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# Controlled Step Growth of Molecularly Linked Gold Nanoparticles: From Metallic Monomers to Dimers to Polymeric Nanoparticle Chains

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# Preparation of Acrylate-Stabilized Gold and Silver Hydrosols and Gold–Polymer Composite Films

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Gold and silver nanoparticles were prepared by reducing aqueous solutions of the respective metal salts with sodium acrylate (SA), which also acts as capping agent. Gold nanoparticles were also prepared using poly(sodium acrylate) (PSA) with various molecular weights (2100, 5100, 15 000, and 30 000 g/mol). These polymers act as both reducing and stabilizing agents for the gold nanoparticles. Gold nanoparticles formed using SA are nearly spherical and have a narrow size distribution (11–17 nm). These particles are similar in size and stability to those formed by the conventional citrate reduction method. PSA-stabilized gold nanoparticles are somewhat less uniform in size but also highly stable. The polymer-stabilized gold particles can be used to form composite polymer films with optical properties that depend on the volume fraction of gold.

## Introduction

Metal nanoparticles have unusual chemical and physical properties which make them attractive for applications such as catalysis, electronics, optics, and biotechnology.<sup>1–10</sup> Gold nanoparticles are versatile building blocks for nanoscale materials and devices.<sup>11–16</sup> Chemical synthesis of metal nanoparticles generally involves the reduction of metal salts followed by nucleation and growth in the presence of stabilizing agents.<sup>17</sup> Faraday was the first to recognize the metallic character of gold nanoparticles in solution.<sup>18</sup> Subsequently, a number of methods have been reported for the synthesis of metal nanoparticles in aqueous solution involving stabilizing agents such as citrates,<sup>17,19</sup> polymers,<sup>20,21</sup> organic solvents such as THF<sup>22</sup>

or THF/MeOH,<sup>23</sup> long chain alcohols,<sup>24</sup> surfactants,<sup>25,26</sup> and organometallics.<sup>27</sup> The first standard protocols for the preparation of metal nanoparticles in aqueous solution were established by Turkevich<sup>17,19</sup> (i.e., the formation of ca. 20 nm gold particles by reduction of [AuCl<sub>4</sub>]<sup>−</sup> with sodium citrate). This has become the most commonly used method for the preparation of gold hydrosols with narrow size distributions. Here we report an alternative procedure for the synthesis of uniform gold and silver hydrosols using sodium acrylate (SA) as reducing and stabilizing agent. The gold nanoparticles are comparable to citrate-stabilized particles with regard to shape, stability, and size distribution.

Polymer protected noble metal colloids are usually prepared from suitable precursors by chemical reduction, photoreduction, or thermal decomposition. Hempenius et al. reported the synthesis of gold nanoparticles in toluene within the core of well-defined polystyrene–oligothiophene–polystyrene (PS–OT–PS) triblock copolymer micelles without the introduction of a separate reducing agent.<sup>28</sup> Youk et al. described the preparation of gold nanoparticles in aqueous solution using a polyelectrolyte complex with a water-soluble terthiophene derivative that reduced HAuCl<sub>4</sub> to produce gold nanoparticles.<sup>29</sup> Poly(sodium acrylate) (PSA) has been used as a stabilizing agent for the synthesis of silver nanoparticles prepared from silver salts using gamma radiation<sup>30</sup> or chemical

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(1) Ciebień, J. F.; Cohen, R. E.; Duran, A. *Supramol. Sci.* **1998**, *5*, 31.

(2) Mayer, A. B. R.; Mark, J. E. *Colloid Polym. Sci.* **1997**, *275*, 339.

(3) Hayward, R. C.; Saville, D. A.; Aksay, I. A. *Nature* **2000**, *404*, 56.

(4) Elghanian, R.; Mucic, C. R.; Storhoff, J. J.; Mirkin, C. A.; Letsinger, R. L. *Science* **1997**, *277*, 1078.

(5) Weller, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 41.

(6) Schmidt, G. *Chem. Rev.* **1992**, *92*, 1709.

(7) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.

(8) Cao, Y.; Jin, R.; Mirkin, C. A. *J. Am. Chem. Soc.* **2001**, *123*, 7961.

