A novel method of preparing thiol-derivatised nanoparticles of gold, platinum and silver forming superstructures

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Thiol-derivatised nanoparticles of Au, Pt and Ag (diameter 1–10 nm) forming superstructures, are prepared by the acid-facilitated transfer of well characterized particles in a hydrosol to a toluene layer containing the thiol.

Nanoparticles of gold and other noble metals are attracting much attention because of their potential applications in microelectronics.[1,2] Several wet chemical methods have been reported in the recent years, for the preparation of colloidal metal sols.[3,4] The methods generally involve the reduction of the relevant metal salt in the presence of a suitable surfactant, the surfactant being useful in the control of the growth of the metal particles. Thiol-derivatised nanoparticles of noble metals are particularly fascinating in that they can be recrystallised from the parent solution; they often self-assemble into cross-linked structures or superlattices on removal of the solvent.[2,5] Since the first report on the synthesis of thiol-derivatised nanoparticles,[6] the common practice is to first extract the metal ions from the aqueous medium to a hydrocarbon (toluene) layer by means of a phase-transfer reagent such as tetraoctylammonium bromide and then to carry out the reduction with $NaBH_4$ in the presence of an alkanethiol. Here, the nucleation and growth of the metal particles as well as the attachment of the thiol molecules occur nearly simultaneously. Metal particles prepared in this manner generally contain nitrogenous surface impurities due to the phase-transfer reagent,[6] which render it difficult to obtain good superstructures. What would be desirable is a procedure wherein one can transfer the well characterized metal nanoparticles from a hydrosol to a non-polar medium containing the thiol. We have indeed found such a direct procedure to be feasible and have successfully prepared thiol-derivatised nanoparticles of Au, Ag and Pt of desired size distributions.

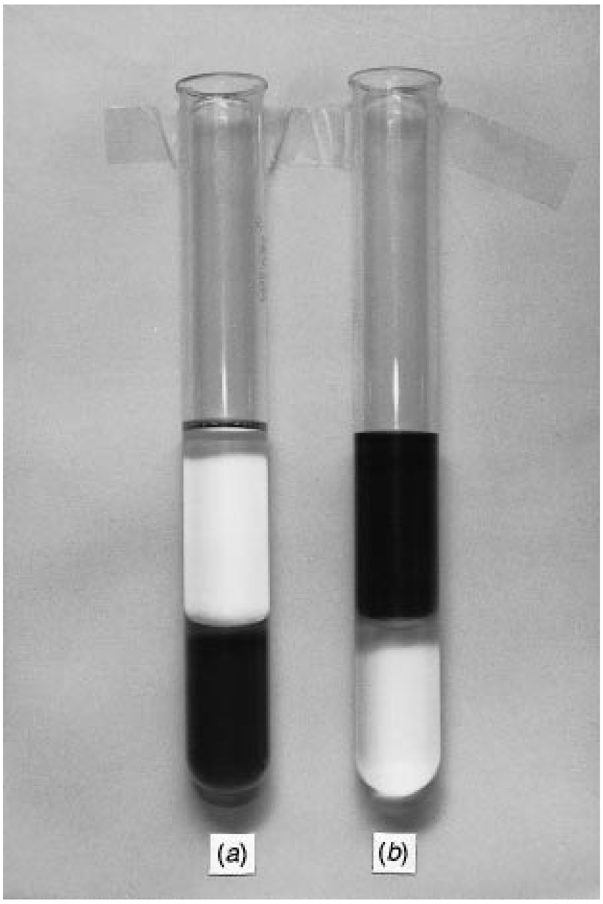

Fig. 1 Immiscible layers of (*a*) the gold hydrosol (at the bottom) and the clean toluene solution containing the thiol (on top). (*b*) Thiol-derivatised Au sol in toluene (on top) and the clean aqueous solution at the bottom.

