

Synthesis and Reactions of Functionalised Gold Nanoparticles

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Stable functionalised gold nanoparticles are prepared by simultaneous reduction of tetrachloroaurate ions and attachment of bifunctional organic thiol molecules to the growing gold nuclei leading to a material whose chemical behaviour is characterised by the vacant functionality of the bifunctional thiol ligand.

The potential application of small metal or semiconductor particles as functional units in innovative microelectronic devices which are based on the quantum confined electronic properties of the particles has inspired much recent research on their synthesis and properties.^{1,2} Schmid *et al.* showed that solid samples of ligand-stabilised Au₅₅ clusters constitute an array of quantum dots, which can be used to manufacture tunnel resonance resistors the smallest working unit of which only comprises a pair of cluster molecules.³

Two important factors which seem to impede the use of metal clusters for the development of a new generation of nano-electronic devices are stability and reactivity. Most of the clusters known so far, lack the stability required for a realistic application in electronic devices.

Very stable clusters on the other hand are devoid of sufficient chemical reactivity to allow the preparation of interconnected one- or two-dimensional structures forming quantum wires and quantum wells, respectively. We reported recently the synthesis of thiol-derivatised gold nanoparticles in a two phase liquid-liquid system.⁴ Materials prepared in this way are extremely stable and do not show any signs of decomposition, such as particle growth or loss of solubility, even after several months storage in air at room temperature. Here, we report the synthesis of similarly stable gold nanoparticles, which are derivatised by means of a bifunctional stabilising thiol ligand. The bifunctional compound employed was *p*-mercaptophenol.

The preparation of the *p*-mercaptophenol-derivatised material was carried out in a single-phase system to avoid the extraction of *p*-mercaptophenol into the alkaline aqueous phase. Hydrogen tetrachloroaurate trihydrate (Aldrich; 300 mg, 0.76 mmol) and *p*-mercaptophenol (Fluka; 230 mg, 1.8 mmol) were dissolved in methanol (150 ml). Acetic acid (3 ml) was added to the mixture to prevent the deprotonation of *p*-mercaptophenol and 30 ml of freshly prepared 0.4 mol dm⁻³ aqueous sodium borohydride were added carefully in small portions of *ca.* 1 ml with vigorous stirring. The solution turned brown immediately indicating the formation of gold clusters in the size range around 2 nm.⁵ After further stirring for 30 min the solvent was removed under reduced pressure without exceeding a temperature of 50 °C, and the dark-brown residue was washed thoroughly with diethyl ether to remove excess *p*-mercaptophenol. After evaporation of the diethyl ether the material was washed (water) to remove borates and acetates, dissolved in propan-2-ol and dried (anhydrous Na₂SO₄). The solvent was removed under reduced pressure to give 162 mg of the pure product as a dark-brown solid.

Elemental analysis gave: C, 19.4; H, 1.88% This corresponds to a C:H ratio of 6:7 rather than the expected 6:5 of *p*-mercaptophenol, considering that derivatisation occurs with the loss of the thiol hydrogen atom. This could indicate that one water molecule is strongly associated with the phenolic surface species. The product was insoluble in water and in nonpolar

