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Purification of dodecanethiol derivatised gold nanoparticles

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Monolayer protected gold nanoparticles synthesised by a two-phase method contain a significant amount of tetraoctylammonium bromide (TOABr), the quaternary ammonium salt used as the phase transfer reagent, as a persistently retained impurity. A simple purification protocol is described.

The two-phase synthesis of core-shell gold nanoparticles reported in 1994 is a straightforward technique for producing relatively monodisperse nanoparticles that are remarkably stable in or out of solution.[1] These materials are of interest in providing a central metal core and a ligand shell, and have attracted considerable interest.[2–4] Both the dimensions of the core, and hence, its electronic properties, and the chemical nature of the capping ligands can be controlled, thus providing a wide range of synthetic opportunities for the preparation of nanoparticles and nanostructures by simple chemical means.[5] Modifications and enhancements to the two-phase preparative technique have been reported and extended to other metals such as silver.[6] Most of these preparations, however, employ quaternary ammonium salts such as TOABr for incorporating the metal ion into an organic phase prior to reduction.

Unusual self-organisation properties and the formation of ring and line nanoscale patterns have been reported. It has been proposed that these effects can originate from dipolar interactions for quaternary ammonium stabilised nanoparticles,[7] or from long-range dispersion forces[8] in the case of ligand shell stabilised material. A problem that has not been extensively highlighted with these materials is the possible presence of TOABr as an impurity in the nanoparticle samples resulting from the two-phase preparation technique. Often methods used for size separation[9] such as precipitation and column chromatography[10] are expected to provide purification. A brief summary of these techniques has been presented by Murray *et al.*[4] Recent work at Liverpool, however, has indicated that even after repeated precipitation of the alkane thiol capped nanoparticles, TOABr was tenaciously retained. The purpose of this communication is to provide evidence for the presence of impurities in these commonly used materials and to describe a simple purification procedure. This is an important step for preparing highly purified and well-characterised nanoscale materials.

Nanoparticles were prepared using the method described by Brust *et al.*[1] using a dodecanethiol to gold ratio of 4 : 1. Hydrogen tetrachloroaurate (Alfa), tetraoctylammonium bromide (Lancaster), dodecanethiol (Fluka) and sodium borohydride (Fischer Scientific) were used as received. After synthesis the nanoparticles were precipitated twice from 400 ml of acetone (Prolabo). Analysis by Micromas LDI-TOF MS gave spectra with groups of nanoparticle peaks centred at 22 570, 29 740 and 39 690 Da (Fig. 1). This Figure also compares the spectra before and after purification and shows that the extraction of the TOABr impurity does not alter the size distribution. The spectra also revealed the presence of a significant amount of tetraoctylammonium cation at 466.5 Da (data not shown).

Soxhlet extraction has been employed for the purification of nanotubes and Buckminster fullerenes.[11] The gold nanoparticles prepared as described above were further purified by Soxhlet extraction. 0.030 g of product from the above synthesis was dissolved in a minimum amount of toluene (BDH) and then placed into a Soxhlet thimble of 25 × 100 mm dimensions. 250 ml of Prolabo AnalaR acetone was used as the cleansing solvent. The Soxhlet extraction was run over a 12 h period and was monitored every 3 h by removing the acetone from the round bottomed flask of the extraction equipment. After four extraction cycles, the product was recovered by dissolving in toluene the particles held within the thimble. The acetone fractions removed after each three-hour stage were evaporated and the residue redissolved in propan-2-ol (BDH).

Positive ion electrospray mass spectrometry was employed as a preferred technique in order to assess quantitatively the amount of TOABr removed at each stage of extraction and to confirm its elimination from the nanoparticle sample. A Micromass Liquid Chromatography Time of flight (LCT) instrument with a syringe pump sample injection system was employed for the analysis. The samples were injected at a flow rate of 10 μl min $^{-1}$ with the sample cone voltage set to 60 V and using a scan rate of one spectrum per second over the mass range 100 to 900 Da. After allowing the system to stabilise for approximately 2 min, the spectrum was scanned for 1 min and the data averaged over 60 scans. Standard solutions of TOABr and didodecyldimethylammonium bromide, DDMABr (Fluka) were used for the quantitative analysis of the TOABr extracted. Its concentration was calculated from the intensity of the TOA^+ mass peak at 466.5 Da. The 382.4 Da mass peak for $DDMA^+$ was employed as the internal calibration standard.

A calibration curve was established from which the quantity of extracted TOABr present in the acetone samples was determined. These results are shown in Table 1 confirming the removal of the quaternary ammonium salt. An exponential extrapolation of these results by non-linear regression showed that approximately 5×10^{-3} % of TOABr remained after 12 h extraction. Although the crude material from the synthesis is

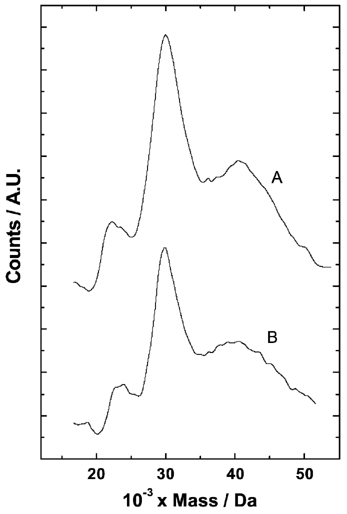

Fig. 1 LDI-TOF spectra of the gold nanoparticle peaks (A) before and (B) after purifications by Soxhlet extraction.

