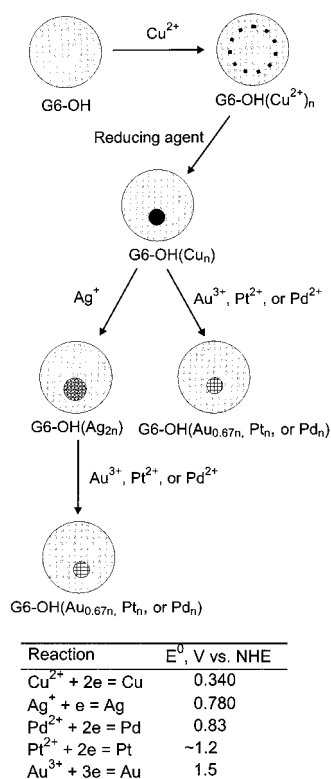
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Scheme 1

Reaction	E^0, V vs. NHE
$Cu^{2+} + 2e = Cu$	0.340
$Ag^+ + e = Ag$	0.780
$Pd^{2+} + 2e = Pd$	0.83
$Pt^{2+} + 2e = Pt$	~1.2
$Au^{3+} + 3e = Au$	1.5

particle for a different, more noble metal. For example, Cu clusters can be displaced by Ag, Au, Pt, or Pd, and Ag clusters can be replaced by Au, Pt, or Pd (but not Cu) (Scheme 1).[5] Thus, this method can yield the types of nanoparticles we have previously prepared by direct reduction of the corresponding ions (Pd and Pt), but more importantly some metals that cannot be prepared by direct reduction can be made using this indirect metal-exchange method (Ag or Au). Moreover, this approach can lead to composite materials in which metal particles and chemically distinct metal ions coexist within individual dendrimers; such materials may have unique properties for some applications such as catalysis. Finally, as we will show in a forthcoming paper, this method can also be used to prepare bi- or trimetallic particles which are important materials for a wide range of catalytic processes.[6–9] Such displacement reactions have previously been used to prepare the bimetallic sulfides of Pb−Cd and Zn−Cd.[10]

Experimental Section

Chemicals. Hydroxyl- and amine-terminated sixth-generation Starburst poly(amidoamine) (PAMAM) dendrimers having an ethylenediamine core (G6-OH) were obtained as 10−25% methanol solutions (Dendritech, Inc., Midland, MI). Prior to use, methanol was removed by rotary evaporation at room temperature. $Cu(NO_3)_2 \cdot 2.5H_2O$ (Acros Organics), $AgNO_3$ (J. T. Baker Inc.), $HAuCl_4 \cdot 3H_2O$ (Sigma Chemical), K_2PtCl_4 (Aldrich), K_2PdCl_4 (Aldrich), $NaBH_4$ (EM Science), ethylenediamine (Aldrich), and triethylamine (Aldrich) were of reagent quality or better and used as received. All solutions were prepared with 18 MΩ·cm deionized water (Milli-Q, Millipore, Bedford, MA). 2 M NaOH or 2 M $HClO_4$ was used to adjust the pH of solutions. Solutions used for preparation of samples for TEM, XPS, and electrochemical measurements were dialyzed against pH 3.0 Milli-Q water for 24 h. Cellulose membranes (Sigma-Aldrich) having a molecular weight cutoff of 12 000 were soaked in water for 30 min and rinsed with Milli-Q water thoroughly before dialysis.

Substrates. For XPS and electrochemical measurements substrates were prepared by electron-beam deposition of 10 nm of Ti followed by 200 nm of Au onto Si(100) wafers. Before use, wafers were rinsed with ethanol, dried in a flowing stream of N_2 gas, and then cleaned in a low-energy ozone cleaner for 10 min (Boekel Industries, Inc., model 135500).

