

## Separation of Dendrimer-Encapsulated Au and Ag Nanoparticles by Selective Extraction

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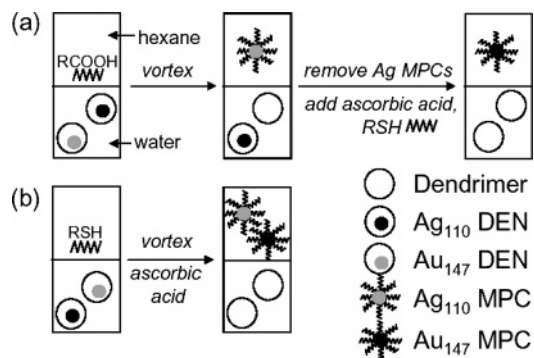
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We report the separation of Au and Ag dendrimer-encapsulated nanoparticles (DENs)<sup>1</sup> from an aqueous mixture of the two using a selective extraction approach (Scheme 1a). In this method, an *n*-alkanoic acid present in an organic solvent and having a high affinity for Ag (but not Au) is added to an aqueous mixture of Ag and Au DENs. Through a strong ligand–nanoparticle interaction, the Ag nanoparticles are selectively extracted into the organic phase resulting in a solution of Ag monolayer-protected clusters (MPCs).<sup>2</sup> Subsequent addition of an organic phase containing an *n*-alkanethiol leads to extraction of the remaining Au DENs. It is also possible to extract both metals simultaneously (Scheme 1b), or selectively extract Au nanoparticles from a mixture of Ag and Au DENs. These results are important, because they demonstrate a simple chemical approach for separating nanoparticles having different chemical compositions. Moreover, as we will show in a forthcoming publication, selective extraction can be used to determine the elemental composition of the outermost metal layer of 1–3-nm-diameter core/shell nanoparticles.<sup>3</sup>

We recently showed that Pd nanoparticles could be extracted from within dendrimer templates and transferred to an organic phase using *n*-alkanethiol surfactants.<sup>4</sup> The model we proposed for this process involves penetration of the dendrimer by the *n*-alkanethiol, adsorption of the thiol to the Pd surface, and extraction of the resulting Pd MPC<sup>2</sup> into the organic phase. It is also possible to extract Au, Ag, and AuAg bimetallic DENs from different generation dendrimers using *n*-alkanethiols.<sup>3,5</sup> We reasoned that if we could find other surfactants that had highly selective affinities for different surfaces, then it would be possible to separate mixtures of nanoparticles. This idea is based on the concept of “orthogonal assembly”, which has its roots in a 1989 paper by Wrighton and Whitesides. They demonstrated that two different surfactants would selectively adsorb to each of two different metal or

Scheme 1



metal-oxide surfaces.<sup>6</sup> Accordingly, we examined the affinity of *n*-alkanoic acids for metal oxide surfaces<sup>7,8</sup> and found that they would extract Ag DENs having a surface oxide layer, but that they would not extract oxide-free Au nanoparticles. The interaction between fatty acids and Ag/AgO surfaces has been studied in detail and has been ascribed to dissociative chemisorption of the acid onto the basic oxide surface.<sup>7</sup>

