

# Phase transfer protocols in nanoparticle synthesis

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**Development of synthesis protocols for realizing nanomaterials over a range of sizes, shapes and chemical compositions is an important aspect of nanotechnology. A number of recipes have been developed for the synthesis of metal nanoparticles in polar (for example, water) and non-polar organic solvents, each method accompanied by characteristic advantages and disadvantages. Specific applications often require the transfer of already formed nanoparticles from a polar to non-polar environment (and vice versa), thereby maximizing the advantages of both methods. In this article, I discuss how such nanoparticle phase transfers may be accomplished through imaginative use of capping molecules that modify the hydrophilicity/hydrophobicity of the nanoparticle surface.**

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WE are witnessing impressive advances in understanding the unusual physicochemical and optoelectronic properties of nanomaterials, their synthesis, assembly and packaging for commercial application<sup>1</sup>. One important area of nanotechnology concerns the development of reliable processes for the synthesis of nanomaterials over a range of sizes (with good monodispersity) and chemical compositions. Very recently, there have been rapid advances in the synthesis of nanoparticles of varying shapes. Nanorods of silver<sup>2,3</sup>/gold<sup>4-6</sup>/CdSe<sup>7</sup>/tungsten sulfide<sup>8</sup>, nanoprisms of silver<sup>9</sup>/gold<sup>10</sup> and CdS<sup>11</sup> are some of the exotic nanocrystalline shapes that may be routinely synthesized in the laboratory today. From a fundamental angle, the ability to control the shape of nanocrystals is particularly exciting and has led to the first observation of two distinct quadrupole plasmon resonance modes in silver nanoprisms<sup>9</sup>. The need for developing eco-friendly synthesis protocols that do away with the use of toxic chemicals has also fuelled research in this direction and bio-related processes that use bacteria<sup>12,13</sup> or fungi<sup>14,15</sup> have been developed to grow nanocrystals of silver and gold.

Gold nanoparticles, in particular, have received considerable attention over the ages and enjoy an interesting history dating back to the pioneering work of Faraday on the synthesis of gold hydrosols (gold nanoparticles dispersed in water)<sup>16</sup>. Gold nanoparticles find application in a variety of fields such as catalysis<sup>17</sup>, as electron microscopy markers<sup>18</sup> and in DNA sequence determination<sup>19</sup>. It

is of little surprise, therefore, that there are many recipes for the synthesis of gold nanoparticles over a range of sizes in an aqueous environment. The procedures for synthesis of gold hydrosols include: (i) reduction of aqueous chloroaurate ions by a variety of reducing agents such as citric acid<sup>20</sup>, sodium borohydride<sup>21</sup>, and alkaline tetrakis (hydroxymethyl)phosphonium chloride<sup>22</sup>, (ii) radiation-induced reduction of gold ions<sup>23,24</sup>, and (iii) sonochemical reduction of gold ions<sup>25</sup> to name just a few. The interested reader is directed to a comprehensive review by Hayat that lists at least one dozen protocols for the syntheses of gold hydrosols with particle sizes in the range 10–640 Å (ref. 21).

The synthesis of gold nanoparticles in non-polar organic media is a considerably newer area of research whose origin may be traced to the seminal work of Brust and co-workers<sup>26</sup>. In this report, the authors have demonstrated the phase transfer of chloroaurate ions into toluene using a phase transfer molecule such as tetra-alkylammonium bromide. Thereafter, the gold ions were reduced using sodium borohydride to yield gold nanoparticles of excellent monodispersity capped with alkanethiol molecules. Analogous to the formation of self-assembled monolayers (SAMs) of alkanethiols on gold thin films<sup>27</sup>, Brust and co-workers<sup>26</sup> used similar thiolate chemistry to cap the gold nanoparticles with alkanethiols present in the organic phase during phase transfer and reduction of the gold ions, thus rendering them hydrophobic and soluble in the organic phase. Such surfactant-stabilized gold nanoparticles behave like new compounds and can be easily separated out of solution in the form of a powder and re-dissolved in different organic solvents without significant variation in the particle size distribution. Very recently, we have considerably simplified the Brust protocol and have shown that the phase transfer of chloroaurate ions from water to chloroform, their spontaneous reduction to yield nanoparticles of controllable size and their surface capping may be accomplished by a single molecule such as hexadecylaniline molecules in one step<sup>28</sup>. The Brust report has been rapidly followed by publications on the self-assembly on gold and silver nanoparticle surfaces of alkanethiol<sup>29,30</sup>, aromatic thiol<sup>31,32</sup>, alkylamine<sup>33,34</sup>, dialkyl disulfide<sup>35</sup>, and thiolated cyclodextrin<sup>36,37</sup> molecules. The surface properties of the gold colloids may be tailored by chemisorption of terminally functionalized thiol molecules resulting in a number of

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interesting applications. One of the exciting areas of research using functionalized colloidal gold particles is the study of the reactivity of monolayer protected colloidal particles (or MPCs as they were termed)<sup>38,39</sup>. Using a simple place-exchange reaction strategy, Murray and co-workers<sup>40</sup> have demonstrated that alkanethiol derivatized colloidal gold particles in an organic solvent could be poly-functionalized. This led to the possibility of using the poly-heterofunctionalized colloidal particles as 'nanofactories' where the metal core scaffolds support complex organic ligand structures that may include polymeric and hyperbranched domains<sup>40</sup>. The use of polar terminal functional groups such as carboxylic acid, ammonium ions, sulphonic acid, etc. in the monolayers chemisorbed onto the gold particle surface may be used to increase the solubility of the particles in polar solvents such as water, thus enabling the synthesis of water-soluble gold nanoparticles that, like their hydrophobic counterparts, may be dried in the form of a powder and re-dispersed in water and other polar solvents without significant degradation in the particle size and monodispersity<sup>41,42</sup>.

The two main approaches for the synthesis of gold nanoparticles, viz. synthesis in water and in non-polar organic solvents, have certain pros and cons that are enumerated below.