(9) Park, S. J.; Lazarides, A. A.; Mirkin, C. A.; Letsinger, R. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 2909.

(10) Braun, E.; Erichen, Y.; Siven, U.; Yoseph, G. B. *Nature* **1998**, *391*, 775.

(11) Schmidt, G.; Hornyak, G. L. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 204.

(12) Dirix, Y.; Bastiaansen, C.; Caseri, W.; Smith, P. *Adv. Mater.* **1999**, *11*, 223.

(13) Brust, M.; Bethell, D.; Kiely, C. J.; Schiffrin, D. J. *Langmuir* **1998**, *14*, 5425.

(14) Lablanc, A.; Astruc, D. *Chem. Commun.* **2000**, 1007.

(15) Templeton, A. C.; Wuelfing, M. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.

(16) Brust, M.; Kiely, C. J. *Colloids Surf., A: Physicochem. Eng. Aspects* **2002**, *202*, 175.

(17) Turkevich, J.; Stevenson, P. C.; Hillier, J. *Discuss. Faraday Soc.* **1951**, *11*, 55.

(18) Faraday, M. *Philos. Trans. R. Soc. London* **1857**, *147*, 145.

(19) Turkevich, J.; Kim, G. *Science* **1970**, *169*, 873.

(20) Hirai, H.; Nakao, Y.; Toshima, N. *Chem. Lett.* **1978**, 545.

(21) Hirai, H.; Nakao, Y.; Toshima, N. *J. Macromol. Sci., Chem.* **1979**, *A13*, 727.

(22) Franke, R.; Rothe, J.; Pollmann, J.; Hormes, J.; Bonnemann, H.; Brijoux, W.; Hindenburg, T. *J. Am. Chem. Soc.* **1996**, *118*, 12090.

(23) Vidoni, O.; Philippot, K.; Amiens, C.; Chaudret, B.; Balmes, O.; Malm, J. O.; Bovin, J. O.; Senocq, F.; Casanova, M. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3736.

(24) Tanori, J.; Pileni, M. P. *Langmuir* **1997**, *13*, 639.

(25) Reetz, M. T.; Lohmer, G. *Chem. Commun.* **1996**, 1921.

(26) Kiwi, J.; Gratzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214.

(27) Sinzig, J.; De Jongh, L. J.; Bonnemann, H.; Brijoux, W.; Koppler, R. *Appl. Organomet. Chem.* **1998**, *12*, 387.

(28) Hempenius, M. A.; Langeveld-Voss, B. M. W.; van Haare, J. A. E. H.; Janssen, R. A. J.; Sheiko, S. S.; Spatz, J. P.; Moller, M.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 2798.

(29) Youk, J. H.; Locklin, J.; Xia, C.; Park, M. K.; Advincula, R. *Langmuir* **2001**, *17*, 4681.

(30) Ershov, B. G.; Henglein, A. *J. Phys. Chem. B* **1998**, *102*, 10663.

reduction.<sup>31</sup> Herein we report the synthesis of gold nanoparticles in aqueous solution using PSA as both reducing and stabilizing agent (i.e., *without* the use of an additional reducing agent).

We further report the formation of polymer films containing gold nanoparticles. The optical properties of these films depend on the local packing density of the particles. Densely packed films have the appearance of golden metallic mirrors, while composite materials with lower filling factors are either red (like solutions of the particles) or blue due to reversible aggregation of the particles within the polymer matrix.

### Experimental Section

All chemicals were purchased from the Sigma/Aldrich Chemical Co. and were used as received. Ultrapure water with a resistivity of  $18.2 \text{ M}\Omega \text{ cm}^{-1}$  was used as the solvent in all preparations.