Characterization. Absorption spectra were recorded on a Hewlett-Packard HP 8453 UV−vis spectrometer. The optical path length was 0.1 cm, and deionized water was used as a reference for all measurements. FTIR-external reflection spectroscopy (FTIR-ERS) measurements were made using a Digilab FTS-40 spectrometer equipped with a Harrick Scientific Seagull reflection accessory and a liquid-N_2-cooled MCT detector. The FTIR-ERS spectra were obtained at 4 cm^{-1} resolution using an average of 256 individual scans; p-polarized light was incident on the substrate at an angle of 84° with respect to the substrate normal.[11] High-resolution transmission electron micrographs (HRTEM) were obtained using a JEOL-2010 transmission electron microscope equipped with an EDAX energy-dispersive X-ray detector. The time duration for collecting spectra was 100 s. Samples were prepared by placing a drop of dilute, aqueous dendrimer solution on a holey-carbon-coated molybdenum TEM grid and allowing the water to evaporate in air. XPS data were acquired using a Perkin-Elmer PHI 5500 spectrometer and employing a pass energy of 29.35 eV, a step increment of 0.125 eV, and a Mg anode power of 400 W. The base pressure was less than 7×10^{-8} mmHg, and photoelectrons were detected at a 45° takeoff angle. Survey scans were acquired between 1100 and 0 eV, and high-resolution spectra were acquired for all metal samples. XPS peak positions were referenced to the Au(4f$_{7/2}$) peak at 83.8 eV. Samples for XPS measurements were prepared by soaking Au-coated Si wafers in aqueous solutions of dendrimers containing metal nanoparticles for 20 h, followed by careful rinsing and drying.

Cyclic voltammetric measurements were carried out using a BAS model 100B electrochemical analyzer (Bioanalytical System, Inc.). The three-electrode cell consisted of a five-necked round-bottomed flask fitted with a Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems) and a Pt−gauze counter electrode, which was separated from the main compartment by a porous glass plug. The working electrode was cut from a Au-coated Si(100) wafer and contained within a Teflon O-ring holder that exposed an area of 0.09 ± 0.009 cm^2. Electrochemical data were obtained in an aqueous electrolyte solution containing 0.1 M $NaClO_4$ or 1.0 M H_2SO_4. The $NaClO_4$ or H_2SO_4 solutions were purged with N_2 or O_2, respectively, for at least 30 min before making measurements. During cyclic voltammetry, N_2 or O_2 was passed through the solutions at the rate of about 2 bubbles/s. All experiments were carried out at 22 ± 2 °C.

Preparation of Dendrimer−Metal Nanocomposites by Displacement Reactions. A 0.01 mM dendrimer solution containing an average of 55 Cu^{2+} ions per dendrimer (G6-OH-$(Cu^{2+})_{55}$) was prepared from an aqueous stock solution containing 0.05 mM G6-OH (from solvent-free dendrimer) and 20 mM $Cu(NO_3)_2$. Prior to reduction, the pH of this solution was adjusted to 7.5 using 2 M NaOH. A 3-fold molar excess of

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NaBH$_4$ was introduced to this solution to reduce the dendrimer-encapsulated Cu^{2+} to the zerovalent metal (G6-OH-(Cu$_{55}$)). The pH of the resulting 0.01 mM G6-OH(Cu$_{55}$) solution was then adjusted to 3, using HClO$_4$, to decompose excess BH$_4^-$.[12] The G6-OH(Cu^{2+})$_{55}$ solution was purged with N$_2$ continuously starting 15 min prior to addition of BH$_4^-$ and continuing until 2 h after reduction. The following control experiment was carried out to ensure that the aforementioned procedure led to complete decomposition of BH$_4^-$. After adjusting the pH of a solution containing 0.01 mM G6-OH and 1.65 mM BH$_4^-$ to pH 3, 1 mL of a 10 mM AgNO$_3$ solution was added every 15 min. The UV–vis absorption spectra of these mixtures were recorded, and the absence of a Ag plasmon peak around 400 nm was taken as an indication that BH$_4^-$ had decomposed. The data indicated that decomposition was complete after 30 min. To ensure that the formation of more noble metal nanoparticles was a consequence of metal displacement, rather than direct BH$_4^-$ reduction, the second metal-ion solution was not added until 1 h after the pH of the 0.01 mM G6-OH(Cu$_{55}$) solution was decreased from 7.5 to 3.

Primary displacement reactions were carried out by adding a stoichiometric amount of AgNO$_3$, HAuCl$_4$, K$_2$PdCl$_4$, or K$_2$PtCl$_4$ to an aqueous 0.01 mM G6-OH(Cu$_{55}$) solution. A UV–vis spectrum was recorded 5 min after mixing. The pH of the solutions was adjusted to 7.5, and then the absorption spectra were recorded again. Secondary displacement reactions involved addition of a stoichiometric amount of HAuCl$_4$, K$_2$PdCl$_4$, or K$_2$PtCl$_4$ to a 0.01 mM, pH 7.5 G6-OH(Ag$_{\sim110}$) solution. UV–vis spectra were recorded 5 min after mixing.