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Table 1 Extraction of TOABr present as an impurity determined by the intensity of the TOA$^+$ peak (mass = 466.5 Da) from the LCT-MS spectra at different stages of extraction

Time from start of extraction/h	$10^4 \times$ Mass of TOABr extracted/g	% of TOABr extracted
3	3.03	1.01
6	0.63	0.21
9	0.31	0.10
12	0.03	0.011

usually purified by precipitation, a content of at least 1% of TOABr is retained. Therefore, an extraction of at least 12 h is required in order to purify the nanoparticles.

XPS measurements were made on similarly sized-gold nanoparticles prepared using a dodecanethiol to gold ratio of 3 : 1. These were purified as described above. Spectra obtained from a Scienta ESCA300 spectrometer at Daresbury, UK, (RUSTI facility) confirmed both the presence of nitrogen before purification by Soxhlet extraction and its elimination after treatment. (Fig. 2) Similar results were observed for nanoparticles prepared using a ratio of dodecanethiol to gold of 1 : 4 and 1 : 2.

It is noticeable that the as-prepared material is very insoluble in acetone–toluene mixtures and can be easily precipitated from them. A systematic study of nanoparticle solubilities in toluene–acetone mixtures indicated that a concentration of 10% in volume of toluene was sufficient to produce significant solubility of the highly purified material, whilst as-prepared samples were totally insoluble in this mixture. It can be concluded that the decrease in solubility must be related to the presence of TOABr, although this salt is completely soluble in the solvents used. To demonstrate that this is the case, TOABr was added in the concentration range 1.3 to 5.1×10^{-4} M to solutions in the above mixture, of nanoparticles purified by 12 h Soxhlet extraction. Complete precipitation was observed in all cases, demonstrating the great sensitivity of the solubility of capped nanoparticles to the presence of TOABr in solution. This unexpected behaviour can be due to either solvent–solute or solute–solute interactions. The concentration of TOABr in solution is very small and hence, the large change in solubility cannot be related to solvent–solute interactions.

It is proposed that both the quaternary ammonium ion and the bromide ion are incorporated within the ligand shell thus providing charged sites leading to strong electrostatic interactions between nanoparticles and therefore, to stabilisation of the solid phase, as schematically illustrated in Fig. 3. There are two possible interactions responsible for this effect. The Br$^-$ ion is known to display strong specific adsorption on gold[12] thus providing electrostatic adsorption sites for the quaternary ammonium ions in the nanoparticle shell. In addition, the alkyl chains of both the capping ligand and of TOA$^+$ can interact strongly as a consequence of alkyl chain interdigitation.[13] It is proposed that both effects are present simultaneously resulting in an increase of the lattice energy with the corresponding decrease in solubility. It can be concluded that TOABr is strongly retained by the nanoparticles and care has to be taken in their purification.

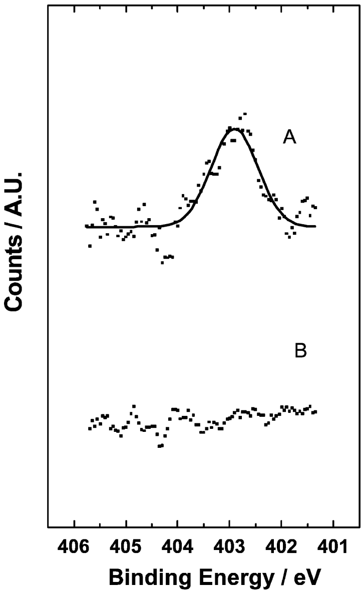

Fig. 2 XPS Nls peak for gold nanoparticles (A) before and (B) after Soxhlet purification.

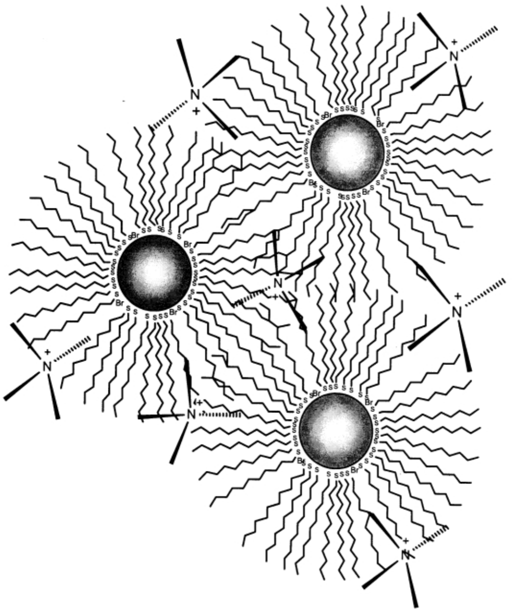

Fig. 3 Schematic diagram showing the stabilization of the solid phase of the nanopharticles due to the presence of TOABr.

This work highlights the fact that nanoparticles synthesised by the two-phase method contain significant amounts of TOABr as impurity that can dramatically affect their properties. Soxhlet extraction with acetone has been shown to be an effective and simple purification method.

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