

# Preparation and Characterization of Dendrimer–Gold Colloid Nanocomposites

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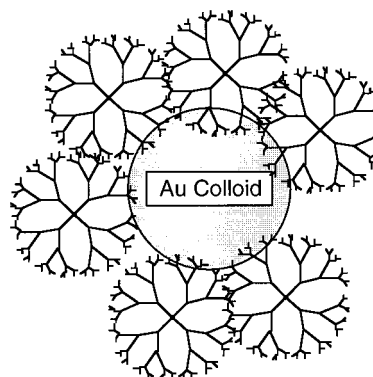
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**Au colloids in the 2–3-nm size regime were prepared by in situ reduction of  $\text{HAuCl}_4$  in the presence of poly-(amidoamine) dendrimers. The dendrimers encapsulate the colloids, imparting stability to the aqueous colloidal solutions. The nanocomposite materials can be isolated by precipitation. The dendrimer generation used in the synthesis controls the size of the resultant colloids: lower-generation dendrimers give rise to larger colloids. The materials were characterized by infrared and UV–vis spectroscopy and transmission electron microscopy.**

We previously showed that nanoclusters containing only a few metal atoms can be encapsulated within single dendrimers;<sup>1</sup> here, we turn this concept around to demonstrate that much larger colloids can be stabilized by multiple, surface-adsorbed dendrimers.<sup>2</sup> Specifically, we report the preparation of nanocomposites consisting of 2–3-nm-diameter Au colloidal particles encapsulated by poly(amidoamine) (PAMAM) dendrimers. These materials are three-dimensional analogues of the two-dimensional dendrimer monolayers we recently reported.<sup>3</sup> A two-dimensional projection of our conceptual model of these new materials is shown in Chart 1. The dendrimers stabilize the colloidal Au particles in aqueous solution at concentrations where unmodified colloids agglomerate. Additionally, the size of the colloids is a function of dendrimer generation. These nanocomposite materials have unique potential for applications such as catalysis, which require stable colloidal particles having surfaces that are not completely passivated by a stabilizing adsorbate. In this sense, the dendrimers serve the dual purpose of acting as a nanofilter and as a stabilizer.

Au nanoclusters modified and stabilized by self-assembled monolayers (SAMs)<sup>4</sup> are generally prepared according to a method first demonstrated by Schiffrin and co-workers.<sup>5</sup> Most recent work has focused on colloidal metals that are stabilized by *n*-alkanethiols,<sup>6–8</sup> but it has also been shown that the interaction of amines with Au can yield stable colloids. For example, Leff et

Chart 1



al. demonstrated that Au colloids can be stabilized by *n*-alkylamines.<sup>9</sup> Au colloids have also been stabilized by cationic polyelectrolytes containing ammonium functional groups.<sup>10</sup> Finally, Esumi et al. recently reported dendrimer stabilization of Au colloids formed by UV irradiation.<sup>11</sup>

Dendrimer/Au nanocomposites are prepared by a very straightforward, one-phase reaction analogous to a literature procedure used to prepare Ag nanoparticles.<sup>12</sup> First, 50 mL of a 0.01 M aqueous (Milli-Q, Millipore) solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was mixed with 50 mL of a methanolic solution of either a second- or fourth-generation (G2 or G4, respectively), amine-terminated PAMAM dendrimer. The molar ratio of Au to the number of primary amine groups of the dendrimers was kept constant at  $\sim 1:11$ , which corresponds to about 5.9 Au atoms per G4 dendrimer or 1.4 Au atoms per G2 dendrimer. Next, the Au complex is reduced by slow addition ( $\sim 10$  mL/min) of 50 mL of a 0.15 M aqueous solution of  $\text{NaBH}_4$ . This treatment yields metallic Au colloids, which are present as wine-red solutions that are stable for several weeks. The same synthetic procedure, but without the dendrimer present, yields only large, insoluble Au particles. The nanocom-

