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Water-dispersible nanoparticles via interdigitation of sodium dodecylsulphate molecules in octadecylamine-capped gold nanoparticles at a liquid–liquid interface[¶]

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Abstract. This paper describes the formation of water-dispersible gold nanoparticles capped with a bilayer of sodium dodecylsulphate (SDS) and octadecylamine (ODA) molecules. Vigorous shaking of a biphasic mixture consisting of ODA-capped gold nanoparticles in chloroform and SDS in water results in the rapid phase transfer of ODA-capped gold nanoparticles from the organic to the aqueous phase, the latter acquiring a pink, foam-like appearance in the process. Drying of the coloured aqueous phase results in the formation of a highly stable, reddish powder of gold nanoparticles that may be readily redispersed in water. The water-dispersible gold nanoparticles have been investigated by UV-Vis spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR). These studies indicate the presence of interdigitated bilayers consisting of an ODA primary monolayer directly coordinated to the gold nanoparticle surface and a secondary monolayer of SDS, this secondary monolayer providing sufficient hydrophilicity to facilitate gold nanoparticle transfer into water and rendering them water-dispersible.

Keywords. Phase transfer; interdigitation; gold nanoparticles; liquid–liquid interface.

1. Introduction

The synthesis of water-dispersible gold nanoparticles is of great interest due of their potential application areas as disparate as electron microscopy markers[1] and in DNA sequence determination.[2] However, these applications require high concentration of monodisperse nanoparticles with no loss of physical or chemical properties over extended periods of time.[3–5] While aqueous phase synthesis of gold nanoparticles is a simple, one-step process facilitating easy conjugation of nanoparticles with biomacromolecules, ionic interactions limit the concentration of gold nanoparticles in the aqueous phase to very dilute levels.[6] Another drawback of aqueous phase synthesis of gold nanoparticles is that little control can be exercised over monodispersity and particle size. An important strategy to overcome this hurdle may be based on the synthesis of nanoparticles in a non-polar organic phase, where high concentrations of monodisperse particles of different

[¶]Dedicated to Professor C N R Rao on his 70th birthday
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sizes may be routinely synthesised and then transfer the nanoparticles to the aqueous phase thereby maximising the advantages of both methods.

Attempts have been made to develop protocols for the phase transfer of nanoparticles and have focused primarily on transfer from aqueous to non-polar organic phases.[7–13] Such movement of nanoparticles may be easily achieved by direct coordination of nanoparticles with octadecanethiol/fatty amine molecules present in the organic phase. Formation of covalently bound monolayers of the alkanethiol/fatty amine molecules on the nanoparticle surface renders the particles hydrophobic and thereby, dispersible in the organic phase. Rao and coworkers[10,11] demonstrated for the first time the acid-facilitated phase transfer of colloidal gold, platinum and silver nanoparticles first synthesised in an aqueous medium into a hydrocarbon environment such as toluene by co-ordination of the particles with alkanethiols present in toluene. They also showed that these hydrophobized nanoparticles form hexagonally close-packed assemblies on solvent evaporation. This method has also been applied to the acid facilitated transfer of oleate stabilised colloidal silver particles by Wang *et al*.[12] Recently some of us have shown the phase transfer of gold nanoparticles from an aqueous phase to organic phase by direct coordination of fatty amine molecules present in organic phase with the nanoparticles.[13] The main advantage of this method is that the phase transfer is achieved without addition of acid.