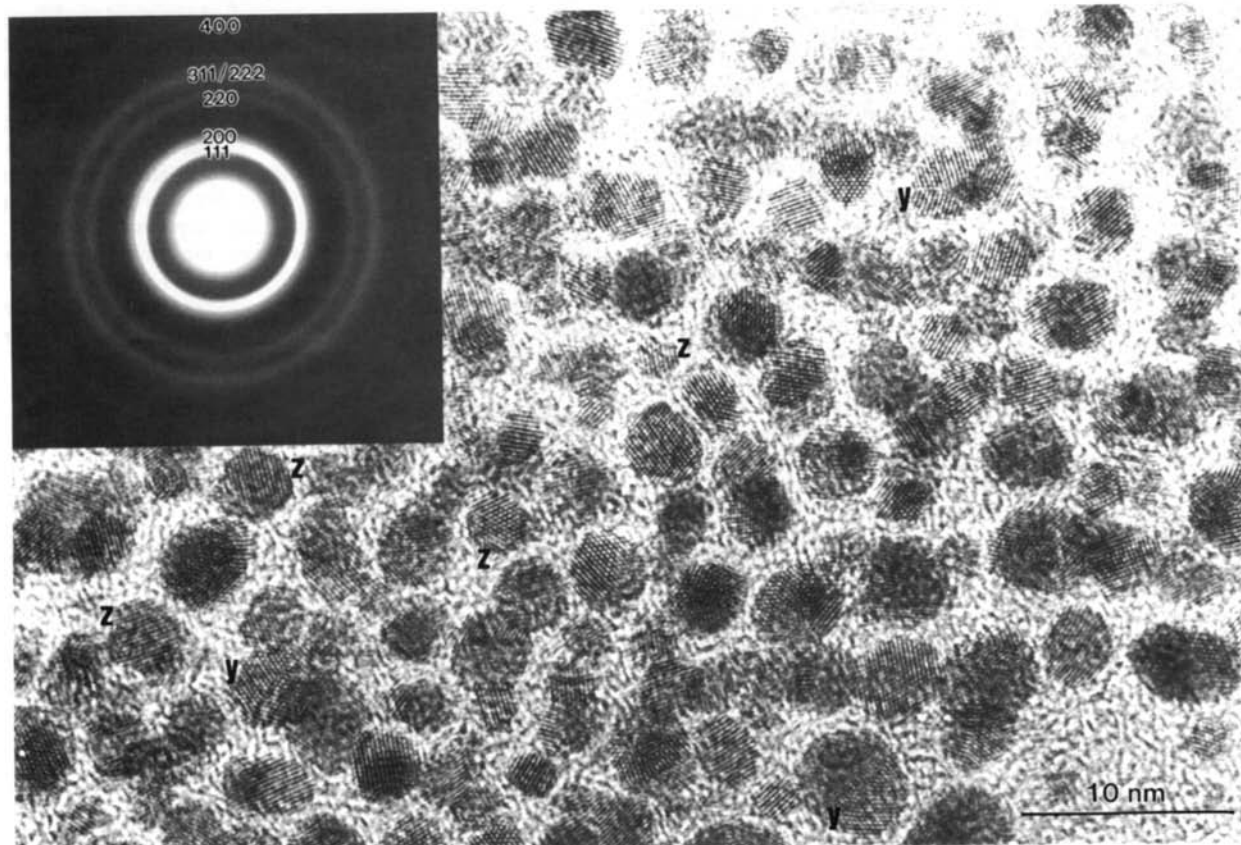


Fig. 1 HRTEM micrograph of the functionalised gold nanoparticles and corresponding polycrystalline electron diffraction ring pattern

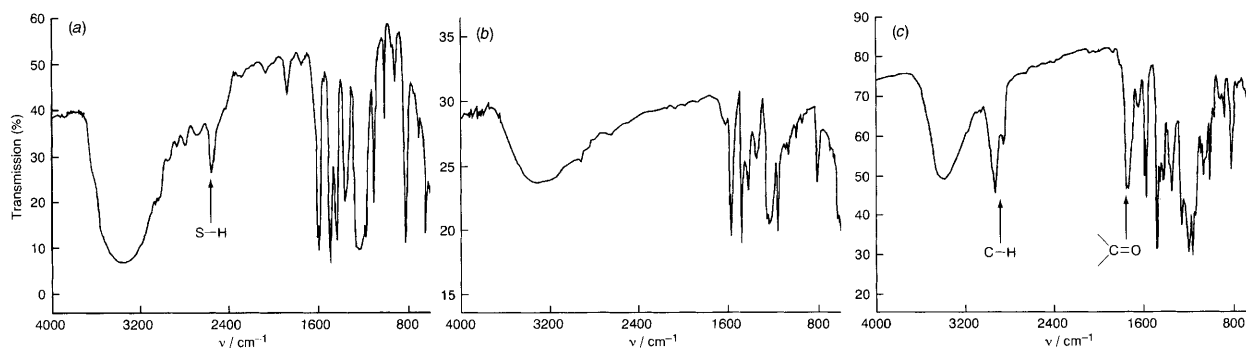


Fig. 2 IR spectra of (a) *p*-mercaptophenol, (b) nanoparticles functionalised with *p*-mercaptophenol and (c) partially esterified nanoparticles after reaction with propionic anhydride. The particles were deposited on an NaCl disc by evaporation of a drop of an ethyl acetate solution. The peak marked C–H in (c) corresponds to C–H stretching vibrations of the propionyl groups. In (a) and (b) the much weaker aromatic C–H stretching vibrations are obscured by the broad hydroxy band.

solvents but dissolved readily in alcohols, ethyl acetate, and in alkaline aqueous solutions ($\text{pH} \geq 13$). When the material was dissolved in ethyl acetate it could be extracted quantitatively into an alkaline aqueous phase and re-extracted into the organic layer after neutralisation of the aqueous phase. This is a simple but significant experiment showing that the phenolic functionality has indeed been transferred to the surface of the gold particles.