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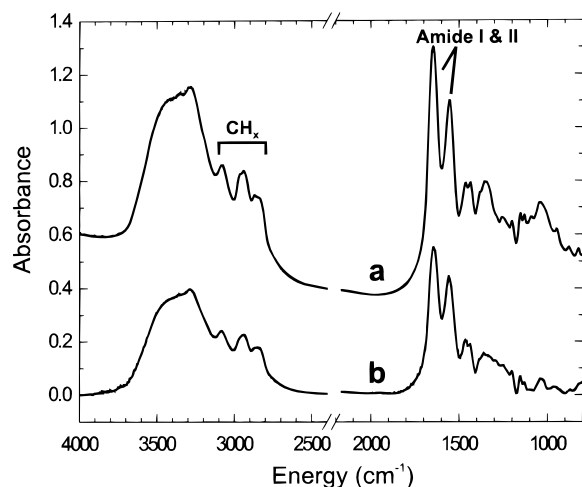


Figure 1. Comparison of FT-IR spectra (KBr pellet) for (a) G4 PAMAM dendrimer and (b) G4-dendrimer/Au-colloid nanocomposite.

posites can be isolated for further characterization by slow precipitation from THF and washing with THF and cold ethanol. Following precipitation they can be redissolved.

The driving force for the interaction of the colloids with the dendrimers is an association of Au with the primary amine terminal groups (and perhaps the interior secondary and tertiary amines) of the dendrimer. It is interesting to note, however, that while amine monolayers on planar Au are unstable in solution,<sup>13</sup> alkylamine monolayers on Au colloids are more robust. That is the equilibrium between amine-terminated dendrimers in solution and on the colloid surface greatly favors the latter. This has been attributed to a finite-size effect that is kinetic in nature.<sup>14</sup> We believe that the materials described here are further stabilized by the large number of amine groups per dendrimer, that is, by chelation. Note, however, that this high degree of functionalization could lead to some aggregation of the colloids via dendrimer-induced cross-linking. This effect can be minimized by using a large excess of dendrimer. In any event, if such cross-linking was a major pathway, we would expect precipitation of the resulting very large aggregates.

Dendrimer/Au nanocomposites can be isolated from alcohol/water solutions by precipitation with THF. We believe that washing with THF and cold ethanol removes most of the free dendrimer, but a small amount of unassociated dendrimer might remain. Part b of Figure 1 shows a transmission infrared spectrum of a nanocomposite prepared from Au and a G4 PAMAM dendrimer isolated in this way. The amide bands present at 1630 and 1540  $\text{cm}^{-1}$  are characteristic of the dendrimer branches.<sup>15</sup> It is clear from a comparison of this spectrum to that of the free dendrimer (part a of Figure 1) that dendrimer is present in appreciable quantities in the composite material and that spectroscopically the dendrimer is essentially identical to the bulk material. Moreover, the spectral data are similar to those observed for dendrimer monolayers adsorbed to planar Au substrates.<sup>3</sup>

The effect of dendrimer generation on the size and shape of the colloids was investigated by comparing nanocomposites synthesized using either G2 or G4 PAMAM dendrimers. Both generations yield stable solutions of colloidal Au. However, the resulting colloids are markedly different, even though the syntheses were carried out in such a way that the ratio of primary amine groups to  $\text{AuCl}_4^-$  was constant. TEM analysis (Figure 2) shows that colloids formed from the G2 dendrimers (part a of Figure 2) are larger, less monodisperse (see histograms), and more aggregated than those prepared using G4 dendrimers (part b of Figure 2). We believe this effect is a consequence not only of the different number of terminal amines for the two materials (64 for G4 and 16 for G2) but also of the size and shape of the dendrimers. For example, G4 is much larger than G2 and may have the capacity to envelop the growing colloid. Also, G4 dendrimers are 4.5-nm-diameter spheroids (whereas G2 is flat), so G4 may serve as a template for particle growth. A similar effect has been reported for the preparation of metal particles within micelles<sup>16,17</sup> and for colloids prepared by UV irradiation that are stabilized by dendrimers.<sup>11</sup>