### Water-based gold nanoparticle synthesis

#### Advantages

- Water is a good solvent for a number of metal ions as well as a variety of capping molecules. The synthesis involves preparation of an aqueous gold salt solution followed by reduction of the metal ions in a single step<sup>21</sup>. It is therefore considerably simpler than the multi-step Brust protocol<sup>26</sup>.
- No additional stabilization against aggregation of the gold nanoparticles is required – surface bound ions (citrate ions, chloraurate ions, etc.) stabilize the nanoparticles electrostatically in solution.
- Electrostatic layer-by-layer assembly involving, for example, oppositely charged polyelectrolytes/surfactants and nanoparticles may be readily accomplished on suitably functionalized surfaces<sup>43–45</sup>.
- Nanoparticle shape control can be easily effected by using suitable micelles (arising due to spontaneous assembly of suitable surfactants in water) as templates<sup>4–6</sup>.
- Perhaps the biggest advantage of a water-based synthesis procedure is that bioconjugation of the gold nanoparticles with DNA<sup>19</sup>, enzymes<sup>46</sup>, etc. may be easily accomplished.

#### Disadvantages

- Ionic interactions limit the concentration of gold nanoparticles in the aqueous phase to very dilute levels, a

big drawback in biological labeling of the nanoparticles.

- Control over the particle size and monodispersity in a particular reduction protocol is not very good.
- The gold nanoparticles do not spontaneously assemble into a close-packed hexagonal arrangement on solvent evaporation.
- The gold nanoparticles are not easily separated from solution in the form of a powder that would be readily re-dispersible in water after storage<sup>41,42</sup>.

### Organic solution-based synthesis of gold nanoparticles

#### Advantages

- High degree of control may be exercised over the gold nanoparticle size, monodispersity<sup>29</sup> and chemical nature of the nanoparticle surface (via capping with terminally functionalized thiols)<sup>38–40</sup>.
- High concentrations of the gold nanoparticles in solution may be easily prepared.
- Functionalized gold nanoparticles may be stored as a powder without sintering of the particles.
- The nanoparticles spontaneously assemble into close-packed, hexagonal monolayers upon solvent evaporation<sup>26,29,34,47,48</sup>. The collective properties of the nanoparticle assembly may be controlled by varying the interparticle separation via capping with different chain length alkanethiols<sup>48</sup>.

#### Disadvantages

- The procedure is a multi-step one involving independent phase transfer of the gold ions followed by their reduction and capping.
- While close-packed monolayers of the gold nanoparticles may be deposited by solvent evaporation, there is little control over the process of assembly. Furthermore, superlattices of the gold nanoparticles cannot be readily deposited, in contrast with the layer-by-layer assembly that is possible for electrostatically stabilized gold nanoparticles in water.
- Formation of bioconjugates with gold nanoparticles is not possible in an organic environment.

It is clear that both methods for the synthesis of gold nanoparticles have characteristic advantages. Depending on the particular application of the nanoparticles, the ideal condition would be to somehow marry the two methods and thus maximize their advantages. This may be conveniently done by effecting a *phase transfer* of gold nanoparticles synthesized in one medium (water/organic solvent) to the second medium (organic solvent/water). In addition to maximizing the benefits accruing from a

combination of the two syntheses methods, the ability to move nanoparticles across liquid interfaces into environments of specific physicochemical properties to probe, for example, variation in the optical properties of the nanoparticle solution<sup>49</sup> is an attractive feature of phase transfer protocols. In the remaining part of this article, I discuss some of the methods developed to carry out the phase transfer of gold nanoparticles in both directions.

## Moving gold nanoparticles around

### *Phase transfer of aqueous gold nanoparticles to non-polar organic solvents*

The movement of aqueous gold nanoparticles into non-polar organic solvents would require hydrophobization of the nanoparticles. The many techniques developed to accomplish phase transfer into organic solvents essentially differ in the nature of the capping molecule employed to hydrophobize the nanoparticles. Possibly the first report on the phase transfer of gold nanoparticles from water to an organic solvent such as butyl acetate was that of Underwood and Mulvaney<sup>49</sup>. In this study, the authors showed that aqueous gold nanoparticles synthesized by the Turkevich method<sup>21</sup> could be quantitatively transferred into butyl acetate by complexation of the particles with a 'comb stabilizer' present in the organic phase<sup>49</sup>. The comb stabilizer used was a co-polymer consisting of a backbone of methyl methacrylate and glycidyl methacrylate with poly(12-hydroxystearic acid) as pendant side chains. Gentle shaking of a biphasic mixture of the gold hydrosol and comb stabilizer in butyl acetate resulted in the emulsification of the gold hydrosol-butyl acetate mixture, this process accelerating the complexation of the polymer with the gold nanoparticle surface. The gold nanoparticles were thereby hydrophobized and were phase transferred to the organic phase. Gold sols possess lovely pink to ruby red colours<sup>49</sup> and therefore, the phase transfer of the gold particles from one phase to another is seen as a dramatic transfer of colour between phases.

