Synthesis of Thiol-derivatised Gold Nanoparticles in a Two-phase Liquid–Liquid System

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Using two-phase (water–toluene) reduction of $AuCl_4^-$ by sodium borohydride in the presence of an alkanethiol, solutions of 1–3 nm gold particles bearing a surface coating of thiol have been prepared and characterised; this novel material can be handled as a simple chemical compound.

Colloidal solutions of metals have been known for a long time[1] and a large variety of preparative techniques is now available.[2,3] Depending on the preparative conditions, the particles have a tendency to agglomerate slowly, eventually lose their disperse character and flocculate. The removal of the solvent generally leads to the complete loss of the ability to reform a colloidal solution. Preparation of colloidal metals in a two-phase system was introduced by Faraday,[4] who reduced an aqueous gold salt with phosphorus in carbon disulfide and obtained a ruby coloured aqueous solution of dispersed gold particles. Combining this two-phase approach with the more recent techniques of ion extraction and monolayer self-assembly with alkane thiols,[5] a one-step method for the preparation of an unusual new metallic material of derivatised nanometre-sized gold particles is described.

The strategy followed consisted in growing the metallic clusters with the simultaneous attachment of self-assembled thiol monolayers on the growing nuclei. In order to allow the surface reaction to take place during metal nucleation and growth, the particles were grown in a two-phase system. Two-phase redox reactions can be carried out by an appropriate choice of redox reagents present in the adjoining phases.[6] In the present case, $AuCl_4^-$ was transferred from aqueous solution to toluene using tetraoctylammonium bromide as the phase-transfer reagent and reduced with aqueous sodium borohydride in the presence of dodecanethiol ($C_{12}H_{25}SH$). On addition of the reducing agent, the organic phase changes colour from orange to deep brown within a few seconds. The overall reaction is summarized by eqns. (1) and (2), where the

$$AuCl_4^-(aq) + N(C_8H_{17})_4^+\ (C_6H_5Me) \rightarrow N(C_8H_{17})_4^+AuCl_4^-(C_6H_5Me) \quad (1)$$

$$m AuCl_4^-(C_6H_5Me) + n C_{12}H_{25}SH(C_6H_5Me) + 3me^- \rightarrow 4mCl^-(aq) + (Au_m)(C_{12}H_{25}SH)_n(C_6H_5Me) \quad (2)$$

source of electrons is BH_4^-. The conditions of the reaction determine the ratio of thiol to gold, *i.e.* the ratio *n*/*m*. The preparation technique was as follows. An aqueous solution of hydrogen tetrachloroaurate (30 ml, 30 mmol dm^{-3}) was mixed with a solution of tetraoctylammonium bromide in toluene (80 ml, 50 mmol dm^{-3}). The two-phase mixture was vigorously stirred until all the tetrachloroaurate was transferred into