Results and Discussion

We,[1-4] and later others,[13] showed that dendrimer-encapsulated metal nanoparticles can be prepared if the corresponding metal ions are extracted into the interior of a dendrimer and subsequently reduced. However, this approach is not suitable for encapsulation of Ag particles, because the equilibrium between PAMAM dendrimers and Ag$^+$ ions does not strongly favor the intradendrimer complex. For example, when an aqueous solution containing 1.10 mM AgNO$_3$ and 0.01 mM G6-OH was reduced with excess BH$_4^-$, the absorption spectrum indicated continuous growth of a Ag plasmon peak at 390 nm over a period of 12 h. After 16 h, Ag precipitated from solution, and after filtering with a 0.2 μm PTFE filter the plasmon band was completely absent from the absorption spectrum (see Supporting Information). The presence of the Ag plasmon peak at 390 nm, and particularly its growth as a function of time, clearly indicates that the nascent Ag colloids are not stabilized by the dendrimer. Rather, the Ag particles aggregate and merge to form larger particles.[14,15] In contrast, when this same experiment is carried out using Cu^{2+}, Pt^{2+}, and many other transition metal ions, reduction results in a stable solution of dendrimer-encapsulated nanoparticles.[1-4]

Other experiments confirm that the interaction between Ag$^+$ and functional groups within the Gn-OH dendrimer is insufficient to yield stabilized nanoparticles. For example, dialysis of a solution containing G6-OH and Ag$^+$ results in retention of only the dendrimer: Ag$^+$ diffuses through the dialysis sack. When the same
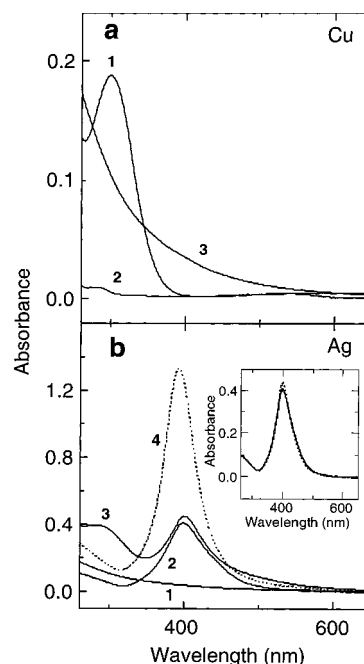
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Figure 1. (a) Absorption spectra of aqueous 0.55 mM Cu-(NO$_3$)$_2$ in the presence of 0.01 mM G6-OH before (pH 7.5, spectrum 1; pH 3.0, spectrum 2) and after (pH 7.5, spectrum 3) reduction with a 3-fold molar excess of BH$_4^-$. (b) Absorption spectra after addition of 11 mmol of AgNO$_3$ to 10 mL of 0.01 mM G6-OH(Cu$_{55}$) (spectrum 2, pH 3.0; spectrum 3, pH 7.5). Spectrum 1 is the same as spectrum 3 in part a for comparison. Spectrum 4 was obtained 1 h after direct BH$_4^-$ reduction of 1.1 mM AgNO$_3$ + 0.01 mM G6-OH: the much higher intensity of this peak (compared to that in spectra 2 and 3) indicates that direct reduction leads to formation of substantially larger Ag particles than do the displacement reactions. The inset in (b) shows spectra obtained at different times after the displacement reaction (solid line, 10 min; dashed line, 18 h).

experiment is performed with Cu^{2+}, which is strongly complexed to the dendrimer interior, both dendrimer and Cu^{2+} are retained. Electrochemical measurements can also be used to evaluate the strength of the interaction between metal ions and ligands, because strong complexation shifts the reduction potential of metal ions to more negative values than would be observed in the uncomplexed state.[5,16] Thus, because of the strong interaction between Cu^{2+} and G6-OH, no reduction peak is observed in an aqueous solution containing Cu^{2+} and dendrimers. In contrast, a large reduction peak is observed in an analogous experiment involving Ag$^+$ reduction in the presence of G6-OH (see Supporting Information).

