Homogeneous silica coating of vitreophobic colloids

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Gold colloids are homogeneously coated with silica *via* a three-step deposition process; the thickness of the silica layer can be completely controlled, and the particles can be transferred into practically any solvent.

Nanosized metal particles have a wide variety of potential uses, ranging from non-linear optical switching and high-density information storage, to immunolabelling and tracer diffusion studies in concentrated dispersions. A major difficulty with large-scale implementation is that metal colloids have complicated double-layer structures, and their stability is controlled by both electronic equilibria and ionic/polymer adsorption. One way to improve the stability of noble-metal particles is to coat them with silica, which is very resistant to coagulation, even at high volume fractions. Furthermore, procedures for incorporating silica particles into polymer latices or transferring them into polar and non-polar solvents are well known. Although silica coating procedures have been reported in the literature,[1–4] these studies generally involved surfaces with significant chemical or electrostatic affinity for silicate. However, gold metal has very little affinity for silica because it does not have an oxide film on its surface, and because there are usually adsorbed carboxylic acids or other organic anions present on the surface to stabilize the particles against coagulation. These stabilizers also render the gold surface vitreophobic.

Previous attempts to overcome this vitreophobic character involved the heterocoagulation of gold colloids on silica colloids dispersed in water, followed by extensive growth in ethanol.[5] This resulted in a mixture of labelled and unlabelled silica particles, with a rather low concentration of the labelled ones. The approach presented here is fundamentally different, and involves modifying the particle surface to make it vitreophilic. The simplest way to do this is using silane coupling agents as surface primers.[6] This results in the direct formation of a hydrated silica monolayer covalently bonded to the metal substrate.

A variety of thioalkane derivatives may be used to stabilize gold colloids,[7] but aminoalkanes also complex strongly with gold metal.[8] The method reported here involves the primer aminopropyltrimethoxysilane (APS). One monolayer of APS is allowed to adsorb onto the gold colloid surface. During this process, the previously adsorbed (negatively charged) citrate groups are displaced by APS molecules, with the silanol groups pointing into solution. This is driven by the large complexation constant for gold amines. Hydrolysis of the surface bonded siloxane moieties to form silane triols occurs within minutes.[6] At pH 7, ionization of the silane triols occurs (their isoelectric point is pH 2–3), and this ensures that there is adequate negative surface charge on the gold sol during stabilizer exchange to maintain sol stability. In the second step, active silica (sodium silicate solution at a pH just low enough to allow a slow polymerization of silicate groups) is added to the dispersion,[1] which promotes the formation of a thin, dense and relatively homogeneous silica layer around the particles, using the silanol groups as anchor points [see Fig. 1(*b*)]. The resulting dispersion can then be transferred without loss of stability into ethanol, where further growth of the particles can be achieved using the well known Stöber method,[9] based on the hydroxide-catalysed hydrolysis of tetraethoxysilane (TES) and condensation of the resulting silanol groups. This final growth step results in smooth, monodisperse spherical silica particles with gold cores placed precisely at their centres, though some gold-free silica particles inevitably form due to the presence of small silica nuclei in the original sodium silicate solution [Fig. 1(*c*)]. However the gold-free nuclei constitute only 1–3% of the colloid particles. In addition, there are a few percent of silica coated gold doublets, formed when the particle growth is allowed to occur too quickly. It is important to note that, if the