In this study, sixth-generation, hydroxyl-terminated PAMAM dendrimers (G6-OH) containing 147-atom Au nanoparticles (G6-OH(Au<sub>147</sub>)) were synthesized using a method we previously reported.<sup>9</sup> Specifically, 0.74 mL of a 20.0 mM solution of HAuCl<sub>4</sub> was added to 42.65 mL of a 2.3 μM solution of G6-OH. This results in encapsulation of an average of 147 Au ions within each dendrimer. Reduction of this composite within 2 min with a 5-fold excess of 10 mM BH<sub>4</sub><sup>-</sup> leads to G6-OH-(Au<sub>147</sub>) DENs having an average diameter of 1.4 ± 0.4 nm, which is close to the calculated value of 1.6 nm.<sup>10</sup> It is not possible to synthesize Ag DENs using this same direct approach. Instead, G6-OH(Ag<sub>110</sub>) DENs were synthesized using an intradendrimer displacement reaction, which converts Cu DENs to Ag DENs.<sup>11</sup> Specifically, a solution of G6-OH(Cu<sub>55</sub>) DENs was synthesized as follows: 0.28 mL of a 20.0 mM solution of Cu(NO<sub>3</sub>)<sub>2</sub> was added to 19.56 mL of a 11.0 μM solution of G6-OH. The solution was purged with N<sub>2</sub> for 15 min prior to reduction with a 3-fold excess of 100 mM BH<sub>4</sub><sup>-</sup>. Excess BH<sub>4</sub><sup>-</sup> was removed by addition of acid, and then 1.1 mL of 0.01 M AgNO<sub>3</sub> was added to the Cu DEN solution. As a consequence of the enhanced nobility of Ag and the stronger oxidizing power of Ag<sup>+</sup> compared to Cu, the Ag<sup>+</sup> ions oxidize the Cu<sup>0</sup> nanoparticles to Cu<sup>2+</sup> and in doing so are themselves reduced to Ag<sup>0</sup>.<sup>11</sup> High-resolution transmission electron microscopy (HRTEM) indicates that the resulting G6-OH(Ag<sub>110</sub>) DENs have an average diameter of 1.7 ± 0.4 nm, which is comparable to the calculated value of 1.5 nm.<sup>10</sup> It is possible

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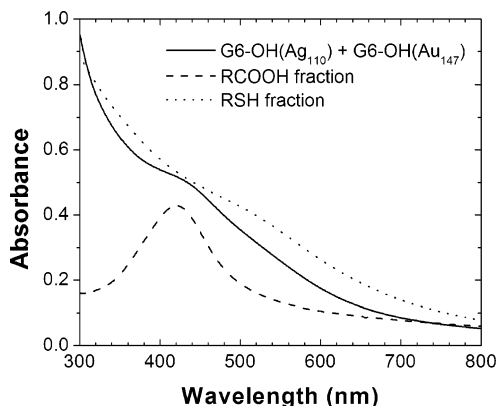
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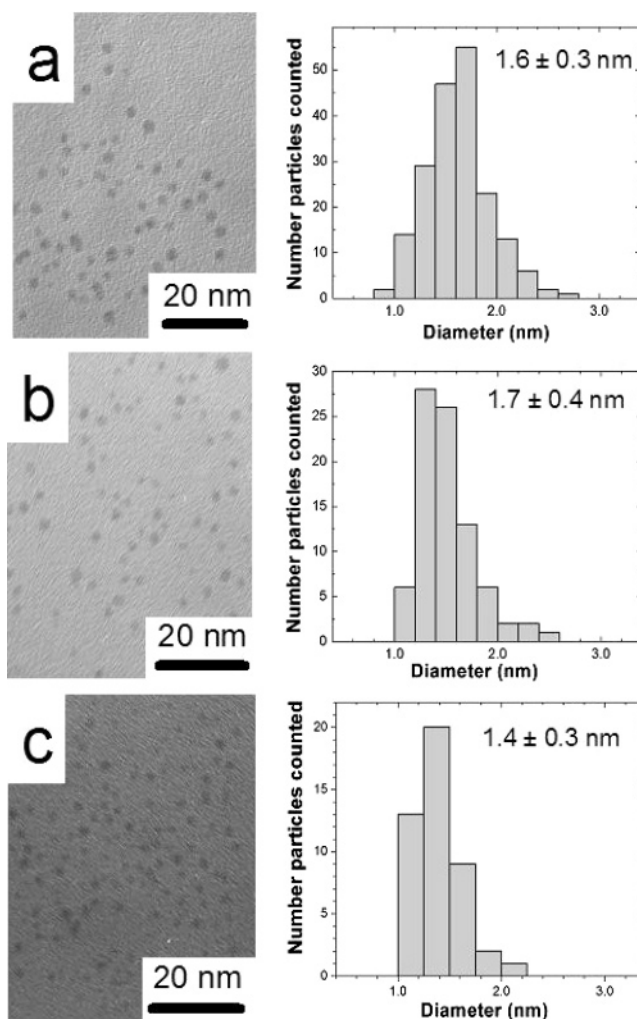