Although it is not possible to prepare intradendrimer Ag nanoparticles by direct reduction of interior ions, stable, dendrimer-encapsulated Ag particles can be prepared by a metal exchange reaction. In this approach, dendrimer-encapsulated Cu nanoclusters are prepared as described in the Experimental Section,[1] and then upon exposure to Ag$^+$ the Cu particles oxidize to Cu^{2+} ions, which stay entrapped within the dendrimer at pH values higher than 5.5, and Ag$^+$ is reduced to yield a dendrimer-encapsulated Ag nanoparticle (Scheme 1). Figure 1a shows UV–vis spectra of an aqueous 0.55 mM Cu^{2+}/0.01 mM G6-OH solution before and after reduc-

(16) It is also possible that metal ions sequestered within dendrimers are electroinactive because they are not accessible to the electrode.

tion. Prior to reduction (curve 1 in Figure 1a, pH 7.5), a strong band is evident at 300 nm ($\epsilon \sim 4000$ M^{-1} cm^{-1}), which is not present in the absence of either the dendrimer or Cu^{2+}. This band arises from a ligand-to-metal charge-transfer (LMCT) transition.[17] Spectrophotometric titrations indicate that each G6-OH can bind as many as 64 Cu^{2+} ions.[1] Because the Cu^{2+}/G6-OH ratio is equal to 55 in the experiments discussed here, we expect that all of the Cu^{2+} is extracted into G6-OH via coordination to interior tertiary amines. We denote this species as G6-OH(Cu^{2+})$_{55}$. Evidence for extraction of Cu^{2+} into the dendrimer comes from the pH dependence of the absorption band at 300 nm, which decreases with decreasing pH until it finally disappears at pH 3.0 (curve 2 in Figure 1a), and the simultaneous appearance of a much weaker band at 810 nm, which corresponds to Cu(H$_2$O)$_6^{2+}$. These pH-dependent spectral changes result from tertiary amine protonation (p$K_a = 5.5$)[18] and concomitant expulsion of Cu^{2+} from the dendrimer at low pH.[1,19]

As signaled by the loss of the band at 300 nm, chemical reduction of a pH 7.5, G6-OH(Cu^{2+})$_{55}$ solution with a 3-fold excess of BH$_4^-$ results in formation of intradendrimer Cu nanoclusters. The new spectrum, curve 3 of Figure 1a, is dominated by a monotonic and nearly exponential slope toward shorter wavelengths, which results from the interband transition of intradendrimer Cu clusters. The measured onset of this interband transition at 590 nm is in agreement with the accepted value,[20] and the nearly exponential shape is characteristic of a bandlike electronic structure, which strongly suggests that the reduced Cu does not exist as isolated atoms, but rather as clusters.[13,15] The absence of a Mie plasmon resonance band around 570 nm suggests that the intradendrimer particles have a diameter smaller than about 4 nm,[21] which is consistent with our view that each dendrimer contains a 1−2 nm diameter cluster composed of, on average, 55 atoms.[22,23] The absorption spectrum of aqueous G6-OH(Cu$_{55}$) solutions is independent of pH in the range 3−7.5.

Ag$^+$ is a stronger oxidizing agent than Cu^{2+}, and therefore eq 1 leads to intradendrimer exchange of the Cu nanoparticle for Ag.[24] Part b of Figure 1 shows the spectroscopic evolution of such a reaction. Spectrum 1 is the UV−vis spectrum of G6-OH(Cu$_{55}$), which is the same as spectrum 3 in part a of Figure 1. When 11 mmol of Ag$^+$ is added to 10 mL of the 0.01 mM G6-OH(Cu$_{55}$) solution (pH 3.0), a new absorbance band centered at 400 nm appears (spectrum 2), which corresponds to the plasmon resonance of Ag nanoparticles.[15] When the pH of the solution is adjusted to 7.5, the Ag plasmon peak does not change much, but a new peak at 300 nm ($\epsilon \sim$
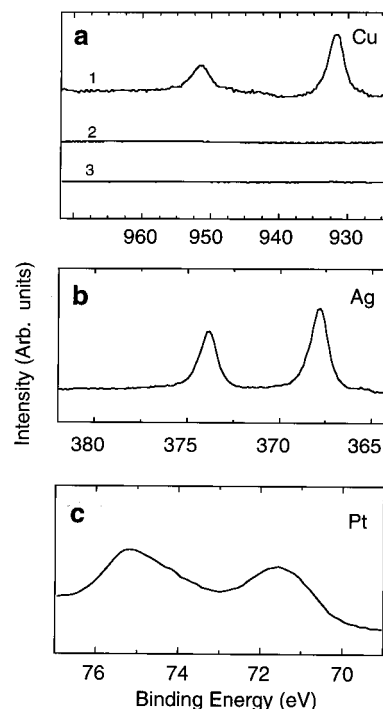

Figure 2. (a) Cu(2p) XPS spectra of G6-OH(Cu$_{55}$) before (spectrum 1) and after reaction with Ag$^+$ (spectrum 2) or Pt^{2+} (spectrum 3). (b) Ag(3d) XPS spectrum of G6-OH(Cu$_{55}$) after reaction with Ag$^+$. (c) Pt(4f) XPS spectrum of G6-OH(Cu$_{55}$) after reaction with Pt^{2+}.