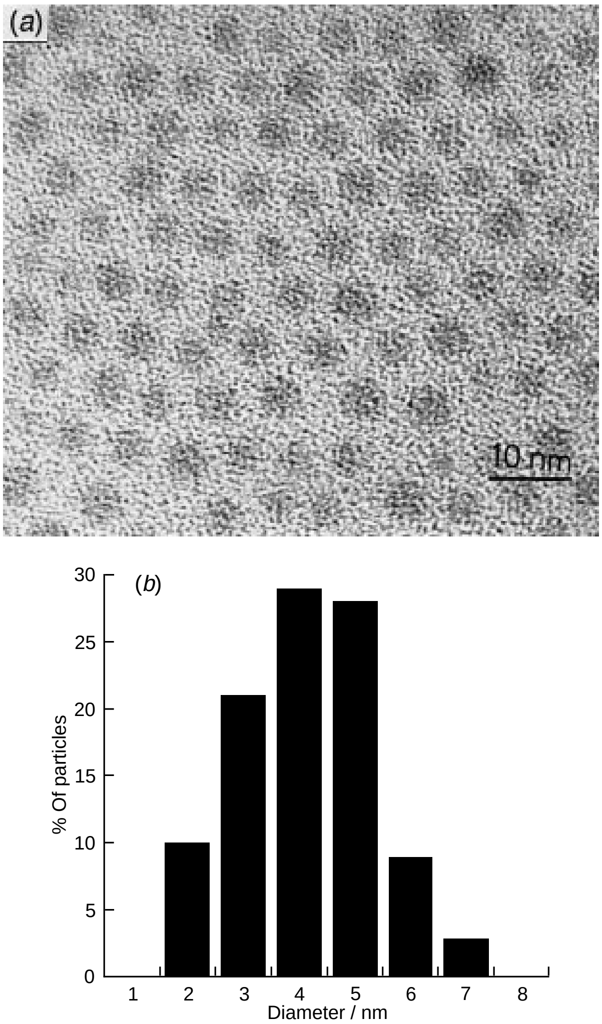

Fig. 2 (*a*) TEM image of the thiol-derivatised Au nanoparticles forming a superstructure. (*b*) Histogram showing the size distribution.

In a typical preparation, a hydrosol containing small clusters of Au was first prepared by the reduction of chloroaurate ions (2.2 ml of 25 mm aqueous solution) using partially hydrolysed tetrakis(hydroxymethyl) phosphonium chloride (THPC),[7] having prepared the latter by adding 1 ml of a fresh 50 mm solution of THPC in water to 47 ml of 6.38 mm NaOH solution. To the gold sol so obtained, 100 ml of a 0.25 mm solution of dodecanethiol in toluene (Au : S = 2 : 1) was added, to obtain two immiscible layers consisting of the transparent organic phase containing the thiol on the top and the coloured hydrosol at the bottom. To this biphasic mixture, 125 ml of conc. HCl was added under stirring. This resulted in a remarkably swift movement (within 3 min) of the Au nanoparticles to the hydrocarbon layer containing the thiol. Clearly, the gold particles have an inherent attraction to the thiol molecules. This could be seen vividly by the complete transfer of colour across the interface to the hydrocarbon layer as shown in Fig. 1. The gold sol in toluene was shaken with water several times to remove traces of HCl and evaporated to *ca.* 2 ml in a rotary evaporator. The excess thiol was removed by the addition of 350 ml of ethanol (95%). The dark brown solid thus obtained was filtered, washed with ethanol and dispersed in 10 ml of toluene for further investigations. The UV–VIS spectrum of the toluene sol of gold showed a broad band at *ca.* 520 nm due to plasmon absorption just as the hydrosol. The core-level X-ray photoelectron spectrum showed the Au $4f_{7/2}$ binding energy at 84 eV, corresponding to the Au^0 state. There was a feature at 163.5 eV due to S 2p showing that the thiol molecules were chemisorbed on the gold surface. There was no evidence of a feature due to P 2p from THPC in the spectrum, unlike in the particles from the hydrosol which showed the feature at *ca.* 133 eV. It appears that the role of HCl in the present procedure is to cleanse the surface of the Au particles and facilitate their transfer to the hydrocarbon layer.