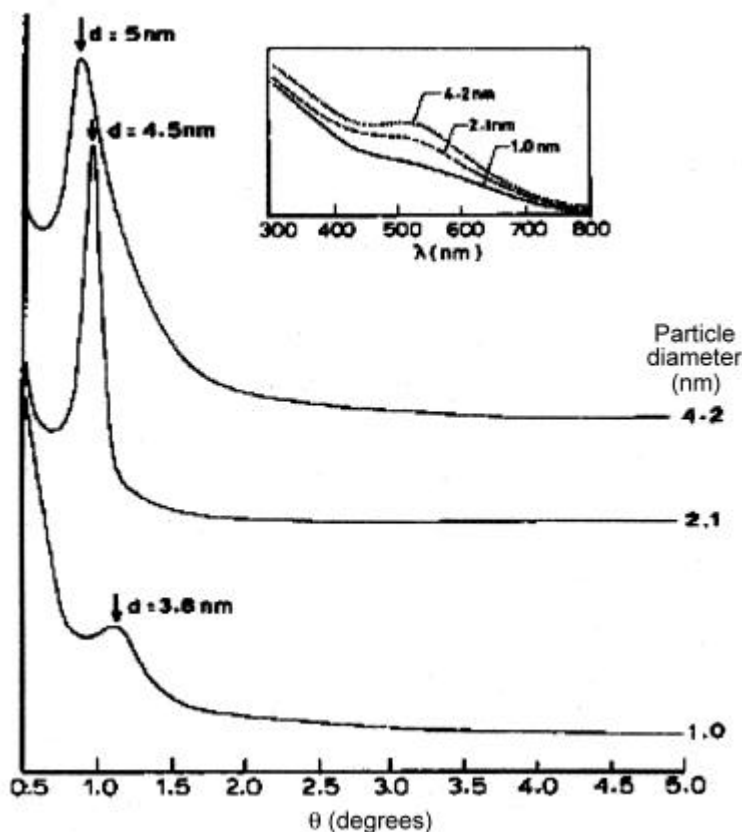
The focus of the work of Underwood and Mulvaney was to study changes in the optical properties of gold colloids as the refractive index of the organic solution was varied. This was done by preparing the gold sols in solutions consisting of mixtures of butyl acetate and CS<sub>2</sub> to obtain solutions possessing refractive indices in the range 1.336 (water) to 1.583. Figure 1 shows pictures of gold nanoparticles in the different butyl acetate-CS<sub>2</sub> solutions<sup>49</sup>. A clear variation in colour with refractive index of the solution is seen and is in quantitative agreement with the Mie theory that is used to understand the optical properties of colloidal solutions<sup>49</sup>. The authors did not perform a detailed characterization of the polymer-gold nanoparticle complex and therefore, little is known of the interaction of the polymer with the particle surface, etc.



**Figure 1.** Five sols of colloidal gold prepared in water and in mixtures of butyl acetate and CS<sub>2</sub>. Refractive indices of the solutions at the absorption band maximum are 1.336, 1.407, 1.481, 1.525 and 1.583 ( $\pm 0.004$ ) respectively. (Reprinted with permission from ref. 49, © 1994, American Chemical Society.)

Recognizing that the strong interaction of alkanethiol molecules with gold nanoparticles may be used to hydrophobize gold nanoparticles at the liquid-liquid interface, Rao and co-workers<sup>50,51</sup> have demonstrated the acid-facilitated phase transfer of aqueous gold and indeed, platinum and silver nanoparticles into organic solvents such as toluene. In a typical experiment, the authors took a mixture of a gold hydrosol and dodecanethiol in toluene. To this biphasic mixture, concentrated HCl was added under stirring. A swift movement of the gold nanoparticles into the organic phase containing the gold nanoparticles was observed indicating capping of the metal nanoparticles with alkanethiol molecules<sup>50,51</sup>. The alkanethiol-stabilized colloidal gold, silver and platinum particles transferred to toluene as described above could be self-assembled by solvent evaporation on different substrates yielding close-packed, hexagonal arrays of the nanoparticles<sup>51</sup>. A concentrated solution of the different sized thiol stabilized-gold particles was placed on glass substrates and the particles assembled on the surface. Figure 2 shows X-ray diffraction patterns from the different films, the size of the particles indicated next to the corresponding diffractogram.

The *d*-spacings obtained from the low angle peaks (indicated by arrows in Figure 2) are also listed in the figure. The low angle diffraction peaks arise from the arrangement of the gold particles in the array formed by solvent evaporation. It is observed that the separation between the clusters decreases as the size of the particles is reduced (Figure 2), in accordance with nanoparticle packing considerations. However, the *d*-spacing is smaller than that expected from the core + surfactant size considera-