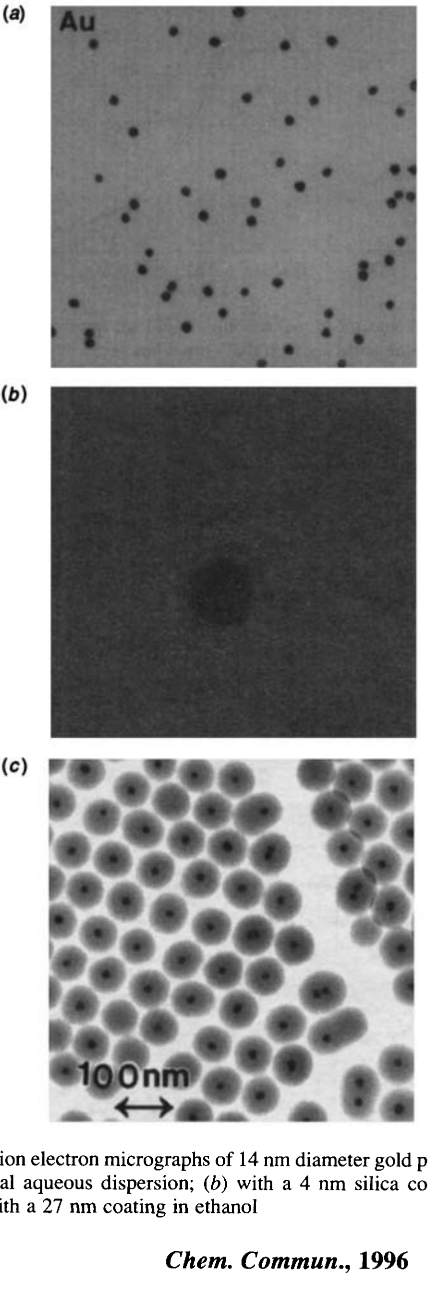

Fig. 1 Transmission electron micrographs of 14 nm diameter gold particles: (*a*) in the original aqueous dispersion; (*b*) with a 4 nm silica coating in water, and (*c*) with a 27 nm coating in ethanol

first silica coating in water is skipped, significant aggregation takes place in ethanol before silica from TES hydrolysis can grow onto the particles. This is mainly due to a reduction in electrostatic stabilization of gold particles in ethanol, when stabilized only with APS/citrate. Philipse *et al.* have previously shown that only a combination of silicate and TES deposition produces homogeneously coated colloid particles.[2,4]

The final growth step allows complete control of the final core : shell thickness ratio, and the coated particles can readily be chemically modified for transfer into organic non-polar solvents.[10] The optical properties of the dispersion can then be tailored through variations in both the coating thickness and the refractive index of the dispersing medium.[11] As an example of the influence of the silica layer on the optical properties, Fig. 2 shows the UV–VIS spectra of dispersions following the three main steps of the synthesis process: the uncoated gold colloid, the gold particles after the initial, thin silica coating in water [Fig. 1(*b*)], and finally after secondary silica deposition in ethanol. Notice that although the gold concentration is the same in all three cases, there is a change in the intensity of the plasmon absorption band, as well as a red-shift in the position of the absorption maximum. If the coated particle size is sufficiently large, scattering becomes important, which results in an enhanced absorbance at low wavelengths. All these effects are in agreement with Mie's theory for coated particles.[5,12]

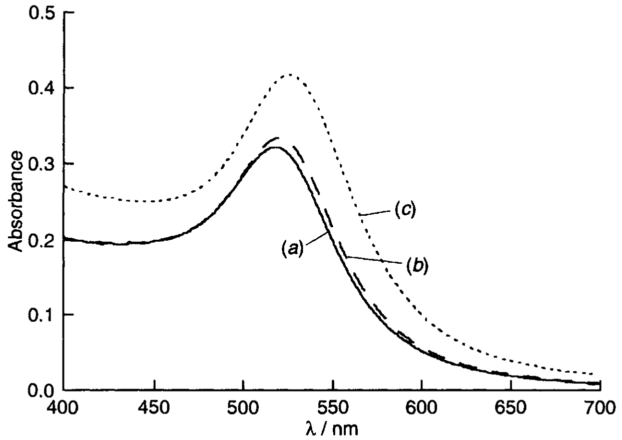

Fig. 2 UV–VIS spectra of: (*a*) the initial gold sol (particle diameter = 14 nm); (*b*) the same particles with the 4 nm silica layer in water, and (*c*) the same particles with the 27 nm silica layer in ethanol. [Au] = 82 μmol dm^{-3}.

Although the method is presented here for gold colloids only, it is readily applied to other kinds of colloids which have typically been difficult to silica coat, such as silver, copper and semiconductor particles. Synthetic routes for the preparation of coated nanosized semiconductors and other metals will be presented elsewhere.

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References

1 R. K. Iler, *US Pat.*, 2 885 366, 1959.
2 A. P. Philipse, M. P. B. van Bruggen and C. Pathmamanoharan, *Langmuir*, 1994, **10**, 92.
3 M. Ohmori and E. Matijević, *J. Colloid Interface Sci.*, 1992, **150**, 594.
4 A. P. Philipse, A. M. Nechifor and C. Pathmamanoharan, *Langmuir*, 1994, **10**, 4451.
5 L. M. Liz-Marzán and A. P. Philipse, *J. Colloid Interface Sci.*, 1995, **176**, 459.
6 E. P. Plueddermann, *Silane Coupling Agents*, 2nd edn., Plenum, New York, 1991.
7 M. Giersig and P. Mulvaney, *Langmuir*, 1993, **9**, 3408.
8 R. J. Puddephatt, *The Chemistry of Gold*, Elsevier, Amsterdam, 1978.
9 W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.
10 A. K. Van Helden, J. W. Jansen and A. Vrij, *J. Colloid Interface Sci.*, 1984, **81**, 354.
11 P. Mulvaney and S. Underwood, *Langmuir*, 1994, **10**, 3427.
12 C. F. Bohren and D. F. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, New York, 1983.

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