**Figure 1.** UV-vis absorbance spectra demonstrating the separation of G6-OH(Au<sub>147</sub>) and G6-OH(Ag<sub>110</sub>) DENs by selective extraction. The solid line corresponds to an aqueous mixture of G6-OH(Au<sub>147</sub>) and G6-OH(Ag<sub>110</sub>), the dashed line corresponds to the hexane phase after the first extraction step with *n*-decanoic acid, and the dotted line corresponds to the hexane phase after a second extraction of the aqueous phase with *n*-dodecanethiol.

to remove the Cu<sup>2+</sup> that results from this process, but that was unnecessary for the experiments described here.

Selective extraction of Ag DENs was carried out by adding 4.0 mL of 0.25 M *n*-decanoic acid/hexane solution to 6.0 mL of an aqueous mixture containing 0.18 mM G6-OH(Ag<sub>110</sub>) and 0.20 mM G6-OH(Au<sub>147</sub>) DENs. The biphasic mixture was vortexed for 30 s and within 5 min a yellow color was observed in the previously colorless hexane phase. The hexane phase was removed and the process was repeated to ensure complete removal of the Ag DENs. The subsequent thiol extraction step was carried out by adding 0.02 g of ascorbic acid to the aqueous phase, which increased the ionic strength sufficiently to enable extraction,<sup>5</sup> followed by 5.0 mL of a 20 mM *n*-dodecanethiol/hexane solution. Alternative salts that have been shown to cause the required increase in ionic strength include NaBH<sub>4</sub>, NaCl, Mg(NO<sub>3</sub>)<sub>2</sub>, and Na<sub>2</sub>SO<sub>4</sub>.<sup>5</sup> Vortexing for 30 s and isolation of the brown hexane phase resulted in a colorless aqueous phase.

Figure 1 shows UV-vis absorption spectra for the aqueous mixture of G6-OH(Au<sub>147</sub>) and G6-OH(Ag<sub>110</sub>) DENs prior to extraction (solid line), the hexane phase after the first extraction with *n*-decanoic acid (dashed line), and a second hexane phase after subsequent extraction with *n*-dodecanethiol (dotted line). After the first extraction, the *n*-decanoic acid/hexane phase reveals a peak at 420 nm, which corresponds to the plasmon absorption of Ag.<sup>12</sup> The position and magnitude of this band are nearly identical to those of the original G6-OH(Ag<sub>110</sub>) solution (Supporting Information, Figure S1), indicating quantitative extraction. Likewise, after the second extraction, the spectrum of Au<sub>147</sub> MPCs is almost identical to that of G6-OH(Au<sub>147</sub>) DENs prior to extraction (Supporting Information, Figure S2). The presence of a much larger plasmon band for Ag DENs compared to Au DENs is in accordance with their fundamental optical properties and previous literature reports.<sup>13,14</sup>



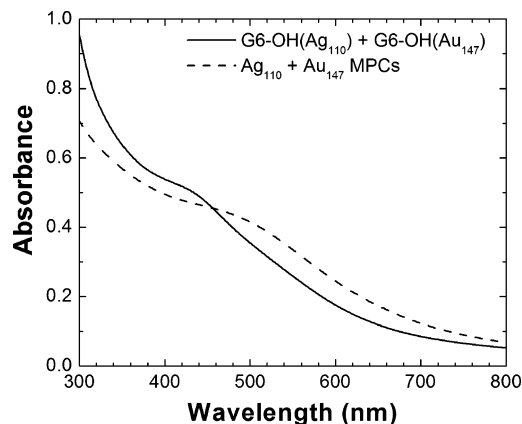
**Figure 2.** HRTEM micrographs and size-distribution histograms prepared using solutions containing the following: (a) an aqueous mixture of G6-OH(Au<sub>147</sub>) and G6-OH(Ag<sub>110</sub>) DENs, (b) the hexane phase after *n*-decanoic acid extraction, and (c) the hexane phase after subsequent *n*-dodecanethiol extraction.