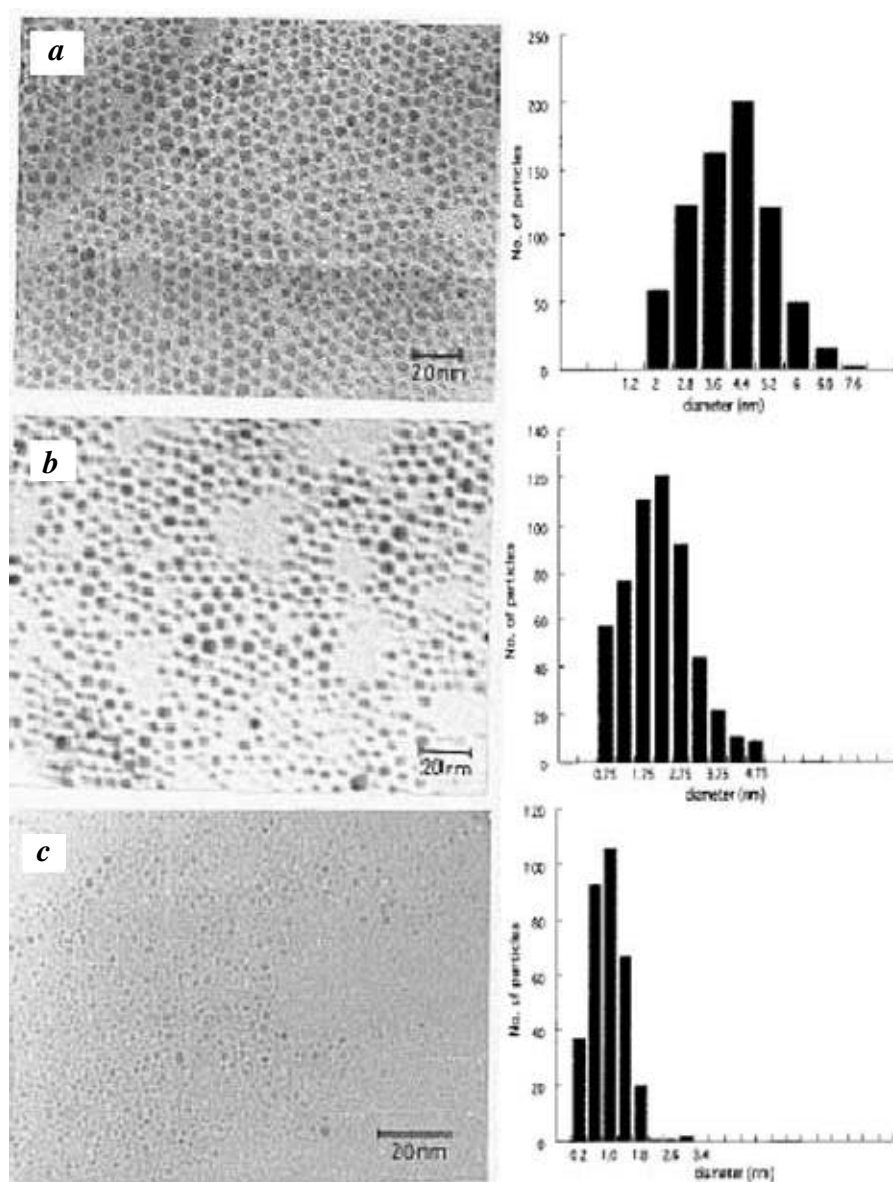


**Figure 2.** XRD patterns from the nanocrystalline arrays of Au particles of different mean diameters (4.2, 2.1 and 1.0 nm). Inset of the figure displays the UV-vis spectra of these particles. (Reprinted with permission from ref. 51. © 1997, American Chemical Society.)

tions indicating some degree of interdigitation of the hydrocarbon chains from neighbouring particles in the array<sup>51</sup>. The inset of Figure 2 shows the optical absorption spectra recorded from the colloidal gold particles in toluene for gold particles of different sizes. The surface plasmon resonance from the colloidal gold particles centered around 525 nm is clearly seen for the 4.2 nm and 2.1 nm sized particles and the intensity of the resonance is higher for the larger sized particles (Figure 2, inset). The resonance could not be detected for the smallest size particles (1.0 nm diameter) and this was attributed to the possibility of the gold particles in this size range being non-metallic<sup>51</sup>.

Transmission electron microscopy images recorded from the self-assembled gold nanoparticle monolayer obtained by solvent evaporation is shown in Figure 3 (ref. 51). It can be seen the thiol-derivatized gold nanoparticles self-assemble into nanocrystalline arrays over tens of nanometer length scales. The spacing between the particles is highly regular and roughly 1 nm between the particles. While the larger particles of mean diameter 4.2 nm assembled into regular, close-packed domains, assemblies of smaller articles show a large fraction of voids within the domains<sup>51</sup>.

It is known that alkylamine molecules also bind to gold nanoparticles quite strongly through a 'weak' covalent bond, as described by Leff *et al.*<sup>33</sup>. Using a process similar to that adopted for phase transfer of gold nanoparticles with alkanethiols, we have recently demonstrated that octadecylamine molecules present in the organic phase may also be used to accomplish the phase transfer of aqueous gold nanoparticles into toluene<sup>52</sup>. Vigorous shaking of a biphasic mixture containing the gold hydrosol and octadecanethiol molecules in toluene resulted in the rapid transfer of gold nanoparticles into the organic phase without the use of acid. This is clearly demonstrated in Figure 4a that shows a picture of two test-tubes with the biphasic mixture before (test-tube to the left) and after shaking (test-tube to the right). The transfer of the red colour from the lower, aqueous phase to the upper, toluene phase is clearly illustrated. UV-vis spectra recorded from the gold hydrosol before (curve 3) and after (curve 1) phase transfer are shown along with the toluene phase after phase transfer (curve 2 in Figure 4b). The almost complete disappearance of the gold nanoparticle plasmon resonance in curve 1 indicates facile phase transfer of the gold nanoparticles into toluene. The UV-vis spectrum recorded from the toluene phase after phase



**Figure 3.** TEM images of the thiol derivatized Au nanoparticles. The particle size distributions are shown in the form of histograms alongside the TEM images. The nanoparticles in (*a*), (*b*), and (*c*) were obtained by using 2.2, 2.0, and 1.8 ml of the 25 mM  $\text{HauCl}_4$  solution, respectively. (Reprinted with permission from ref. 51. © 1997, American Chemical Society.)

transfer of the gold nanoparticles (curve 2) shows a fairly sharp plasmon resonance from the nanoparticles, indicating little aggregation of the particles. The gold nanoparticles could be separated in the form of a dry powder by rotary evaporation of the toluene phase and could be readily redispersed in organic solvents such as chloroform, benzene, carbon tetrachloride, etc.<sup>52</sup>

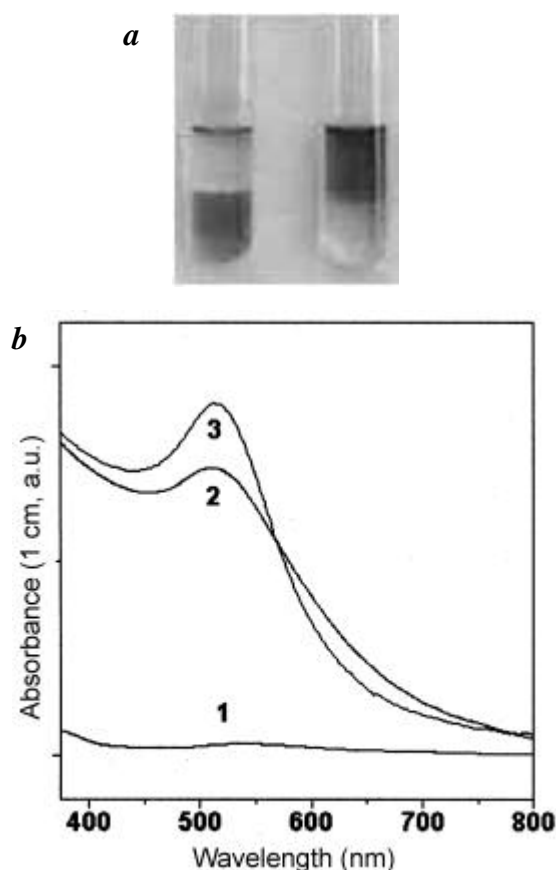
A drop of the toluene phase with the gold nanoparticles was placed on a TEM grid and analysed after solvent evaporation. Figure 5 shows the image obtained wherein well ordered hexagonal, close-packed configuration of gold nanoparticles can be seen. The ordered domains are not particularly large due to the fact that the monodisper-

sity of the gold particles in the aqueous phase was 15%. It is interesting to observe the separation of the gold nanoparticles into domains based on their size (Figure 5).