On the other hand, reports on the phase transfer of nanoparticles in the reverse direction (i.e. from the organic to aqueous phase) are relatively scarce.[6,14,15] One of the approaches for phase transfer from organic to aqueous phase is based on a place exchange of alkanethiolate monolayer protected clusters (MPCs) with *w*thiol carboxylic acid molecules.[14] However this process permanently changes the chemistry of the particle surface and results in only a small percentage of transferred material.[14] Recently, Gittins and Caruso[6] have reported a facile and rapid one-step method for the direct and complete transfer of gold and palladium nanoparticles synthesised in toluene and stabilised by tetraalkylammonium salts across the phase boundary (organic to aqueous).[6] This was accomplished by addition of an aqueous 0·1 M 4-dimethlyaminopyridine (DMAP) solution to aliquots of the gold/palladium nanoparticles in toluene. The DMAP molecules replace the tetraalkylammonium salts and form a labile donor-acceptor complex with the gold atoms on the surface of the nanoparticles through the endocyclic nitrogen atoms.[6] These authors have shown that the aqueous gold and palladium solutions are extremely stable with no sign of degradation even after storage for several months. Gittins and Caruso[7] have also demonstrated the phase transfer of silver, gold, platinum and palladium nanoparticles using a number of exchanging ligands such as mercaptoundecanioc acid (MUA), mercaptosuccinic acid etc. An important aspect of the work was the non-specific bioconjugation of the protein, bovine serum albumin (BSA) with MUA-functionalized gold nanoparticles, possibly through electrostatic and hydrogen bonding interactions between the protein and the ionised carboxylate ions on the nanoparticle surface.[7]

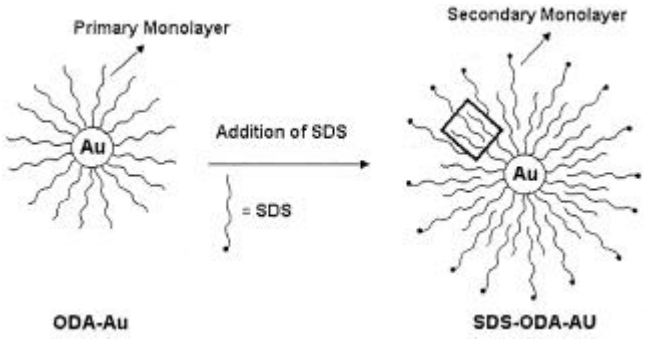
We have recently demonstrated the formation of water-dispersible gold nanoparticles by phase transfer of dodecylamine (DDA)-capped colloidal gold particles in an organic solvent into water containing the cationic surfactant, cetyltrimethylammonium bromide (CTAB).[16] In the present study we demonstrate that octadecylamine-capped gold nanoparticles (ODA-Au) dispersed in chloroform can be quantitatively transferred into water containing an anionic surfactant, sodium dodecylsulphate (SDS). Vigorous shaking of the biphasic mixture (ODA-Au-in-chloroform/SDS-in-water) results in the swift transfer of the hydrophobized nanoparticles (ODA-Au) into the aqueous phase. These nanoparticles are exceptionally stable in the aqueous phase at high concentration and can be stored as a

reddish powder, which can be readily redispersed in water. Analysis of the phase-transferred gold nanoparticle solution and the purified powder of nanoparticles by UV-Vis spectroscopy, differential scanning calorimetry (DSC) thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy indicated that the nanoparticles are capped with an interdigitated bilayer of ODA (primary monolayer, directly coordinated to the gold nanoparticle surface, scheme 1) and SDS (secondary monolayer, the polar sulphonic acid group extending towards water, scheme 1). While interdigitated bilayers have been used to stabilise Ag,[17] magnetite nanoparticles[18] and gold nanorods[19] in water, here we demonstrate the use of interdigitated bilayers in the phase transfer of gold nanoparticles and thereby, the formation of water dispersible nanoparticles. Presented below are details of the investigation.

2. Experimental details

ODA-capped gold nanoparticles in chloroform were synthesised as described in a previous report.[13] To 100 ml of the gold colloidal solution prepared by borohydride reduction of chloroauric acid, 100 ml of a 2×10^{-4} M solution of octadecylamine (ODA) in chloroform was added to yield immiscible layers of the colourless organic solution at the bottom of the red-coloured gold hydrosol. Vigorous shaking of the biphasic mixture resulted in extremely rapid transfer (within 30 s) of the gold colloidal particles into the organic phase. The organic phase was separated out and the powder of ODA-capped gold nanoparticles was obtained by evaporating the solvent by rotavapping. The powder was purified by ethanol washing and redispersed in chloroform.