4000 M^{-1} cm^{-1}) appears. This is the G6-OH(Cu^{2+})$_{55}$ LMCT band discussed earlier, and it indicates that when the interior tertiary amines are deprotonated, Cu^{2+} resides within the dendrimer. Thus, both the metallic Ag nanoparticles and the Cu^{2+} ions generated by the displacement reaction are present within the dendrimers simultaneously. Ag particles synthesized by this displacement reaction are very stable; for example, spectra taken 10 min and 18 h after reduction are nearly identical (Figure 1b, inset), and no precipitation is observed even after storage in air for >2 months. Such stability strongly suggests dendrimer encapsulation of the Ag nanoparticles.

$$Cu + 2Ag^+ = 2Ag + Cu^{2+} \qquad (1)$$
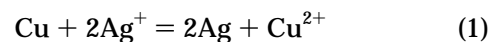
X-ray photoelectron spectroscopy (XPS) can be used to provide information about the elemental composition of dendrimer nanocomposites. Prior to XPS analysis, the dendrimer nanocomposites are immobilized on a Au surface via polydentate chemisorption[25,26] by immersing in a dilute, aqueous pH 3.0 solution for 20 h, followed by careful rinsing and drying.[27] All XPS data indicate the presence of carbon and nitrogen arising from the dendrimer. Figure 2 shows XPS data for G6-OH(Cu$_{55}$) before and after exposure to Ag$^+$ (Ag$^+$/Cu = 2). Prior to

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(27) FTIR-external reflection spectroscopy (FTIR-ERS) is also used to confirm the attachment of dendrimers to substrates. FTIR-ERS data of a substrate coated with dendrimer−metal particle composites exhibit peaks at 1665 and 1555 cm^{-1}, characteristic of the high density of amide bonds present within the PAMAM dendrimers.
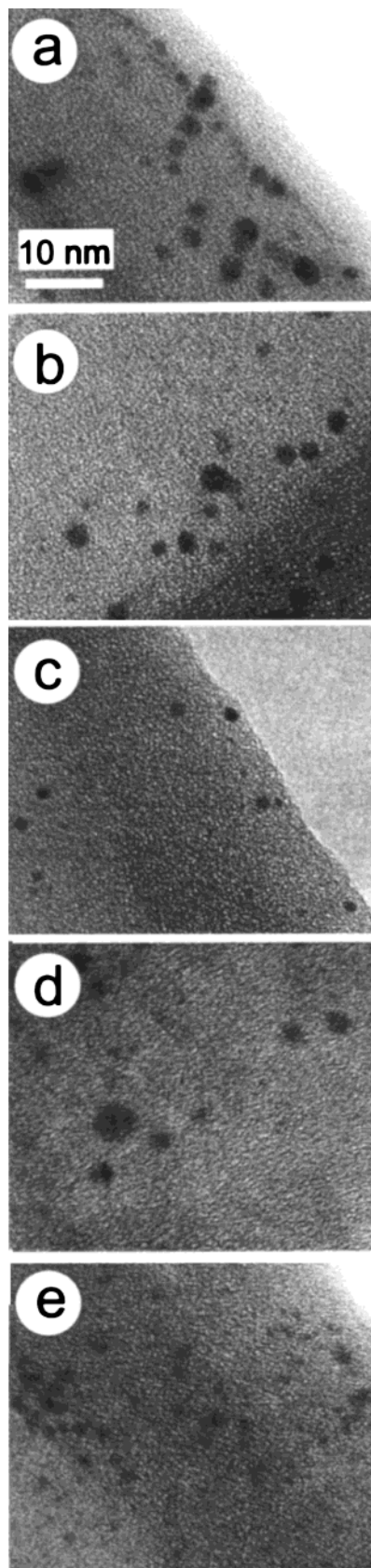
Figure 3. HRTEM images of metal nanoparticles prepared by primary displacement reactions—(a) Ag, (b) Au, and (c) Pt—and secondary displacement reactions—(d) Au and (e) Pt. In the primary displacement reactions, Ag^+, Au^{3+}, or Pt^{2+} ions react with G6-OH(Cu_{55}) to yield the corresponding zerovalent metals, and in the secondary displacement reactions, Au^{3+} or Pt^{2+} ions react with Ag nanoparticles prepared from G6-OH-(Cu_{55}) by a primary displacement reaction.
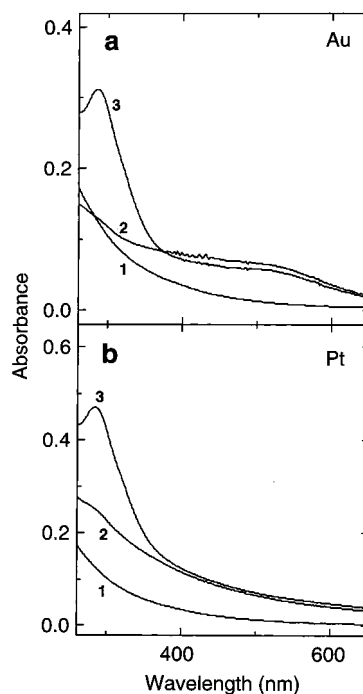