Cyclodextrins (CDs), which are cyclic oligosaccharides consisting of six, seven or eight glucopyranose units (*a*-, *b*- and *g*-CDs respectively), are versatile host molecules for 'guests' such as alkanethiols, forming what are known as 'inclusion complexes'. Inclusion complexes of CD and alkanethiols in water have been self-assembled on gold thin films<sup>53</sup> as well as on gold nanoparticles<sup>54</sup>. We have shown recently that gold nanoparticles may be capped with octadecanethiol (ODT) molecules threaded with cyclodextrin and furthermore that during

vigorous shaking of a biphasic mixture of this hydrosol with chloroform, the gold nanoparticles were rapidly transferred to the organic phase<sup>55</sup>. The inset of Figure 6 shows the test tubes before (test tube to the left) and after (test tube to the right) phase transfer of gold nanoparticles capped with inclusion complexes of ODT and CD into chloroform. The process of phase transfer proceeds via detachment of the CD molecules from the alkanethiol molecules capping the gold nanoparticles during stirring of the biphasic mixture. The gold nanoparticles become sufficiently hydrophobic at this stage and are phase transferred into chloroform. The schematics accompanying the picture illustrate the changes occurring in the monolayer of ODT on the surface of the gold nanoparticles during the shaking process leading to hydrophobization of the gold nanoparticles<sup>55</sup>.

Just as in the case of gold nanoparticles, appropriate choice of the capping agent for modification of the surface of nanoparticles may be used to accomplish the phase transfer of aqueous silver nanoparticles. Wang, Efrima

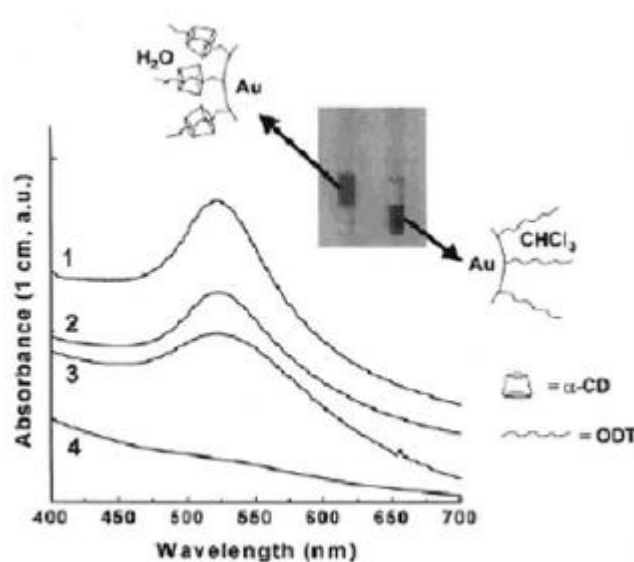


**Figure 4.** *a*, Picture showing the two-phase gold hydrosol-ODA containing toluene layers before (test tube on the left) and after (test tube on the right) phase transfer of the gold particles into toluene. *b*, UV-vis spectra recorded from the toluene phase (curve 2) and the aqueous phase before (curve 3) and after (curve 1) phase transfer of the gold colloidal particles into toluene (Figure 4 *a*, solutions taken from the test tube on the right). (Reprinted with permission from ref. 52, © 2001, Elsevier Science.)

and Regev have shown that silver nanoparticles can be phase-transferred from water to organic solvents by binding the nanoparticles to sodium oleate present in cyclohexane/dodecane<sup>56</sup>. Similar to the acid facilitated phase transfer of gold nanoparticles using alkanethiols<sup>50,51</sup>,

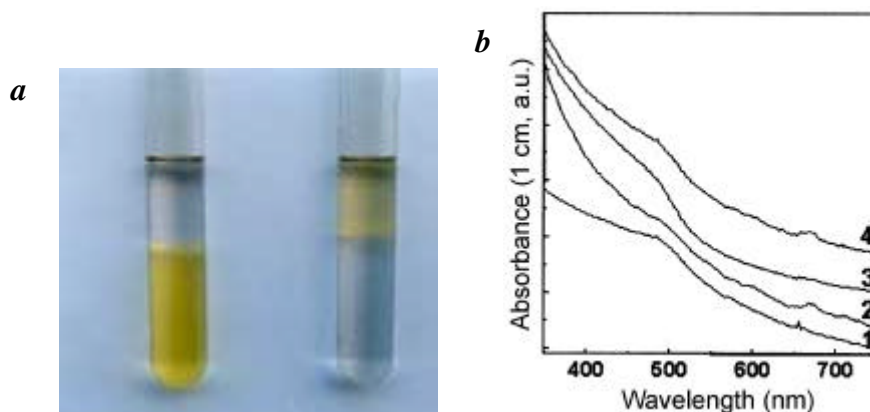


**Figure 5.** TEM micrograph of gold nanoparticles phase transferred into toluene self-assembled by solvent evaporation.



**Figure 6.** UV-vis spectra recorded from the as-prepared gold colloidal solution (curve 1), the gold colloidal solution after capping with  $\alpha$ -CD threaded ODT molecules (curve 2), the chloroform solution after phase transfer of the gold nanoparticles (curve 3), and the aqueous gold colloidal solution after phase transfer of the gold nanoparticles into chloroform (curve 4). *Inset*, Test tubes containing solutions of chloroform and  $\alpha$ -CD threaded ODT-capped gold hydrosol before (test tube on the left) and after phase transfer of the gold nanoparticles into chloroform (test tube on the right). The cartoons illustrate the nature of surface modification of the gold nanoparticles in the aqueous phase and in the organic phase. (Reprinted with permission from ref. 55, © 2001, American Chemical Society.)