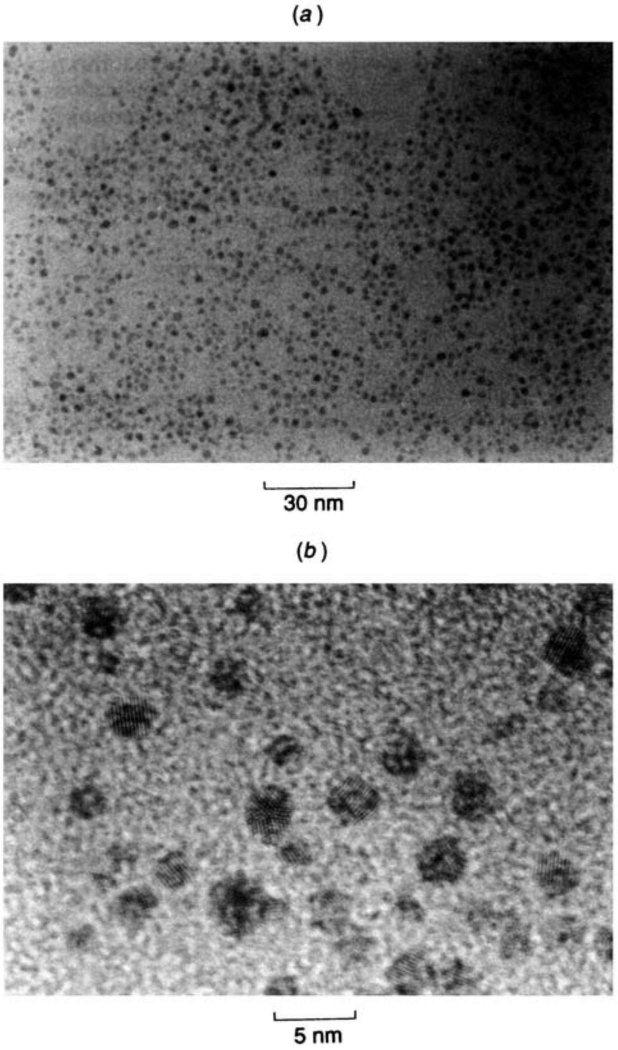

Fig. 1 TEM pictures of the thiol derivatised gold nanoparticles at (*a*) low and (*b*) high magnification

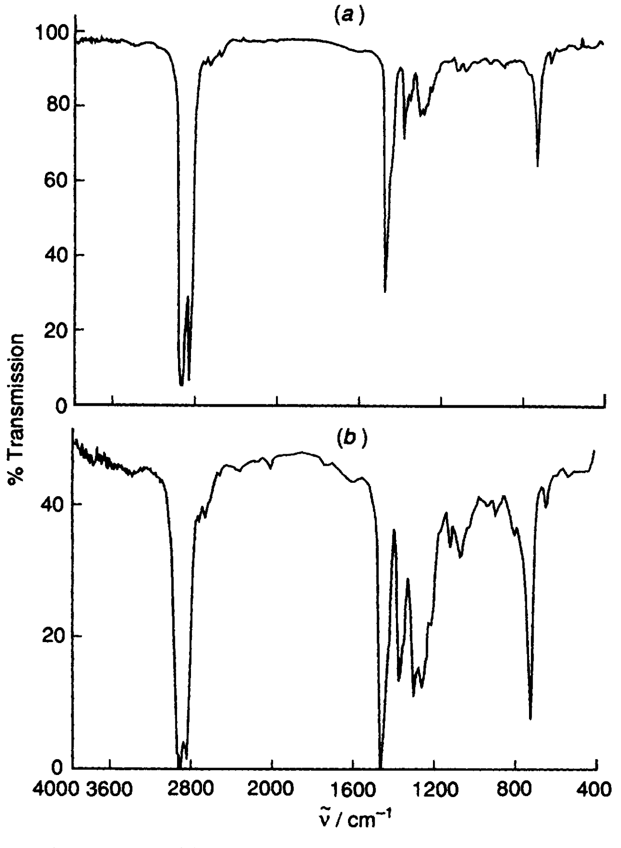

Fig. 2 IR spectra of (*a*) dodecanethiol and (*b*) nanoparticles prepared in the present work. The particles were deposited on an NaCl disc by evaporation of a drop of a toluene solution.

the organic layer and dodecanethiol (170 mg) was then added to the organic phase. A freshly prepared aqueous solution of sodium borohydride (25 ml, 0.4 mol dm^{-3}) was slowly added with vigorous stirring. After further stirring for 3 h the organic phase was separated, evaporated to 10 ml in a rotary evaporator and mixed with 400 ml ethanol to remove excess thiol. The mixture was kept for 4 h at -18 °C and the dark brown precipitate was filtered off and washed with ethanol. The crude product was dissolved in 10 ml toluene and again precipitated with 400 ml ethanol. Yield: 214 mg (93% assuming from elemental analysis a product composition of 75% gold and 25% dodecanethiol). The specimens for examination by electron microscopy were prepared by evaporation of one or two drops of a toluene solution of the nanoparticles on to holey carbon films supported on standard copper grids. Phase contrast images of the nanoparticles were obtained using a top-entry JEOL 2000EX electron microscope at an accelerating voltage of 200 kV (point resolution 0.21 nm). The UV-VIS spectrum of the gold solution was similar to that obtained by Duff *et al.*[7] for gold hydrosols of 1.5 nm average particle diameter. The colloidal solutions obtained were very stable and did not show signs of decomposition or aggregation over a period of several weeks.

