Communication

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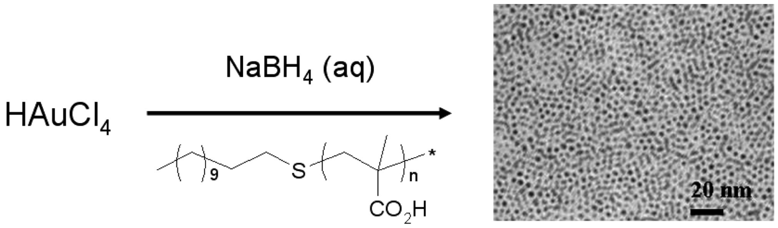

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Size-Controlled Synthesis of Near-Monodisperse Gold Nanoparticles in the 1−4 nm Range Using Polymeric Stabilizers

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Gold nanoparticles are among the oldest and best-studied nanoscale materials known.[1] They are commercially available in many forms, and numerous preparative methods for particles from about 1 nm to several micrometers diameter are documented in the literature.[2] Nevertheless, only a handful of standard procedures are employed routinely to prepare gold particles for a multitude of applications. These methods are reliable, simple to carry out, and lead to uniform particles with a narrow size distribution in the desired range. The most widely applied procedures to obtain gold hydrosols are variations of the classic Turkevich−Frens citrate reduction route.[3] Most hydrophobic (and some hydrophilic) particles are prepared by borohydride reduction in an organic solvent in the presence of thiol capping ligands using either a two-phase liquid/liquid system or a suitable single-phase solvent.[4] The latter approach is usually employed for particles in the 1 to ca. 8 nm range.

Gold nanoparticles are useful in a broad range of applications,[5] but practical limitations are apparent when monodispersity is required, for example, in electrochemical quantized capacitance charging,[6] single-electron transistor assembly,[7] and in advanced applications of thermal gradient optical imaging.[8] In many cases, monodisperse *fractions* of particles must be prepared, usually in low yield following cumbersome size separation procedures, such as size exclusion chromatography.[9] The availability of a simple protocol for the gram-scale preparation of uniform MPCs below 5 nm would thus be of great practical value for numerous applications. We report here a single-step method which leads to near-monodisperse gold nanoparticles in the 1−4 nm size range. In contrast to previous procedures, the particle size is controlled precisely by the ratio of Au to capping ligand, and the particles are readily obtainable in both aqueous and nonaqueous solutions.

To prepare the particles, an aqueous solution of hydrogen tetrachloroaurate (20 mL, 0.5 mM) was reduced by the addition of a freshly prepared solution of sodium borohydride (2 mL, 50 mM) in the presence of a water-soluble alkyl thioether end-functionalized poly(methacrylic acid)[10] stabilizer (Scheme 1, $n \sim 50$, $M_w/M_n = 1.1$; see Supporting Information for GPC data).

The polymer concentrations used for the preparations and the resulting particle sizes are given in Table 1.

The as-prepared particles were characterized by UV−vis spectroscopy (Figure 1).

Scheme 1

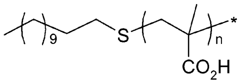

Table 1. Synthesis of Au Nanoparticles Using a Thioether-Terminated Polymeric Stabilizer[a]

polymer (mM)	particle diameter (nm)	Au:S	approximate sum formula
0.006	4.0 ± 0.1	4.6 (A)	Au_{2406} (thiol)$_{523}$
0.03	3.0 ± 0.1	4.1 (B)	Au_{976} (thiol)$_{238}$
0.18	2.5 ± 0.3	4.1	Au_{586} (thiol)$_{143}$ Au_{459} (thiol)$_{112}$ Au_{309} (thiol)$_{75}$
0.6	2.0 ± 0.2	3.3 (C)	Au_{225} (thiol)$_{68}$ Au_{309} (thiol)$_{94}$
1.8	1.8 ± 0.3	2.6	Au_{140} (thiol)$_{54}$ Au_{201} (thiol)$_{77}$ Au_{225} (thiol)$_{87}$
3.6	1.5 ± 0.2	2.2 (D)	Au_{79} (thiol)$_{36}$ Au_{116} (thiol)$_{53}$ Au_{140} (thiol)$_{64}$

[a] Effect of polymer concentration on particle size (from TEM) and Au:S ratio (from AES). Suggested sum formulas were calculated from the number of Au atoms per particle of a given size (obtained from ref 4c) and the corresponding experimental Au:S values (see Supporting Information for details).

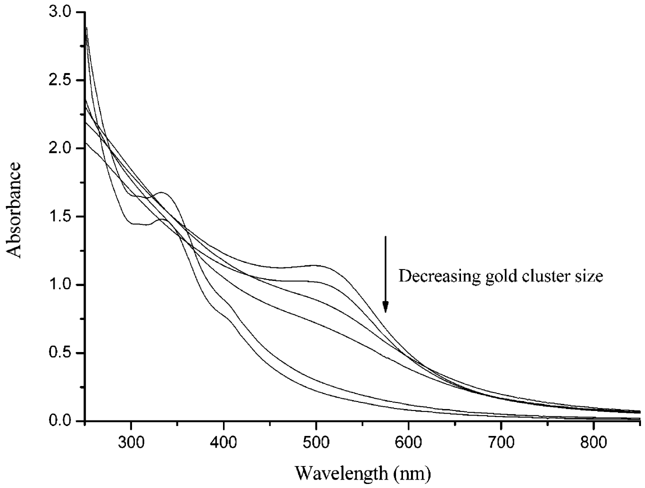

Figure 1. UV−visible spectra of as-prepared gold nanoparticles of six different sizes as shown in Table 1.