**Figure 7.** *a*, Test-tubes containing the biphasic mixture of aqueous CdS and ODT in pet ether before (test-tube on the left) and after (test-tube on the right) phase transfer of the CdS nanoparticles into the organic phase. *b*, UV-vis spectra recorded from CdS nanoparticles dispersed in different solvents. Curve 1, as-prepared CdS nanoparticle solution in water; Curve 2, ODT-stabilized CdS nanoparticles in toluene; Curve 3, ODT-stabilized CdS in chloroform and Curve 4, ODT-stabilized CdS in benzene. (Reprinted with permission from ref. 58. © 2001, American Chemical Society.)

the phase transfer of silver particles occurs when a small amount of orthophosphoric/perchloric acid is added to the reaction medium<sup>56</sup>. As observed by other workers, the silver particles assembled into large domains of hexagonally packed nanoparticles<sup>56</sup>. What is interesting about this study is the change in conformation of the surface-bound oleate ions on transfer between the two phases. From FTIR studies, the authors inferred the presence of carboxylate ions on the surface of the silver particles in water that, upon phase transfer into the organic solvent, reversed direction to expose the hydrophobic tails of the oleate molecules towards the solvent. Detailed studies of the position of the double bond in the capping molecule in relation to the carboxylate ions indicated that this factor was crucial for efficient phase transfer of the silver nanoparticles<sup>56</sup>.

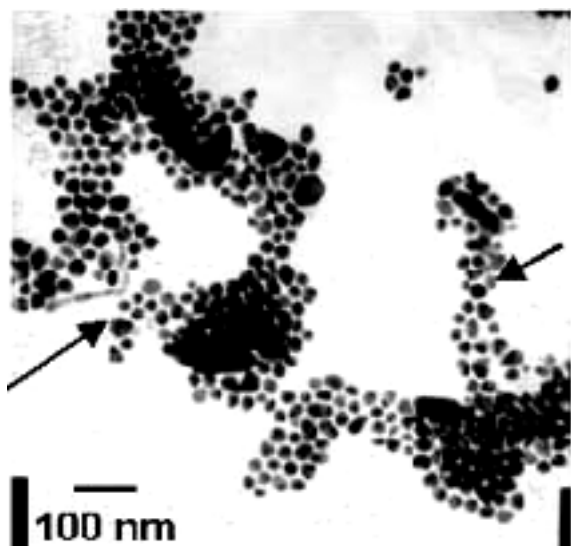
There is much interest in the synthesis and electronic application of semiconductor nanoparticles, or quantum dots as they are more popularly known<sup>57</sup>. It is well known that thiols bind to quantum dots of CdS and therefore, it should be possible to phase transfer aqueous CdS nanoparticles into organic solutions by complexation with alkanethiols and has been demonstrated by us<sup>58</sup>. The experimental conditions for phase transfer of aqueous CdS into toluene containing octadecanethiol were slightly more stringent than that used for phase transfer of gold nanoparticles. It was observed that pre-formed CdS nanoparticles upon complexation with octadecanethiol molecules at the liquid-liquid interface assembled at the interface and were not transferred to the organic phase<sup>58</sup>. Bubbling of H<sub>2</sub>S gas in a biphasic mixture of aqueous CdCl<sub>2</sub> solution and petroleum ether containing octadecanethiol during vigorous stirring nanoparticles of CdS capped with the thiol molecules that were rapidly transferred to organic phase (Figure 7a)<sup>58</sup>. The CdS nanopar-

ticle powder was extremely stable and could be readily redispersed in a number of organic solvents such as chloroform, benzene and toluene without any indication of sintering of the particles (Figure 7b)<sup>58</sup>. In the UV-vis spectra of hydrophobized CdS in the different solvents, the onset of absorption occurs at 475 nm and corresponds to a particle size of 6 nm. This size is in good agreement with that determined from TEM studies of CdS nanoparticles transferred into pet ether (Figure 8). A fairly regular close-packed assembly of the CdS quantum dots can be observed in the TEM micrograph. A number of triangular CdS nanoparticles can also be seen in the figure (identified by arrows).

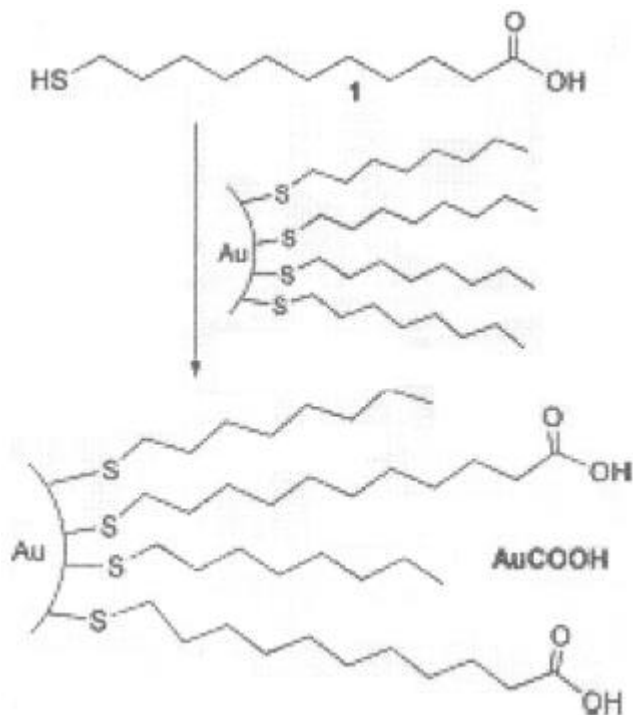
### Transfer of organically soluble gold nanoparticles to water