An unusual property of these thiol-derivatised metal nanoparticles is that they can be handled and characterised as a simple chemical compound. The dry product is dark brown and has a waxy texture; it is soluble in non-polar solvents such as toluene, pentane and chloroform and can be further purified by gel-filtration chromatography (Sepharose 6B/toluene).

High resolution TEM photographs of the nanoparticles (Fig. 1) show that they have diameters in the range 1–3 nm and a maximum in the particle size distribution at 2.0–2.5 nm. Examination of the specimens at higher resolution [Fig. 1(*b*)] reveals a mixture of particle shapes with a preponderance of cuboctahedral and icosahedral structures, similar to previous observations.[8,9] In contrast with many preparations of colloidal gold, multiply twinned particles comprise only a minority species. It is proposed that this could result from the conditions of growth employed, where the formation of a self-assembled thiol layer on the growing nuclei inhibits twinning.

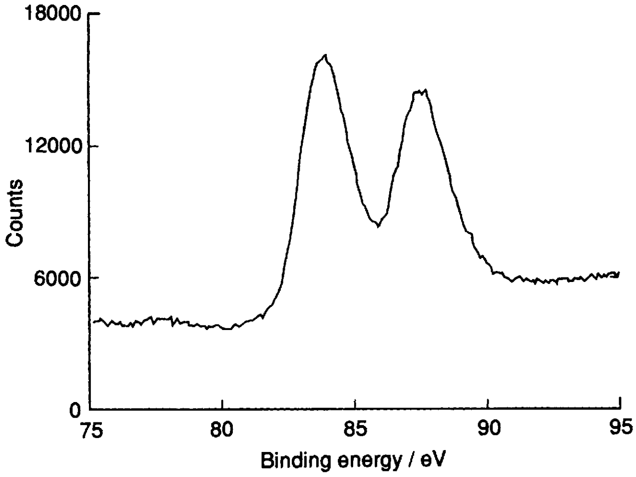

Fig. 3 XPS spectrum of the nanoparticles showing the Au $4f_{7/2}$ and $4f_{5/2}$ doublet with binding energies of 83.8 and 87.5 eV respectively. These are typical values for Au^0.

The IR spectra of the particles and of dodecanethiol are similar (Fig. 2), which indicates that the thiol is indeed part of the composite. Elemental analysis gave: Au, 75.0; C, 17.6: H, 3.0; S, 4.4% (by difference). The C:H and C:S ratios are, within the experimental uncertainties, those of dodecanethiol. The oxidation state of gold in the nanoparticles was determined by X-ray photoelectron spectroscopy. The binding energies of the doublet for Au $4f_{7/2}$ (83.8 eV) and Au $4f_{5/2}$ (87.5 eV) shown in Fig. 3 are characteristic of Au^0. The absence of a band at 84.9 eV as found for Au^I in a gold octanethiol complex[10] indicates that the gold atoms in the clusters must be present largely as Au^0. This is a remarkable result, bearing in mind that, from the elemental analysis, about a third of the gold atoms are at the surface of a particle and bonded to a thiol molecule. Consequently, it is suggested that the gold–thiol bond does not have the character of gold sulfide. As expected, weak sulfur signals were observed in the XPS spectrum.

The interest in the preparation technique described here is three-fold. First, it could lead to a simple way for the direct synthesis of surface-functionalised metallic clusters. Secondly, since the kinetics of cluster growth are expected to be determined by the surface coverage, cluster size can be controlled by the reaction conditions and not by the metal ion reduction kientics as is usually the case in condensed-phase colloidal metal preparations. Finally, these new hydrophobic metal clusters are of intrinsic interest since in some respects, they behave like simple chemical compounds; they can be precipitated, redissolved and chromatographed without any apparent change in properties. It is envisaged that this type of new material could find a wide range of applications, for instance, in catalysis, sensors and molecular electronics.

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