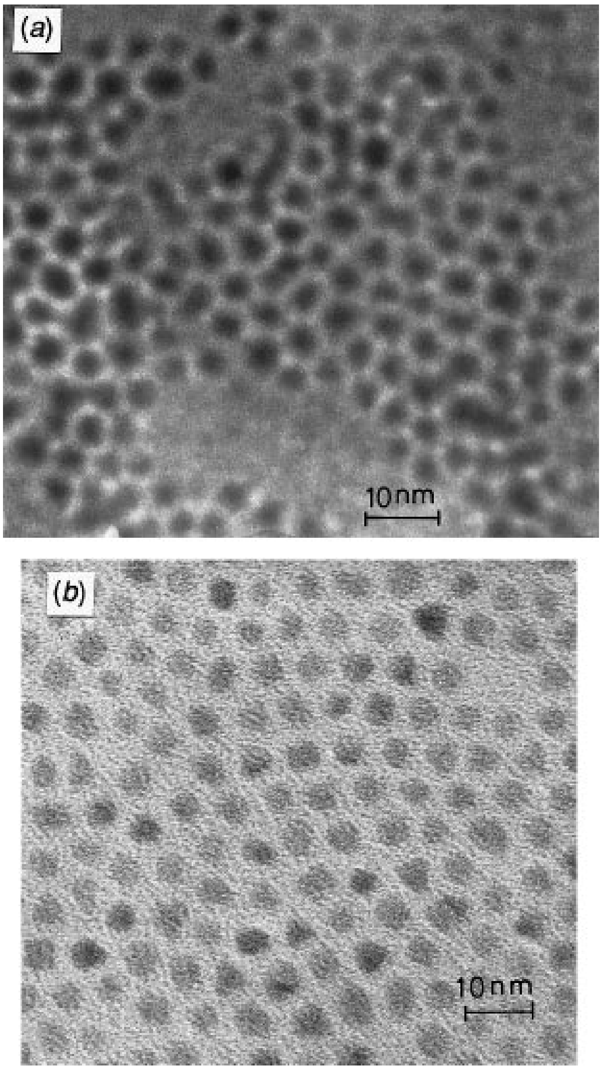

Fig. 3 TEM images of thiol-derivatised Pt (*a*) and Ag (*b*) nanoparticles

Fig. 2(*a*) shows the transmission electron microscope (TEM) image (recorded with JEOL JEM3010, Japan) of the thiol-derivatised Au nanoparticles obtained by placing a drop of the toluene sol on the holey carbon grid. The particles are nearly spherical with a mean diameter of 4.1 nm. The size distribution obtained, with the help of a Quantimat image analyser, is quite narrow as can be seen from the histogram in Fig. 2(*b*). Furthermore, the nanoparticles assemble into a superstructure as revealed by Fig. 2(*a*). The centre-to-centre nearest-neighbour distance between the nanoparticles is nearly constant at *ca.* 5.5 nm, throughout the superstructure domain. The X-ray diffraction pattern of a film of this material exhibits a low-angle peak corresponding to a *d*-spacing of *ca.* 5 nm. In order to examine whether the individual nanoparticles were crystalline or not, nanoparticles deposited on thin flakes of layered $MoSe_2$ were observed by TEM. The images showed Moiré patterns arising from the interference between the crystallographic planes of $MoSe_2$ and those of the nanoparticles, thereby establishing the crystallinity of the individual particles.

We have been able to prepare thiol-derivatised nanoparticles of Au with different mean diameters in the 1–10 nm range, by varying the concentration of $HAuCl_4$ in the initial hydrosol, by employing the present procedure. We have also prepared Au hydrosols with other reducing agents such as citric acid[8] and thiol-derivatised them by this procedure. The citric acid procedure, however, seems to yield nanoparticles of different shapes (spherical, triangular, pentagonal, hexagonal and rod-like) with varying sizes (*ca.* 25–50 nm).

We have prepared thiol-derivatised nanoparticles of Pt and Ag by the present procedure, by starting with hydrosols obtained with $NaBH_4$ as the reducing agent. Fig. 3(*a*), shows a typical TEM image of thiol-derivatised Pt nanoparticles. These particles are spherical with a narrow size distribution, the mean diameter being 4.4 nm. The figure also reveals a superstructure similar to that of Au in Fig. 2(*a*). A TEM image of thiol-derivatised Ag nanoparticles is shown in Fig. 3(*b*). The image shows that the Ag particles are not as spherical as those of Au and Pt and resemble the Ag particles prepared under vacuum.[9]

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