Figure 4. (a) Absorption spectra of 0.01 mM G6-OH(Cu_{55}) before (spectrum 1, pH 7.5) and after (spectrum 2, pH 3.0 and spectrum 3, pH 7.5) addition of a stoichiometric amount of Au^{3+}. (b) Absorption spectra of 0.01 mM G6-OH(Cu_{55}) before (spectrum 1, pH 7.5) and after (spectrum 2, pH 3.0; spectrum 3, pH 7.5) addition of a stoichiometric amount of Pt^{2+}.

metal exchange, strong peaks arising from Cu are observed at 931.7 eV ($2p_{3/2}$) and 951.6 eV ($2p_{1/2}$) (curve 1 of Figure 2a). After exposure to Ag^+ at pH 3.0, the Cu(2p) peaks are absent (curve 2 of Figure 2a), but two new Ag peaks appear at 367.9 eV ($3d_{5/2}$) and 373.9 eV($3d_{3/2}$) (Figure 2b). Taken together, these results confirm that Cu displacement by Ag is nearly complete.

Transmission electron microscopy (TEM) results provide additional information about metal particles prepared by displacement. Figure 3a shows that Ag particles prepared by displacement have an average size of 2.8 ± 0.6 nm, which can be compared to the 6.7 nm diameter G6-OH dendrimer in which we contend they are confined. In contrast, Ag particles prepared by direct reduction (corresponding to spectrum 4 of Figure 1b) are 15 ± 5 nm in diameter: far too large to be within the dendrimer interior. Although the Ag particle size resulting from the displacement reaction is much smaller than from the direct method, it is still significantly larger than the theoretical value of 1.5 nm, calculated by assuming that the Ag atoms form a single cluster and are encompassed within the smallest sphere containing a 110-atom fcc crystal. This inconsistency between the observed and calculated values for the Ag particle size may be due to interdendrimer exchange of Ag atoms, nonspherical particles, or multiple smaller particles per dendrimer.

This displacement method can be used to prepare other noble-metal particles, such as Au, Pt, and Pd, because the standard potentials ($E°$) of the corresponding half-reactions are more positive than for Cu^{2+}/Cu.[24] Figure 4 shows UV–vis spectra resulting from dendrimer-encapsulated Au and Pt particles prepared by the sort of metal exchange reaction just described for Ag. The absorption spectrum of G6-OH(Cu_{55}) is shown

as spectrum 1 in both parts of this figure for comparison. When 3.7 mmol of $HAuCl_4$ is added to 10 mL of a pH 3 aqueous solution containing 0.01 mM G6-OH(Cu_{55}) ($Au^{3+}/Cu = 2/3$), a new, broad absorption feature appears centered at ~520 nm (spectrum 2, Figure 4a), which corresponds to the plasmon resonance absorption of Au.[15] When the pH of this solution is increased to 7.5, a new band centered at 290 nm appears (curve 3 in Figure 4a). This feature arises from the dendrimer–Cu^{2+} LMCT transition and therefore confirms the presence of both Au and Cu^{2+} within the dendrimer. Note that there is little change in the dendrimer–Cu^{2+} LMCT transition arising from the presence of the Au nanoparticles. It is also interesting to note that the peak intensity of the LMCT transition in curve 3, after correction for the baseline, indicates that the displacement reactions are nearly complete (compare to spectrum 1 in Figure 1a).