In a typical experiment, 25 ml of ODA-Au nanoparticles in chloroform was added to 25 ml of 10^{-2} M SDS solution in water. The concentration of gold in chloroform was estimated to be 2×10^{-4} M by UV-Vis spectroscopy. Vigorous shaking of the biphasic mixture resulted in phase transfer of the gold nanoparticles from chloroform to water, giving a pink, foam-like appearance to the aqueous layer. This layer was then separated from the organic layer, dried and the resulting dry powder was redispersed in 25 ml of distilled water. The redispersed solution was centrifuged three times at 10,000 rpm and 25°C for 20 min to remove uncoordinated SDS molecules from solution. Further removal



Scheme 1. Diagram showing the formation of an interdigitated secondary monolayer of SDS molecules on the surface of ODA-modified gold particles (SDS-ODA-Au). The box encloses ordered, interdigitated regions of the bilayers (see text for details).

of water from the solution by rotavapping and drying under vacuum in N_2 atmosphere gave a reddish, dry powder of surface modified gold nanoparticles free from uncoordinated SDS molecules. UV-Vis spectra of the hydrophobized gold nanoparticles and redispersed nanoparticles after phase transfer from the organic phase to aqueous phase by SDS were recorded on a Shimadzu dual-beam spectrophotometer (model UV-1601 PC) operated at a resolution of 0·5 nm. FTIR spectroscopic measurements of a drop-coated film of the phase-transferred gold nanoparticles on Si (111) substrate were done on a Perkin–Elmer Spectrum 1 instrument operated at 4 cm^{-1} resolution in the diffuse reflectance mode. Calorimetric measurements of the purified powder of phase-transferred Au nanoparticles were done using a DSC-7 Perkin–Elmer unit from 10 to 250°C at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) of the phase-transferred gold nanoparticle powder was done on TGA-7 Perkin–Elmer instrument from 50–700°C at a scanning rate of 10°C/min. TEM measurements of the phase-transferred gold nanoparticle solution were performed on a JEOL Model 1200EX instrument operated at an accelerating voltage of 120 kV. Samples for TEM were prepared by placing drops of the purified phase-transferred gold nanoparticle solution on carbon-coated TEM copper grids. The drops were allowed to dry for 1 min and the extra solution was removed using a blotting paper.

3. Results and discussion

Figure 1a shows pictures of the gold nanoparticle solution at different stages of surface modification. Test tube 2 contains ODA-capped gold nanoparticles in chloroform prepared by a method of phase transfer described in an earlier report.[13] As mentioned in the experimental section, vigorous shaking of the biphasic mixture (ODA-Au-in-chloroform/SDS-in-water) resulted in the swift transfer of the hydrophobized nanoparticles

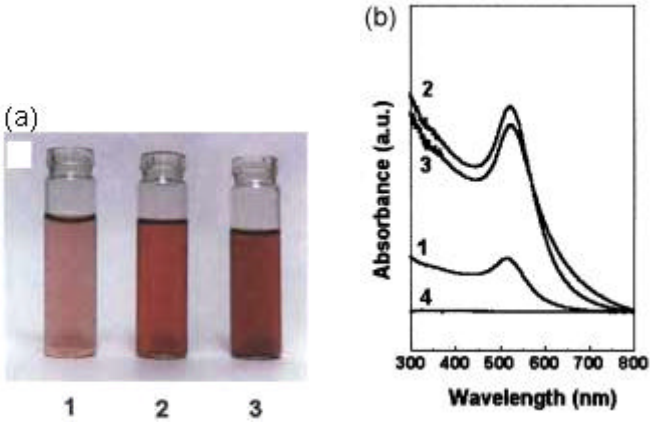


Figure 1. (**a**) Picture showing the as-prepared borohydride reduced gold hydrosol (test tube 1), ODA-modified gold nanoparticle solution in chloroform (test tube 2), and ODA modified nanoparticles after phase transfer into an aqueous solution of SDS (test tube 3). (**b**) UV-Vis spectra corresponding to the three gold nanoparticle solutions shown in (a); curves 1, 2, 3 correspond to solutions from tubes 1, 2, 3 respectively. Curve 4 corresponds to the spectrum recorded from the organic layer after phase transfer of the ODA-capped gold nanoparticles into water.