While many different procedures have been developed for the transfer of aqueous gold nanoparticles into organic solvents, the number of reports on the phase transfer of gold nanoparticles in the reverse direction is much less. The key step is to replace the hydrophobic groups bound to the gold nanoparticle surface with polar functional groups, thus rendering the nanoparticles water-soluble. Rotello and co-workers<sup>59</sup> used a place exchange mechanism to functionalize alkanethiol capped organically soluble gold nanoparticles with carboxylic acid groups. The process is illustrated in Figure 9 which depicts replacement of octanethiol molecules bound to the surface of 2 nm diameter gold nanoparticles by 11-thioundecanoic acid. Under the experimental conditions adopted by Rotello *et al.*, the ratio of thiol carboxylic acid:octanethiol on the gold nanoparticle surface after place exchange was found to be 1:1. The carboxylic acid deri-

vated gold nanoparticles were washed with dichloromethane and were found to be soluble in water. One advantage of using carboxylic acid functionality to render the gold nanoparticles water-soluble is that the charge on the nanoparticle surface can be modulated by varying the pH of the gold colloidal solution. Interesting variation



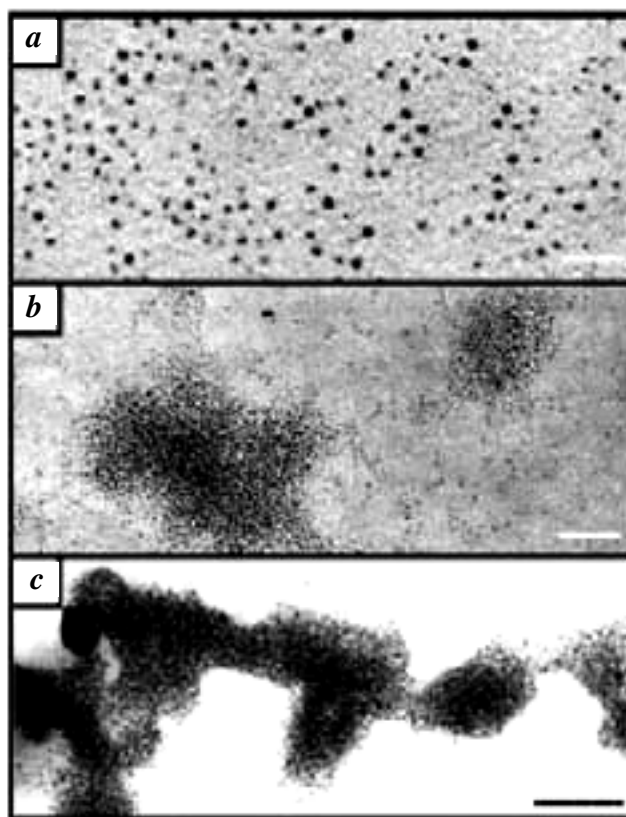
**Figure 8.** TEM picture of CdS quantum dots capped with octadecanethiol and phase transferred into pet ether. The arrows in the figure identify some triangular shaped CdS nanoparticles.



**Figure 9.** Schematic showing the place exchange of octanethiol molecules on the surface of gold nanoparticles by  $\omega$ -thiol carboxylic acid molecules. (Reprinted with permission from ref. 59. © 2000, Royal Society of Chemistry.)

in the optical properties of carboxylic acid derivatized gold<sup>32</sup> and silver nanoparticles<sup>60</sup> as a function of solution pH have been studied by us earlier. Rotello and co-workers have shown that as the pH of the gold colloidal solution was reduced below 7, the particles aggregated into close-packed assemblies, the size of the aggregates being largest at the lowest pH value (Figure 10).

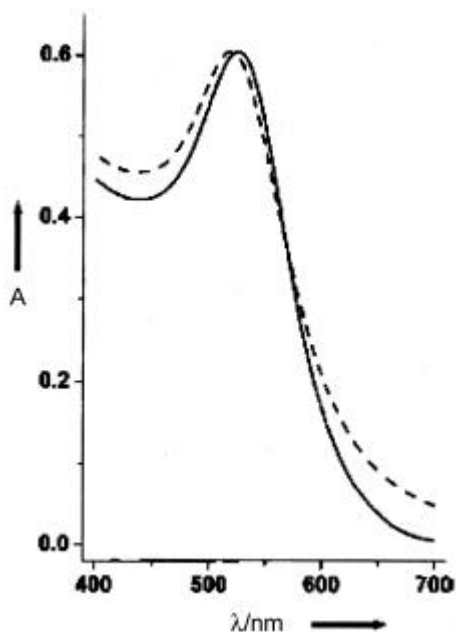
A more direct method for the phase transfer of gold nanoparticles into water along the lines discussed earlier for phase transfer of aqueous particles into organic solvents involving a biphasic mixture has been demonstrated by Gittins and Caruso<sup>61</sup>. More specifically, Gittins and Caruso showed that gold and palladium nanoparticles synthesized in toluene by the Brust method and stabilized by tetraalkyl ammonium salts could be rapidly and completely phase transferred to water by addition of an aqueous 0.1 M 4-dimethylaminopyridine (DMAP) solution to aliquots of the gold nanoparticles in toluene. As in previous studies (Figures 4 and 6), the process of phase transfer is seen as a transfer of colour from the organic phase to the aqueous phase. That the movement of the gold particles between phases was almost 100% can be seen from the UV-vis spectra recorded from toluene before phase



**Figure 10.** TEM micrographs of  $\omega$ -thiol carboxylic acid functionalized gold colloid at (a) pH 10, (b) pH 7, and (c) pH 4. Scale bars represent 10 nm, 25 nm and 50 nm, respectively. (Reprinted with permission from ref. 59. © 2000, Royal Society of Chemistry.)



transfer (full line, Figure 11) and water after phase transfer (dashed line, Figure 11). The UV-vis spectra recorded from the two phases are almost identical. There is little broadening of the surface plasmon resonance after phase transfer indicating no aggregation of the nanoparticles consequent to their movement<sup>61</sup>. The authors have shown that the aqueous gold and palladium solutions were extremely stable with no sign of degradation even after storage for several months<sup>61</sup>. This is graphically illustrated in