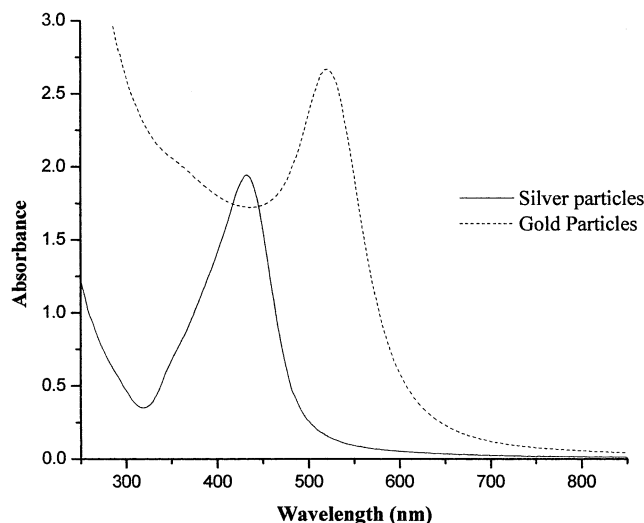
**Preparation of Gold Nanoparticles using SA.** An aqueous solution of  $\text{HAuCl}_4$  (50 mL, 1 mM) was refluxed for 5–10 min, and a warm (50–60 °C) aqueous solution of SA (15 mL, 80 mM) was added quickly. Reflux was continued for another 30 min until a deep-red solution was observed. The particle solution was filtered through  $0.45 \text{ }\mu\text{m}$  Millipore syringe filters to remove any precipitants, and the filtrate was stored at room temperature.

**Preparation of Silver Nanoparticles using SA.** An aqueous solution of  $\text{AgNO}_3$  (50 mL, 3 mM) was refluxed for 5–10 min under an argon atmosphere, and a warm (50–60 °C) aqueous solution of SA (25 mL, 160 mM) was added quickly. Reflux was continued until a yellowish-brown solution was obtained (approximately 30 min). This solution was filtered through  $0.45 \text{ }\mu\text{m}$  Millipore syringe filters to remove any precipitants, and the filtrate was stored at room temperature in the dark under an argon atmosphere.

**Preparation of Gold Nanoparticles using PSA.** An aqueous solution of  $\text{HAuCl}_4$  (50 mL, 1 mM) was refluxed for 5–10 min, and a warm (50–60 °C) aqueous solution of PSA was added rapidly (PSA-2100,  $M_w = 2100 \text{ g/mol}$ , 25 mL, 40 mM, or PSA-5100,  $M_w = 5100 \text{ g/mol}$ , 40 mL, 20 mM). Reflux was continued until a red solution was obtained (approximately 1 h). To make gold nanoparticles using PSA-15000 ( $M_w = 15\,000 \text{ g/mol}$ ), 9 mL of 0.7% PSA-15 000 was added to a boiling  $\text{HAuCl}_4$  solution (60 mL, 1 mM) and refluxed for 1 h. In both cases, the solutions were filtered through  $0.45 \text{ }\mu\text{m}$  Millipore syringe filters to remove any insoluble material and the filtrate was stored at room temperature. Viscous solutions of gold nanoparticles were prepared by adding a hot (50–60 °C) aqueous solution of 12% PSA-30 000 (20 mL,  $M_w = 30\,000 \text{ g/mol}$ ) to 40 mL of boiling  $\text{HAuCl}_4$  solution (5 mM). This solution was then refluxed for 10 min.

**Preparation of PSA–Gold Nanoparticle Composite Films.** Two aliquots of the viscous PSA-30 000-stabilized gold nanoparticle solution (4 mL each, as prepared above) were mixed with 0.5 and 1 mL, respectively, of a solution of PSA-30 000 (20 w/v %). These two mixtures, along with a 4 mL aliquot of the original PSA-30 000-stabilized gold nanoparticle solution, were slowly evaporated at room temperature in separate rectangular glass troughs to obtain three gold-loaded polymer films (film thicknesses = 75–175  $\mu\text{m}$ ). To produce polymer films with higher gold loadings, 3 mL, 5 mL, and 10 mL aliquots of PSA-15 000-stabilized gold nanoparticles were concentrated by centrifuging, decanting, and redispersing in 1 mL of PSA-30 000 solution (0.07 w/v %). These three solutions were then further concentrated by slow evaporation under vacuum to a volume of 300  $\mu\text{L}$ . These solutions, which all contained the same amount of PSA-30 000 but varying concentrations of gold, were then slowly evaporated on glass slides within a cover ring to form highly loaded gold–polymer composite films.