(ODA-Au, test tube 2) into the aqueous phase. Test tube 3 in figure 1a contains gold nanoparticles in water phase-transferred from chloroform. For comparison, the gold hydrosol prepared by borohydride reduction of chloroauric acid (10^{-4} M) is also shown (test tube 1). The ruby red colour of gold nanoparticle solutions is due to excitation of surface plasmon vibrations in the nanoparticles. Figure 1b shows the UV-Vis spectra of the gold solutions, curves 1, 2 and 3 corresponding to test tubes 1, 2 and 3 respectively in figure 1a. A strong absorption centered at ca. 520 nm is observed in all cases and is characteristic of gold nanoparticles. Curve 4 corresponds to the spectrum of the chloroform layer after phase transfer of ODA-capped gold nanoparticles into water. The almost complete loss in intensity of the surface plasmon vibration band attests to the fact that close to 100% phase transfer of the ODA-capped gold nanoparticles from chloroform to water had occurred. It is clear that SDS in the organic phase plays an important role in accomplishing the phase transfer of ODA-capped gold nanoparticles to water and could occur by two conceivable methods. The first possibility is replacement of surface-bound ODA molecules by SDS molecules, which would thus make the particle surface hydrophilic. The second possibility is the formation of interdigitated bilayers consisting of a primary monolayer of ODA in contact with the gold surface and a secondary monolayer of SDS as shown in scheme 1.

In order to understand how SDS molecules interact with ODA-capped gold nanoparticles and facilitate nanoparticle phase transfer, TGA and DSC measurements of the purified powder of the phase-transferred Au nanoparticles were done. Figures 2a and b show the DSC thermograms and TGA data obtained for the surface modified Au nanoparticles respectively. In both figures, curve 2 corresponds to data recorded from the phase-transferred powder and curve 1 is that recorded from pure SDS. Figure 2a shows four endothermic peaks at 55, 100, 183 and 218°C for the phase transferred Au nanoparticles (curve 2) and, barring the feature at 55°C, are similar to those observed for the pure SDS sample (curve 1). The corresponding TGA data (figure 2b) shows the close to 75% weight loss occurs at 215°C for pure SDS (curve 1) while the weight loss for the

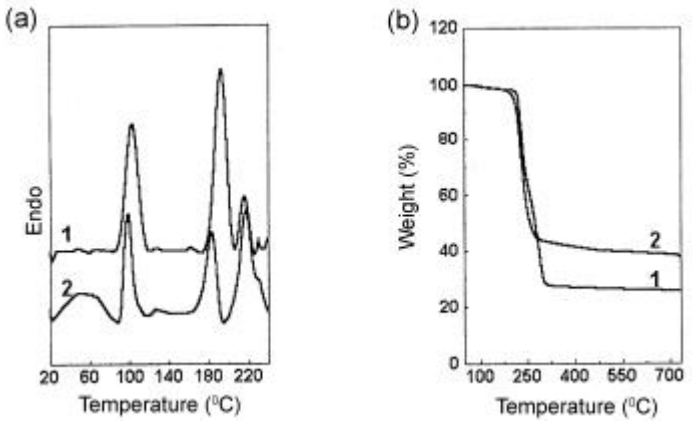


Figure 2. (**a**) DSC data recorded from powders of pure SDS (curve 1) and ODA-capped gold nanoparticles after phase transfer into water (curve 2). The curves have been shifted vertically for clarity. (**b**) TGA data recorded for powders of pure SDS (curve 1) and ODA-capped gold nanoparticles after phase transfer into water (curve 2).