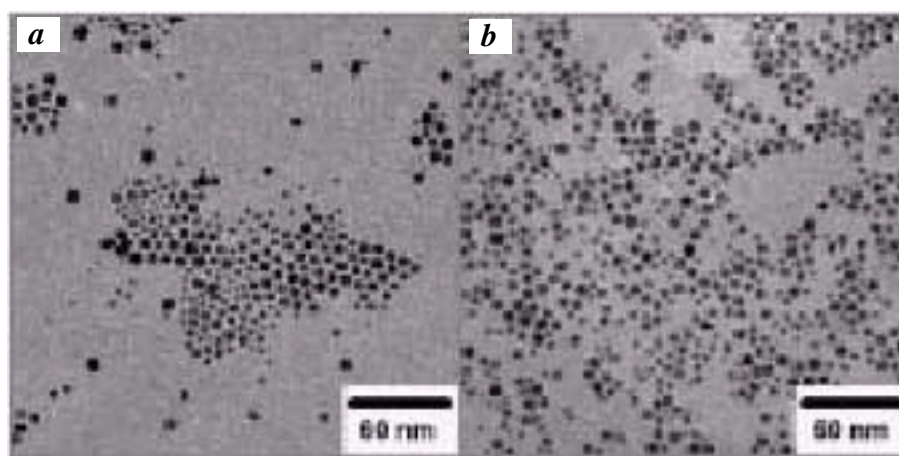
**Figure 11.** UV/Vis spectra of a diluted solution of gold nanoparticles in toluene (solid line) and the same sample transferred into an equal volume of 0.1 M DMAP solution at pH 10.5 (dashed line). (Reprinted with permission from ref. 61. © 2001, Wiley-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.)

the TEM micrographs recorded from the gold nanoparticles in the toluene phase (Figure 12a) and the aqueous phase one month after phase transfer of the gold nanoparticles (Figure 12b). A comparison of the two TEM pictures shows that little sintering/aggregation of the gold nanoparticles had occurred after one month of storage.

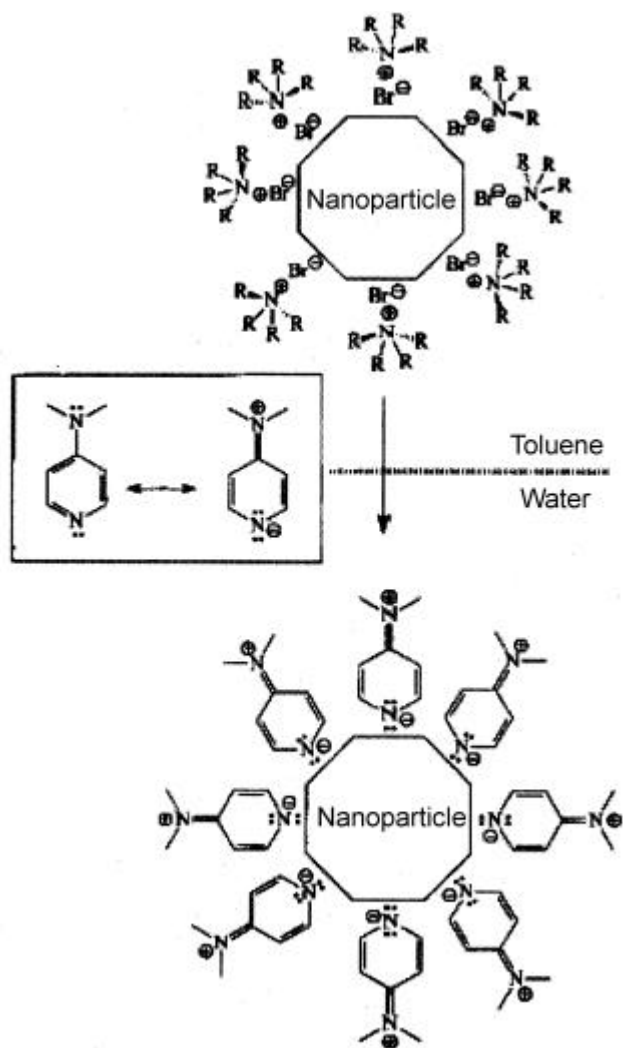
Gittins and Caruso have speculated on the mode of binding of the DMAP molecules on the gold nanoparticle surface during the phase transfer process<sup>61</sup>. Based on a series of control experiments, they have proposed a mechanism for the phase transfer as illustrated in Figure 13. Addition of an aqueous DMAP solution to the nanoparticle dispersion in toluene leads to partitioning of the DMAP molecules across the toluene/water boundary as shown in Figure 13. The DMAP molecules replace the tetraalkyl ammonium salts and form a labile donor-acceptor complex with the gold atoms on the surface of the nanoparticles through the endocyclic nitrogen atoms. The surface charge on the gold nanoparticles that stabilizes the particles in water arises due to partial protonation of the exocyclic nitrogens that extend away from the nanoparticle surface towards the solvent (Figure 13).

Gittins and Caruso have developed on their approach and recently demonstrated the phase transfer of silver, gold, platinum and palladium nanoparticles using a number of exchanging ligands such as mercaptoundecanoic acid (MUA), mercaptosuccinic acid, etc.<sup>62</sup>. A highlight 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 ionized carboxylate ions on the nanoparticle surface<sup>62</sup>.

In conclusion, I have tried to outline the advantages of carrying out phase transfer of inorganic nanoparticles (gold nanoparticles in particular) from aqueous to non-



**Figure 12.** Transmission electron micrographs of gold nanoparticles synthesized in toluene (a) and the same sample one month after being transferred into water by the addition of DMAP (b). (Reprinted with permission from ref. 61. © 2001, Wiley-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.)



**Figure 13.** Proposed mechanism for the spontaneous phase transfer of gold and palladium nanoparticles from an organic reaction medium (toluene) to water by the addition of DMAP.  $R = C_8H_{17}$ . (Reprinted with permission from ref. 61. ©, 2001 Wiley-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.)

polar organic environments and vice versa. Various methods in the literature including work from my group in this fascinating area have been covered and if there are any omissions, it is unintentional. Future work will focus on phase transfer of nanoparticles of well-controlled shapes and investigation into their liquid crystalline behaviour.

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