Pt particles can also be prepared by displacement. In this case, a stoichiometric amount of K_2PtCl_4 ($Pt^{2+}/Cu = 1/1$) is added to a 0.01 mM G6-OH(Cu_{55}) solution at pH 3. This results in particles that are spectroscopically distinct from the starting material. For example, the interband transition of the resulting dendrimer-encapsulated Pt nanoparticles (spectrum 2 in Figure 4b) is stronger than that of G6-OH(Cu_{55}) (spectrum 1, Figure 4b).[3] XPS data also confirm intradendrimer replacement of Cu by Pt: the Cu(2p) peaks originally present (spectrum 1 of Figure 2a) disappear (spectrum 3 of Figure 2a), and new Pt(4f) peaks at 71.5 and 75.2 eV appear (Figure 2c). When the pH of the displacement solution is adjusted to 7.5, a strong new band centered at 290 nm ($\epsilon \sim 4000$ M^{-1} cm^{-1}) emerges in the optical spectrum (spectrum 3 in Figure 4b). As for the Au displacement reaction just discussed, this band corresponds to the LMCT transition of the dendrimer–Cu^{2+} complex, and here too its magnitude confirms that the Pt displacement reaction goes nearly to completion. Although not shown here, Pd particles can be synthesized in the same manner as Ag, Au, and Pt, and the resulting spectra are similar to those of Pt.

The HRTEM images in parts b and c of Figure 3 reveal the shape and size distribution of the Au and Pt clusters, respectively, prepared by the previously described primary displacement reactions. Analysis of 100 randomly selected particles indicates that the average diameters for the Au and Pt nanoparticles are 2.3 ± 0.3 and 1.4 ± 0.2 nm, respectively. The particle size for Pt is very close to the theoretical value of 1.2 nm calculated by assuming the Pt atoms are encompassed within the smallest sphere containing a 55-atom fcc crystal. The size is also in good agreement with that of dendrimer-encapsulated nanoparticles containing 60 atoms (1.6 ± 0.2 nm) prepared by direct reduction of Pt^{2+}.[2,3] The size of Au particles prepared by displacement is larger than the calculated value (1.1 nm, using the same assumptions as for Pt, except for the slightly smaller atom size). As discussed for the Ag nanoparticles, there are a number of possible explanations for this slight discrepancy.

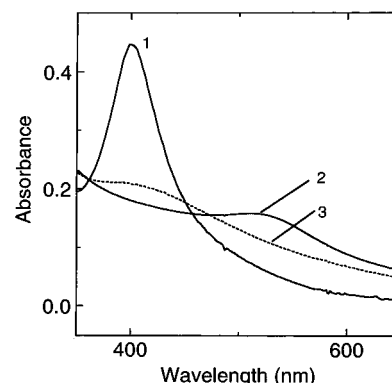Ag nanoparticles synthesized by primary displacement of dendrimer-encapsulated Cu nanoparticles can

Figure 5. Spectrum 1: absorption spectrum of a solution containing 0.01 mM G6-OH(Ag_{110}) prepared by primary displacement of Cu in G6-OH(Cu_{55}). Spectra 2 and 3: absorption spectra of G6-OH(Au_{37}) and G6-OH(Pt_{55}), respectively, prepared by secondary displacement of Ag from G6-OH(Ag_{110}). Note the disappearance of the Ag plasmon peak following the secondary displacement reactions.

themselves be displaced to yield Au, Pt, or Pd nanoparticles by a secondary displacement reaction (Scheme 1). Figure 5 provides spectroscopic evidence for the second displacement of Ag by Au^{3+} or Pt^{2+}. In the absence of Au^{3+} or Pt^{2+} ions, the spectrum of the G6-OH-stabilized Ag particles is dominated by the previously discussed plasmon peak at 400 nm (spectrum 1). When a stoichiometric amount of Au^{3+} (spectrum 2) or Pt^{2+} (spectrum 3) is added to this solution, the magnitude of the Ag plasmon peak is reduced to a negligible value, and it is replaced by the Au plasmon absorption band or Pt interband transition, respectively, described earlier.

TEM and EDS results confirm that particles of Au and Pt can be prepared by secondary displacement reactions between dendrimer-encapsulated Ag particles and Au^{3+} or Pt^{2+}, respectively. For example, the TEM images shown in parts d and e of Figure 3 indicate that the average diameters of Au and Pt particles are about 2.5 and 1.8 nm, respectively, and the EDS results definitively show that the particles are composed of Au or Pt.