The UV-visible spectra of the six preparations listed in Table 1 are all significantly different from each other, indicating that particles of different average sizes have been prepared in each case. Remarkably, all spectra suggest that the average particle size is below 5 nm since larger particles would exhibit a sharper and more intense plasmon absorption band close to 525 nm.[11] Some of the spectra do not show a plasmon band at all, indicating that most particles are below ca. 3 nm in size. The series of spectra obtained is well-known for size-separated (fractionated) particles in the range

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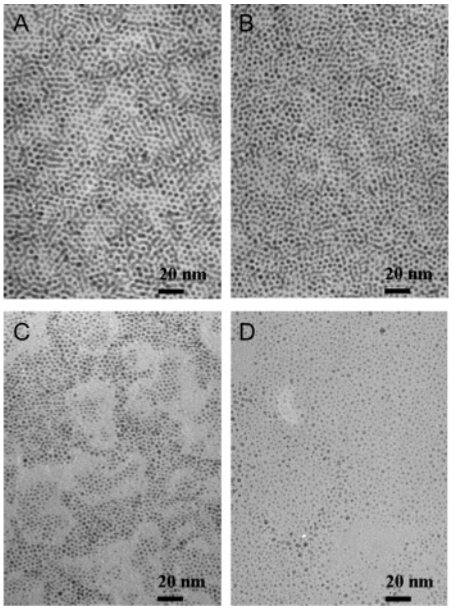

Figure 2. TEM micrographs of gold nanoparticles of four different sizes.

below 5 nm but unprecedented for as-prepared samples. The ability to prepare six spectroscopically distinct samples with diameters less than 5 nm strongly suggests a narrow size distribution for each sample. To confirm this by transmission electron microscopy (TEM), it was convenient to first isolate the particles from excess polymer. For this purpose, the particles were capped with 1-dodecanethiol and transferred into *n*-hexane (see Supporting Information). The UV−vis spectra in hexane were very similar to those in water (see Supporting Information, Figure S1) except for some small systematic changes which are due to the different refractive index of the organic medium.[12] Most importantly, the spectra retained their characteristic differences relative to each other, indicating that the ligand exchange process did not cause a significant broadening of the particle size distribution.

Specimens for inspection by TEM were prepared by evaporating a droplet of the hexane solutions onto a carbon-coated copper mesh grid (Figure 2).

All images confirm very narrow size distributions which are unprecedented in the sub-5 nm size range. The particles shown in Figure 2a and b have diameters of 4.0 ± 0.1 and 3 ± 0.1 nm, respectively, and are near-monodisperse. The smaller particles in Figure 2c and d also exhibit very narrow size distributions in the range of 2 ± 0.2 and 1.5 ± 0.2 nm, respectively. Since size nonuniformities can easily be underestimated by TEM due to size segregation phenomena during sample preparation, large and representative areas were imaged to support our claim of near-monodispersity. The particle size and particle size distribution for selected samples were also examined for the native aqueous hydrosols by laser diffraction, and these measurements agreed well with the TEM observations (see Supporting Information, Figure S4). Examining the Au:S ratio of each preparation by ICP-AES further confirmed the particle sizes found by UV−vis and TEM and, in addition, allows the assignment of an average sum formula for each preparation (Table 1).

Although the synthetic method reported here does not differ fundamentally from previous preparations of MPCs, no other methods lead to comparable results in a single step. The causes of polydispersity in MPC samples (and hence the limited scope for size control by adjustment of reaction conditions) is not well understood.[4c] As such, it is hard to give a precise rationalization for the apparent superiority of our new method. Most likely, the polymeric ligands establish a hydrophilic protective shell around the growing metal nuclei that is permeable to tetrachloroaurate ions (to allow further growth) while preventing the fusion of two or more particles. The poly(methacrylic acid) chains can clearly function as steric stabilizers by binding to the gold surface through the thioether but may also (unlike, for example, PEG-SH)[4d,h] play an electrostatic role due to the potential for this water-soluble ionizable polymer to carry a negative charge.

We also considered the possibility that the clusters are pre-organized within monodisperse micelles formed by the polymer which has a C_{12} hydrophobic “headgroup”. This mechanism was ruled out by determining the critical micelle concentration of the polymer (∼0.8−0.9 mM), which was well above the concentrations used in the majority of the experiments.

In conclusion, a simple protocol for the preparation of near-monodisperse gold hydrosols in the small size regime below 5 nm has been developed. The particle size is controlled by varying the concentration of the stabilizing polymer, which can be readily displaced by thiol ligands to yield MPCs of the usual type. We believe that this new protocol will replace previous methods whenever precise size control and monodispersity are required.

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Supporting Information Available: Experimental details, details of polymer synthesis, UV−visible absorption spectra of gold nanoparticles in *n*-hexane, and particle sizing. This material is available free of charge via the Internet at http://pubs.acs.org.

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