**Characterization.** Transmission electron microscopy (TEM) was carried out with a JEOL-2000EX TEM operating at 200 kV. Specimens for inspection by TEM were prepared by slow



**Figure 1.** UV–visible absorption spectrum of an aqueous solution of gold and silver nanoparticles formed using sodium acrylate (SA).

evaporation of one drop of a dilute aqueous solution of the particles on a carbon coated copper mesh grid. The Ag particles (which are air sensitive) were deposited under a nitrogen atmosphere. UV–visible spectra were recorded using a Genesys 10-S spectrophotometer (Thermo Spectronic, USA).

### Results and Discussion

**Gold Nanoparticles.** Gold nanoparticles prepared using SA were found to be comparable to the citrate-stabilized gold nanoparticles with regard to shape, size, and stability. A plasmon absorption band, characteristic of gold nanoparticles, was observed at 522 nm (Figure 1). We also attempted to form gold nanoparticles using sodium propionate and sodium butyrate as reducing/stabilizing agents, but this resulted only in the decolorization of the solution, indicating reduction of  $\text{Au}^{3+}$  to a water-soluble  $\text{Au}^{1+}$  complex.

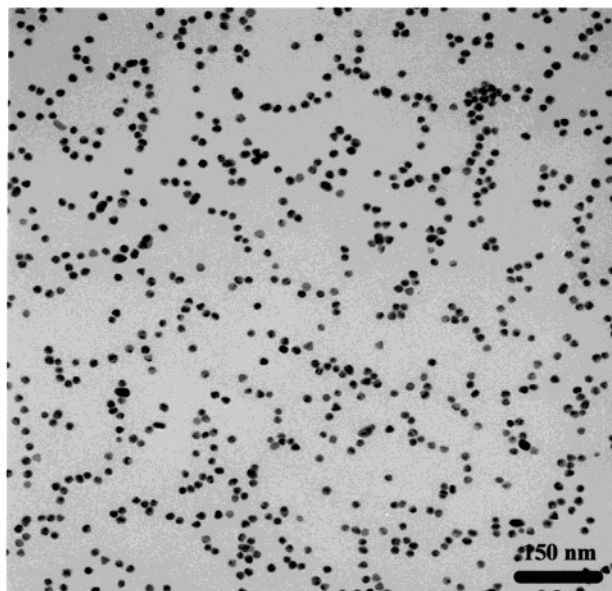
Gold nanoparticles formed using PSA-2100, PSA-5100, PSA-15 000, and PSA-30 000 (2100, 5100, 15 000, and 30 000 g/mol, respectively) also exhibited typical plasmon absorption in the range 516–534 nm (see Supporting Information). These polymers act as both reducing and stabilizing agents for the gold nanoparticles. The precise mechanism of stabilization is unclear, but since these polymers are polyelectrolytes, it is possible that both electrostatic and steric stabilization are involved.

Figure 2 shows a TEM image of gold nanoparticles formed using SA. The particles were found to be spherical with a narrow size distribution (11–17 nm), as shown in Figure 3. The average particle diameter was 14 nm. Figure 4 shows the TEM image of gold nanoparticles synthesized using PSA-2100. In general, the particles formed using polymers were found to be less uniform in size and shape than those formed using SA (see Supporting Information). The gold particles formed using PSA-2100 were found to be spherical and predominantly in the size range 20–30 nm. When PSA-15 000 was used as the stabilizing agent, particles of two size ranges were formed: approximately half fell in the size range 45–65 nm while the remainder were between 10 and 20 nm in diameter. Gold nanoparticles formed using PSA-30 000 had smaller diameters (5–20 nm).

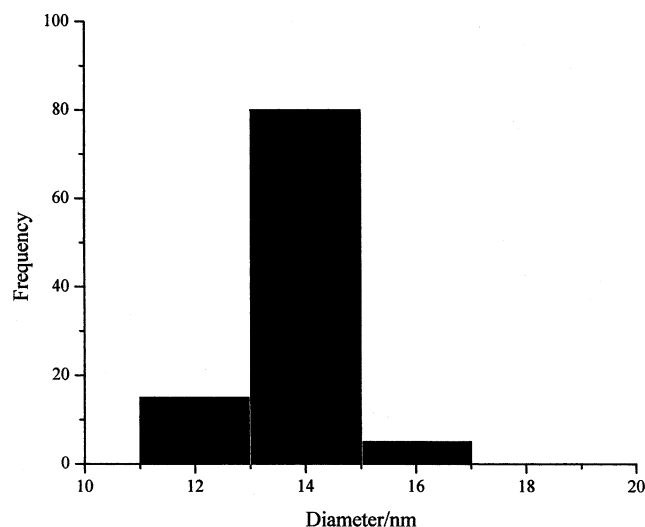
**Quantification of SA on the Surface of Gold Nanoparticles.** Since the concentration of SA can be determined by UV–visible spectroscopy, it was possible to measure its total concentration in the hydrosol by UV