We previously showed that dendrimer-encapsulated metal particles could be used for both heterogeneous and homogeneous catalysis.[2-4] Indeed, the observation of catalytic rate enhancements demonstrates that substrates can enter the dendrimer interior and undergo chemical reactions therein. Such reactions also prove that the surfaces of encapsulated nanoparticles are not fully passivated. Catalytic reactions can also be used to confirm the presence of an encapsulated metal and assist in identifying its composition.

Pt and Pd are efficient electrocatalysts for O_2 reduction in acid electrolytes, while Ag and Cu demonstrate no such catalytic effect under the same conditions.[28,29] Accordingly, we expect that dendrimers containing nanoparticles of Pt and Pd will accelerate the rate of O_2 reduction, while Ag and Cu dendrimer-encapsulated nanoparticles will not. Figure 6 shows cyclic voltammograms (CVs) obtained from Au electrodes modified with single monolayers of G6-OH(Cu_{55}), G6-OH(Ag_{110}), G6-OH(Pt_{55}), and G6-OH(Pd_{55}) in 1 M H_2SO_4 saturated

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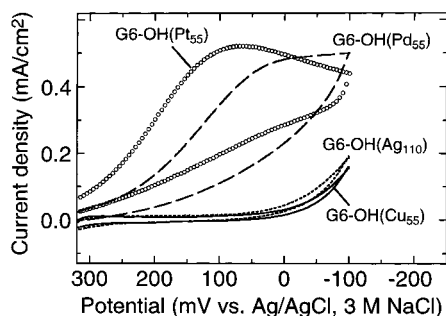
Figure 6. Cyclic voltammograms of Au electrodes coated with G6-OH(Cu_{55}) prepared by direct reduction and G6-OH(Ag_{110}), G6-OH(Pd_{55}), and G6-OH(Pt_{55}) prepared by primary displacement reactions. Catalytic reduction of O_2 is observed only on the G6-OH(Pd_{55})- and G6-OH(Pt_{55})-modified electrodes. Electrode area, 0.09 cm^2; scan rate, 50 mV/s; electrolyte, 1.0 M H_2SO_4.

with O_2.[3,25] The latter three composite materials were prepared by a primary metal displacement reaction followed by dialysis against pH 3.0 water for 24 h (to remove Cu^{2+}). Electrodes modified with G6-OH(Cu_{55}) and G6-OH(Ag_{110}) yield a relatively small current and no peak attributable to O_2 reduction, indicating a kinetically slow electrode reaction.[5] However, when the Cu particles in G6-OH(Cu_{55}) are displaced by Pt or Pd and then immobilized on a Au electrode surface, a significant diffusion-controlled catalytic current is observed. In the absence of O_2, only a small background current is observed for the G6-OH(Pt_{55})- and G6-OH-(Pd_{55})-modified electrodes, confirming that the relevant Faradaic process in this potential range is O_2 reduction. We previously reported similar behavior for dendrimer-encapsulated Pt nanoparticles prepared by direct reduction of Pt^{2+}.[3]

Summary and Conclusions

We have demonstrated that dendrimer-encapsulated metal particles can be prepared by an in-situ exchange process driven by differences in the electrochemical potentials of the two metals involved. In all cases described here, UV–vis, EDS, XPS, and electrochemical data strongly suggest that the exchange reactions go to completion. These findings are important because many metal ions do not partition into dendritic interiors sufficiently well to yield stable composites. Equally important, we have shown that both the exchanged metal particle and the ions corresponding to the original nanoparticles can, under appropriate conditions, simultaneously exist within the dendrimer interior. The resulting well-defined microenvironments are ideally suited for a wide range of fundamental studies and technological applications, especially those related to catalysis.

It is also possible to do secondary intradendrimer displacement reactions. Certain metals, such as Pt, can be encapsulated within dendrimers by direct reduction of Pt^{2+}, as well as by primary and secondary reactions. In this case, the spectroscopic and catalytic behavior of the composites is largely independent of how they are prepared. Although we have not reported the results here, bi- and trimetallic dendrimer-encapsulated metal particles can be prepared by exposing the original nanocluster to substoichiometric amounts of the ions used for the primary or secondary displacement reactions.

Supporting Information Available: Spectroscopic and electrochemical data related to Ag nanoparticles prepared by direct reduction. This material is available free of charge via the Internet at http://pubs.acs.org.

CM990435P