Specimens suitable for examination by TEM were prepared by evaporating a drop of propan-2-ol solution containing the nanoparticles onto an amorphous carbon film supported on a copper mesh grid. Specimens were examined in a JEOL2000EX High Resolution Electron Microscope operating at 200 keV. A typical phase-contrast image obtained from the material, along with the corresponding selected area diffraction pattern is shown in Fig. 1. The characteristic rings in the polycrystalline diffraction pattern can be indexed to the {111}, {200}, {220}, {311}, {222} and {400} allowed reflecting planes expected from fcc Au. The diffuse nature of the rings is a simple manifestation of the crystal shape effect due to the nanoscale size of the particles. Discrete Au particles were observed in electron micrographs, some of which exhibit characteristic {111} and {200} lattice fringes. A particle size distribution was carried out using a sample of 120 particles showing a Gaussian distribution with a particle range of 2.4 to 7.6 nm and a mean diameter of 5 nm. A significant number of particles (*e.g.* *y*) exhibit multiple twinning and preferential {111} surface facet planes are clearly visible in some instances (*e.g.* see *z*). (Fig. 1).

The IR spectrum of the nanomaterial [Fig. 2(b)] resembles that of *p*-mercaptophenol [Fig. 2(a)] giving clear evidence that *p*-mercaptophenol forms part of the composite. The absence of an S–H stretching mode in the spectrum of the particles gives further spectroscopic evidence for the absence of the thiol hydrogen in self-assembled monolayers on gold surfaces, which has been a subject of some discussion in the past.^{6–8} More importantly for this communication, it shows that all detectable *p*-mercaptophenol present in the sample is attached to the particle surface by its thiol function.

To demonstrate clearly that the synthesis of functionalised Au clusters had been achieved, the reactivity of the material was investigated by esterification of the surface bound phenolic hydroxy groups. *p*-Mercaptophenol derivatised clusters (30 mg) were suspended in aqueous sodium acetate (100 ml 0.15 mol dm^{-3}). Propionic anhydride (0.1 mol) was added and the mixture was stirred vigorously. After 15 min stirring another 0.1 ml propionic anhydride was added and the mixture was stirred for a further 15 min. The solution was extracted with ethyl acetate and the organic phase was washed ($5 \times$ water) and dried (anhydrous Na_2SO_4). The solvent was removed under reduced pressure at $< 50^\circ\text{C}$ to give the product (37 mg) as a dark-brown solid.

Elemental analysis gave: C, 29.4 and H, 3.21% which corresponds approximately to a C : H ratio of 10 : 13 rather than 10 : 11, which would be expected for complete esterification of the surface bound *p*-mercaptophenol.

The IR spectrum of the material [Fig. 2(c)] shows that indeed only a partial esterification had been achieved. The characteristic C–H stretching modes and a carbonyl band appear as new features in the IR spectrum, but the OH band at 3400 cm^{-1} is still present, indicating the presence of free hydroxy groups. The repetition of the esterification procedure described above, using the partially esterified particles as starting material, did not result in a detectable further esterification. However, after shaking the product with D_2O , it could be shown by IR spectroscopy that the remaining hydroxy groups were accessible to H/D exchange. It is, therefore, assumed that the incomplete esterification is due to steric hindrance encountered on the particle surface tightly packed with *p*-mercaptophenol. Further investigations using either sterically less demanding reagents, or a lower ratio of bifunctional thiols in the ligand shell of the cluster, are under way.

This is a clear example of a controlled chemical modification of a ligand-stabilised metal cluster achieved by the reaction of functional groups in the ligand shell. It is expected that this new strategy will pave the way for the chemical synthesis of superclusters by attachment of individual clusters to one another *via* functionalities in their ligand shells. If it is possible to construct one-, two- or three-dimensional structures by interlinkage of metal clusters following this approach, the results presented here can be seen as a further step towards closing the continually narrowing gap between the smallest micromachined, and the largest chemically designed structures.

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References

- 1 Clusters and Colloids, ed. G. Schmid VCH, Weinheim 1994.
- 2 T. Vossmeier, L. Katsikas, M. Giersig, I.G. Popovic, K. Diesner and A. Chemseddine, *J. Phys. Chem.*, 1994, **98**, 7665.
- 3 U. Simon, G. Schön and G. Schmid, *Angew. Chem., Int. Engl.*, 1993, **32**, 250.
- 4 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801.
- 5 D. G. Duff, A. Baiker, P. P. Edwards, *Langmuir*, 1993, **9**, 2301.
- 6 R. G. Nuzzo, L. H. Dubois and D. L. Allara, *J. Am. Chem. Soc.*, 1990, **112**, 558.
- 7 C. A. Widrig, C. Cheng and M. D. Porter, *J. Electroanal. Chem.*, 1991, **310**, 335.
- 8 Y. Li, J. Huang, R. T. Jr McIver, and J. C. Hemminger, *J. Am. Chem. Soc.*, 1992, **114**, 2428.