(31) Shiraishi, Y.; Toshima, N. *Colloids Surf., A: Physicochem. Eng. Aspects* **2000**, 169, 59.



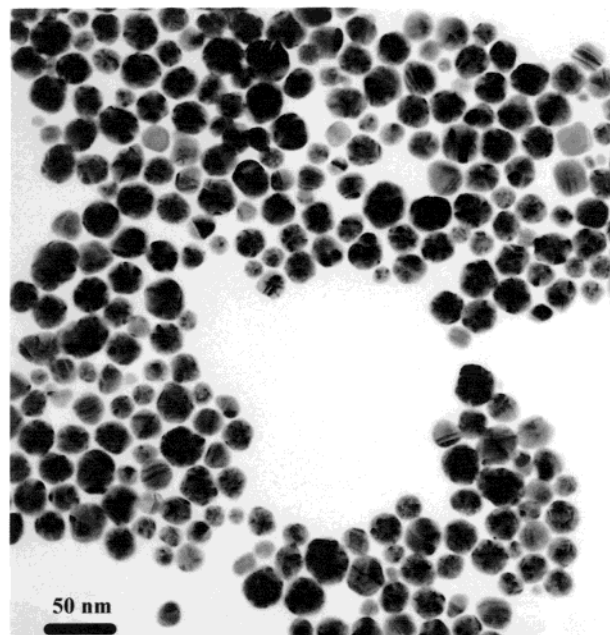


**Figure 2.** TEM micrograph of gold nanoparticles formed using sodium acrylate (SA).



**Figure 3.** Histogram for the size distribution of gold nanoparticles formed using sodium acrylate (SA).

analysis. These measurements were also confirmed by elemental analysis. Since SA residing on the surface of the gold particles exists in equilibrium with that in solution, it is still difficult to know exactly the concentration of SA at the surface of particles. To estimate the amount of SA on the particle surfaces and in the solution, the particle solutions were centrifuged for 0.5 h at 13 000 rpm using a Sigma (1-13) benchtop centrifuge. The supernatant was then removed by decanting. The particles were redissolved in an equivalent volume of milli-Q water, and the same procedure was repeated to remove most of the SA from the surface of particles. Analysis of SA in the supernatant after the second wash indicated the removal of 94% of the initial SA. After two washings we obtained stable gold nanoparticles in a solution with a total SA concentration of 1.34 mM. Even at this low SA concentration, the particles were stable for at least 1 month. A third centrifugation resulted in the irreversible precipitation, and this separated gold aggregate contained about 1.15 mM SA. The molar amount of gold nanoparticles in solution before precipitation was estimated from UV-visible spectra to be 524 nM, assuming that the molar



**Figure 4.** TEM micrograph of gold nanoparticles formed using poly(sodium acrylate), 2100 g/mol (PSA-2100).

extinction coefficient for these particles was  $4.2 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ , as calculated by Demers et al. for citrate stabilized particles of  $15.7 \pm 1.2 \text{ nm}$  diameter.<sup>32</sup> Thus, we estimate that a minimum of around 2300 SA molecules per gold nanoparticle is required for stabilization and that approximately 80% of these are molecules adsorbed at the surface of the particles (see Supporting Information).