phase transferred ODA-capped Au nanoparticle powder is ≈60% and occurs at roughly the same temperature (curve 2). A small weight loss is seen for both samples at close to 100°C (figure 2b). Negligible weight loss in the range 325–700°C is observed in both samples. From the DSC and TGA data, it is seen that the one significant difference between the SDS sample and ODA-capped gold nanoparticle powder is the presence of broad endothermic peak at 55°C in the phase transferred gold nanoparticle sample (curve 2, figure 2a) that is not accompanied by a weight loss (curve 2, figure 2b). This feature is attributed to the melting of ordered regions formed due to interdigitated segments of the primary ODA and SDS secondary monolayers (boxed regions, scheme 1). In a previous study, some of us have shown that silver nanoparticles capped with interdigitated bilayers of lauric acid show similar endothermic no weight-loss features at ≈50°C.[17] An interdigitated structure is expected to be energetically favourable in an aqueous environment due to the maximisation of hydrophobic interactions between the interdigitated hydrocarbon chains.[20] Based on this result, we propose that the phase transfer of the ODA-capped gold nanoparticles and their redispersibility in water arises due to formation of an interdigitated structure as shown in scheme 1. The DSC and TGA data of pure SDS and SDS-ODA-Au nanoparticle powder show another endothermic process at 215°C accompanied by a weight loss in both cases (figures 2a and b). These features correspond to desorption of free SDS molecules as well as a fraction of the surface-bound SDS-ODA bilayers. This desorption temperature is near to that reported for dodecylamine-modified gold nanoparticles by Leff *et al*.[21] The endothermic feature seen at ≈100°C in both samples (figure 2a) is due to the desorption of water entrapped in SDS and the SDS-ODA-Au nanoparticle powder. The origin of the features at 183°C (curve 2) and 192°C (curve 1) of figure 2a is not clear at this moment. That they occur in the broad weight loss region attributed to desorption of gold nanoparticle-surface bound SDS and ODA molecules (figure 2b) indicates that they are associated with breaking of bonds between the interdigitated bilayers and the gold surface. The TGA data reveals that the percentage weight contribution of the surface bound ODA and SDS molecules is higher than a theoretical estimation of ca. 24% (by assuming the area occupied by ODA molecule as 25 $Å^2$ on the surface of gold nanoparticles with diameter 35 Å and the ratio of ODA: SDS to be 1 : 1). The higher weight loss observed in this study is most likely due to the presence of uncoordinated SDS molecules in the powder, that in spite of repeated washing and centrifugation remains in the sample. Another important observation is the residual weight in the case of SDS even after heating to 700°C. We believe this is due to the formation of stable sodium-sulphur compounds after burning away of the hydrocarbon component in SDS. The difference in the residual weights of the two samples at 700°C is attributed to the presence of gold nanoparticles along with sodium and sulphur residue in the phase-transferred gold nanoparticle powder (figure 2b).

A drop-coated film of the aqueous solution of purified powder of SDS-ODA-Au nanoparticles was prepared on a Si (111) substrate and analysed by FTIR spectroscopy. The spectra obtained from an SDS-ODA-Au nanoparticle film (curve 3), ODA-Au nanoparticles (curve 2) as well as a solution-cast pure SDS film (curve 1) in the spectral range 3500–2500 cm^{-1} and 1500–600 cm^{-1} are shown in figures 3a and b respectively. The spectrum of pure SDS (curve 1) shows peaks at 1252 cm^{-1} (feature a) and 1083 cm^{-1} (feature b), which are assigned to S=O stretching vibrational modes of sulphonic acid groups present in SDS (figure 3b). These two features are not observed in the ODA-Au (curve 2, before phase transfer of the gold nanoparticles with SDS) while they are clearly seen in SDS-ODA-Au (curve 3, after phase transfer of the ODA-capped gold nano-

particles with SDS) indicating that SDS molecules are bound to the surface of the gold nanoparticles after phase transfer. The fact that the S=O stretch vibrational frequencies do not change in the phase-transferred gold nanoparticle sample clearly indicates that SDS is not directly coordinated to the gold nanoparticles. This rules out the possibility of an exchange of surface-bound ODA molecules by SDS during phase transfer as a possible mechanism for hydrophilization of the gold surface. Together with the DSC and TGA data, we conclude that that an inderdigitated bilayer structure as shown in scheme 1 best describes the structure of the surface modifiers for the gold nanoparticles. Curves 2 and 3 (figure 3b) corresponding to FTIR spectra of ODA-Au and SDS-ODA-Au show a resonance at 1470 cm^{-1}, which can be assigned to methylene scissoring vibrations in the hydrocarbon segment of the molecule.[22] The methylene antisymmetric and symmetric