The UV-vis spectra of solutions of these colloids is also indicative of the size and morphology differences observed by TEM. Figure 3 shows UV-vis spectra in the surface-plasmon region for Au.  $\lambda_{\text{max}}$  is similar for the two samples, but the plasmon band is red-shifted by 12 nm for the G2 dendrimers.<sup>18</sup> This shift is most likely due to the larger size of the colloids prepared using G2.<sup>19–21</sup>

Preliminary experiments suggest that it is possible to form monolayers of dendrimer-functionalized colloids on planar Au substrates functionalized with a dithiol linker.<sup>19,22</sup> We term these materials “monolayers of monolayers”, because the colloids are coated with the dendrimers and the planar Au substrate is coated with the composites. These materials are useful because the colloids effectively increase the roughness of the planar Au surface, and therefore the surface concentration of dendrimers is proportionately higher than that on planar Au. The presence of the composites on the planar Au could be confirmed by external-reflectance FT-IR spectroscopy. Additionally, AFM data indicate that substrates prepared in this way are covered by roughly one monolayer of the composites. These monolayers of supramolecular monolayers are useful for applications to chemical sensors and catalysis presently underway in our laboratories.<sup>1,23</sup>

To summarize, we have shown that 2–3-nm-diameter Au colloids can be prepared in the presence of PAMAM dendrimers. The dendrimers stabilize the colloids by sorbing to their exterior. Solutions of these materials are stable for periods of weeks. In solution, we think it likely that free dendrimers are in equilibrium

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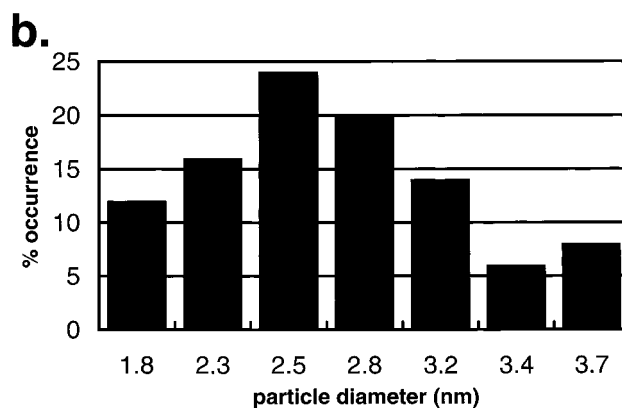
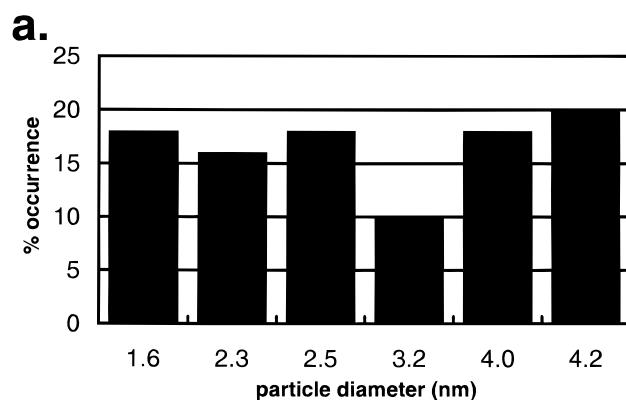
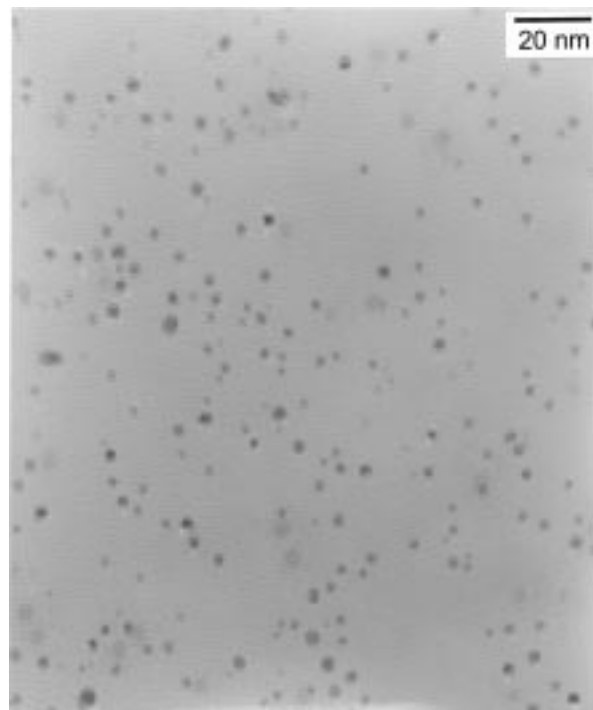
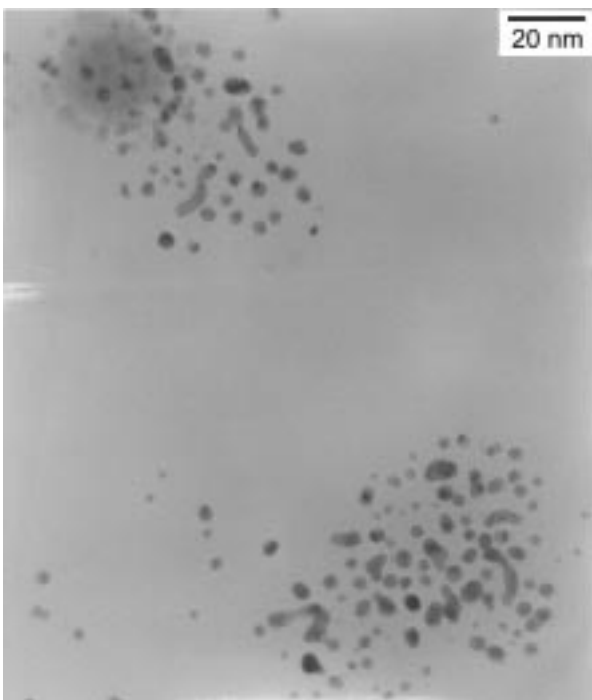