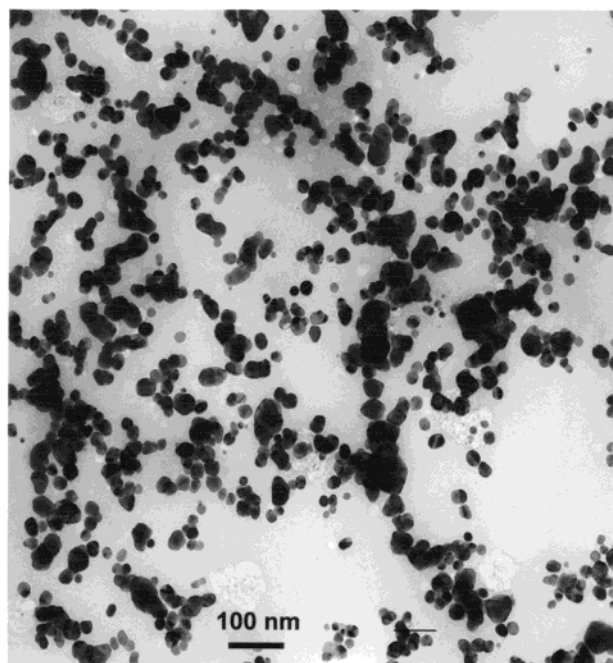
**Silver Nanoparticles.** Due to the high sensitivity of colloidal silver toward oxygen, it is usually difficult to obtain stable silver nanoparticles with narrow size distributions. At low concentrations of SA, aggregated silver particles were formed with starlike or leaflike structures (see Supporting Information), similar to those observed by Henglein and Giersig in the preparation of silver nanoparticles by reduction of silver salts using  $\gamma$  radiation in the presence of citrate.<sup>33</sup> We, therefore, prepared silver nanoparticles using SA under anaerobic conditions. Under these conditions, we were able to synthesize relatively stable silver nanoparticles with a characteristic plasmon resonance band at 432 nm, as shown in Figure 1. Figure 5 shows a TEM image of these silver particles. About 70% of the particles are in the range 18–40 nm.

**Polymer Films.** An interesting aspect of the polymer stabilized gold particles is the possibility of obtaining composite gold–polyelectrolyte films simply by allowing their aqueous solutions to evaporate on a suitable substrate, for example, glass. As predicted by Maxwell–Garnett theory and recently demonstrated by Ung et al.,<sup>34,35</sup> the optical properties of such composite materials can be controlled by the packing density of gold particles. Films with a low filling factor, in general, will be of the same color as solutions of the particles, while very high filling factors lead to reflective golden mirrors, which appear blue in transmission. Our systems exhibit behavior

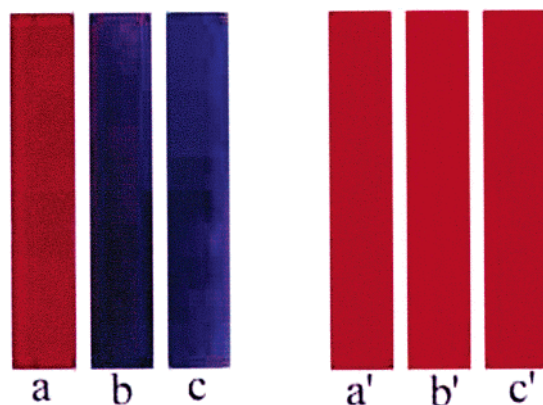
(32) Demers, L. M.; Mirkin, C. A.; Mucic, R. C.; Reynolds, R. A.; Letsinger, R. L.; Elghanian, R.; Viswanadham, G. *Anal. Chem.* **2000**, *72*, 5535.

(33) Henglein, A.; Giersig, M. *J. Phys. Chem. B* **1999**, *103*, 9533.  
(34) Ung, T.; Liz-Marzan, L. M.; Mulvany, P. *Colloids Surf., A: Physicochem. Eng. Aspects* **2000**, *202*, 119.

(35) Ung, T.; Liz-Marzan, L. M.; Mulvany, P. *J. Phys. Chem. B* **2001**, *105*, 3441.