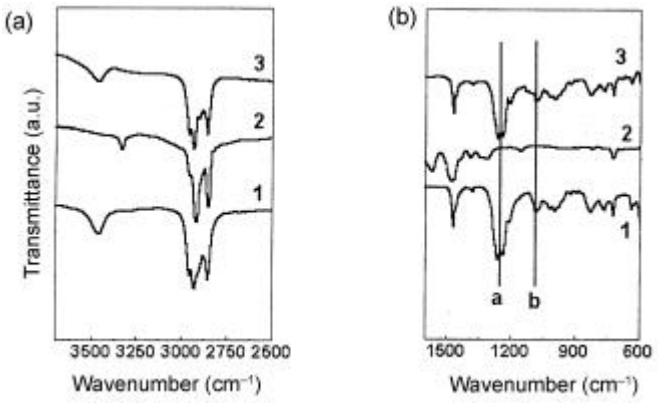


Figure 3. (**a**) and (**b**) FTIR spectra of pure SDS (curve 1), ODA-capped gold nanoparticles (curve 2) and surface modified gold nanoparticles with interdigitated bilayers of ODA and SDS (curve 3) in different spectral windows.

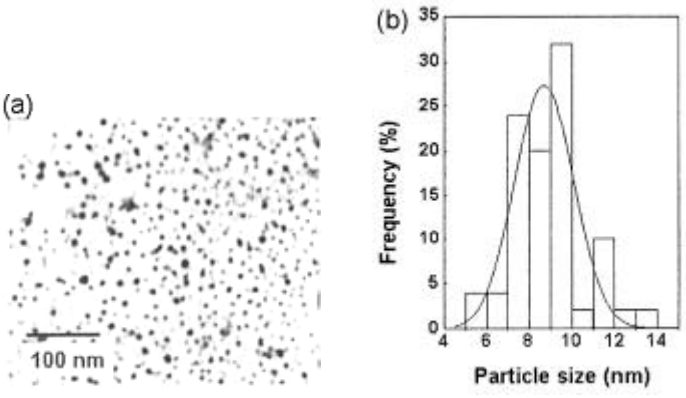


Figure 4. (**a**) Representative TEM micrograph of a film of gold nanoparticles phase transferred into water (SDS-ODA-Au). (**b**) Histogram showing the particles' size distribution measured from figure 4a. The solid line represents a Gaussian fit to the data.

vibrations are observed at 2920 and 2850 cm^{-1} respectively in both the cases and are clearly seen in figure 3a.[22] Another prominent resonance at 3456 cm^{-1} is observed in the case of SDS and SDS-ODA-Au samples and corresponds to O–H stretching vibration mode from moisture entrapped in both powders.

A drop-coated film of the aqueous solution of purified SDS-ODA-Au nanoparticles was formed on a carbon-coated copper grid by solvent evaporation and analysed by transmission electron microscopy (TEM). Figure 4a shows a representative TEM image of SDS capped gold nanoparticles while figure 4b is a plot of the particle size distribution (PSD) histogram measured from figure 4a. It is clear from the picture that the particles are fairly polydisperse. A Gaussian fit to the PSD histogram resulted in an average particle size of 9 ± 2 nm. The average size of the nanoparticles is roughly two times that of the as-prepared gold nanoparticles formed by borohydride reduction of chloroauric acid.[23] Murray and co-workers have shown that the particle size of *N*,*N*-trimethyl (undecylmercapto)ammonium chloride protected cluster is higher than the actual individual cluster due to ionic association between terminal trimethylammonium groups and counter anions during solvent evaporation.[24] This association leads to clumping of particles which hinders imaging of the core sizes of individual MPCs in the TEM. We believe that the larger particle size of the phase transferred gold nanoparticles relative to the ODA-capped nanoparticles in the organic solvent observed in the present study may be due to a similar process of screening of electrostatic interactions by sodium counterions.

In summary, the formation of water-dispersible gold nanoparticles by phase transfer of ODA-capped gold nanoparticles from chloroform to water-bearing SDS molecules has been demonstrated. The phase transfer is achieved by interdigitation of hydrocarbon tails of SDS molecules with that of the hydrocarbon sheath formed by primary monolayer of ODA on gold nanoparticle surface. This method shows promise for obtaining high concentrations of gold nanoparticles in water for with important application in nanoparticle bioconjugation methodologies.

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