Figure 2. TEM micrographs of nanocomposites formed using (a) G2 and (b) G4 dendrimers. Histograms of the particle size distributions are also shown (determined by counting at least 50 particles). Note the higher degree of monodispersity for the materials prepared using the G4 dendrimers. Average particle diameter: (a)  $3.0 \pm 1.0$  and (b)  $2.7 \pm 0.6$  nm.

with the colloid-confined materials, but this is very difficult to confirm. The composites can be isolated as solids and character-

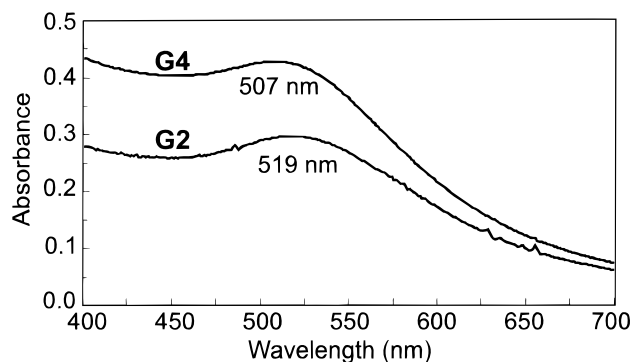


Figure 3. UV-vis spectra of ethanolic solutions of Au-colloid prepared using G4 and G2 dendrimers. The peaks arise from the surface-plasmon absorption for Au. Spectra are normalized to an absorbance of  $\sim 1$  at 250 nm (not shown) to facilitate comparison.

ized using traditional analytical methods. At present, we are studying monolayers of these materials prepared on planar substrates and their applications to chemical sensing and catalysis.

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