Figure 2a is a HRTEM micrograph of a mixture of G6-OH(Au<sub>147</sub>) and G6-OH(Ag<sub>110</sub>) DENs prepared from an aqueous solution. These DENs have an average size of  $1.6 \pm 0.3$  nm, and quantitative standardless analysis using large-area energy-dispersive X-ray spectroscopy (EDS) of 10 areas on the grid indicates a composition of 43% Ag and 57% Au. HRTEM analysis of the hexane phase following the first extraction with *n*-decanoic acid results in particles with a diameter of  $1.7 \pm 0.4$  nm (Figure 2b), and EDS analysis yields an average composition of  $95 \pm 6\%$  Ag and  $5 \pm 6\%$  Au. This is convincing evidence that *n*-alkanoic acids preferentially extract G6-OH(Ag<sub>110</sub>) from the DEN mixture. HRTEM and EDS analyses of the particles resulting from the second hexane extraction with *n*-dodecanethiol (Figure 2c) indicate a particle-size distribution of  $1.4 \pm 0.3$  nm and a metal composition of  $8 \pm 6\%$  Ag and  $92 \pm 6\%$  Au. From these results we conclude that similarly sized Au and Ag DENs can be separated.

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**Figure 3.** UV-vis spectra demonstrating the simultaneous extraction of both 0.20 mM G6-OH(Au<sub>147</sub>) and 0.18 mM G6-OH(Ag<sub>110</sub>) DENs when the extracting ligand is *n*-dodecanethiol in the presence of excess ascorbic acid. The solid line corresponds to the aqueous mixture of G6-OH(Au<sub>147</sub>) and G6-OH(Ag<sub>110</sub>) and the dashed line corresponds to the hexane phase after the extraction step with *n*-dodecanethiol.

Figure 3 compares the UV-vis absorption spectrum of an aqueous mixture of G6-OH(Au<sub>147</sub>) and G6-OH(Ag<sub>110</sub>) DENs prior to extraction (solid line) with the hexane phase after simultaneous extraction of Au and Ag nanoparticles with *n*-dodecanethiol in the presence of a reducing agent (dashed line). Under these conditions there is no oxide present on the Ag surface, which enables the thiol-based extraction of both metals. Further confirmation of the need for a Ag oxide layer for selective extraction with *n*-decanoic acid was obtained

by adding NaBH<sub>4</sub> to the mixture of Ag and Au DENs. Under these reducing conditions, neither Au nor Ag DENs extract with *n*-decanoic acid, presumably due to the absence of the Ag oxide layer. NMR spectroscopy was used to confirm that BH<sub>4</sub><sup>-</sup> did not reduce or otherwise react with the acid.

To summarize, we have shown that orthogonal assembly of self-assembled monolayers onto metal nanoparticles having different compositions provides a basis for selective separation. Additionally, we will shortly report that this process can also be used to distinguish between bimetallic core-shell nanoparticles having different surface compositions.<sup>3</sup> In this sense, the approach described here is useful as an analytical method for determining the structure of nanoparticles having sizes that are too small for conventional methods to be useful.<sup>15</sup>

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**Supporting Information Available:** UV-vis absorbance spectra of Ag<sub>110</sub> DENs and the *n*-decanoic acid/hexane extract; and Au<sub>147</sub> and Ag<sub>110</sub> DENs before and after mixing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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