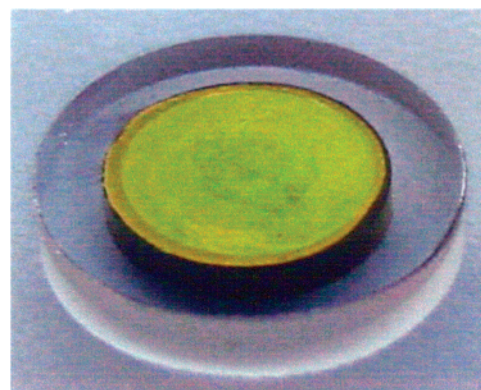


**Figure 5.** TEM micrograph of silver nanoparticles formed using sodium acrylate (SA).

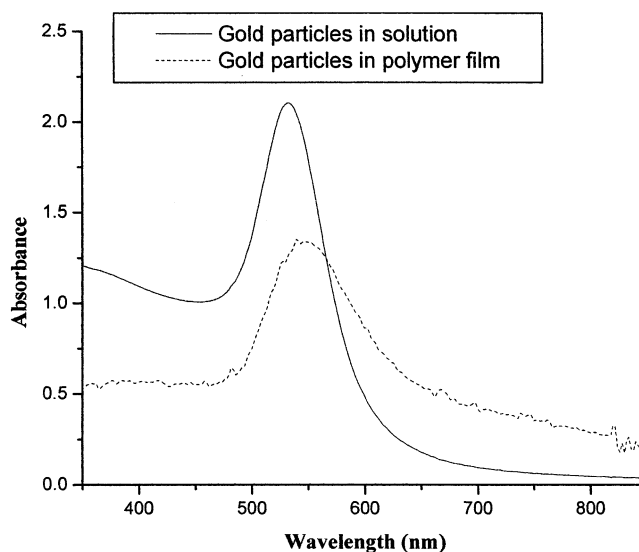


**Figure 6.** Photographs of polymer films with low gold filling factor containing (a) 0 mL, (b) 0.5 mL, and (c) 1.0 mL of additional PSA-30 000 solution (20% w/v). a', b', and c' are the photographs of the respective films after dissolution in water.

that is consistent with these observations. We have prepared two different types of polymer films, highly dilute thick films (ca. 75–170  $\mu\text{m}$ ) and densely packed thinner films (ca. 9  $\mu\text{m}$ ). The thick, dilute films have gold volume fractions of 0.04–0.08% v/v that are comparable with the volume fraction of gold in a concentrated colloidal *liquid* solution. Thus, these films can be thought of as “solutions” of gold nanoparticles in a polymer phase, and one might expect the color of the films to be the same as that of a liquid solution, that is, red. Photographs of these films (Figure 6) show that this is not always the case: some of the films appear blue, as would only be expected for a much higher filling factor of gold. This observation can be explained by aggregation of the gold particles within the polymer matrix, that is, by a localized increase in the filling factor. Interestingly, the aggregation is completely reversible, as demonstrated by the reappearance of the typical red color upon dissolution of the films in water (Figure 6). The color of thinner films with relatively high volume fraction of gold (4–12% v/v) was purple in transmission. In reflection, the films had the appearance of golden metallic mirrors, as shown in Figure 7. To obtain



**Figure 7.** Photograph of a densely packed thin film showing golden metallic reflection.



**Figure 8.** UV-visible spectra of polymer-stabilized gold nanoparticles before and after thin film formation.

UV-visible spectra of the densely packed films (which were almost opaque), the reference beam was recorded while attenuating the beam with milky glass (Figure 8). The plasmon peak is slightly shifted toward higher wavelength (red shift) due to close packing of the particles. Even these highly gold loaded films dissolve readily in water to give wine-red solutions, indicating complete recovery of the colloidal gold.

## Conclusions

We have demonstrated the synthesis of gold and silver nanoparticles using a simple polymerizable ligand as both reducing and stabilizing agent. These particles, especially gold, are comparable to citrate-stabilized particles regarding their shape, stability, and size distribution. We have also synthesized gold (and silver) nanoparticles in aqueous media using a series of polyelectrolytes, which act as reducing and capping agents for these particles. Formation of gold-loaded polymer films and their dissolution in water to regenerate solutions of gold nanoparticles is also reported. Moreover, the methods described here present a simple, one-step approach to the formation of gold-polyelectrolyte nanocomposites using readily available reagents.

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**Supporting Information Available:** UV-visible spectra and TEM images of gold nanoparticles and calculations for quantification of surface ligand concentration. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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