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Trialkylphosphine oxide/amine stabilised silver nanocrystals—the importance of steric factors and Lewis basicity in capping agents

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The preparation of specifically passivated silver quantum dots is reported. Investigations into the surface-capping agents have highlighted the importance of both the chain length and bonding strength of the individual ligands. Capping agents traditionally utilised to stabilise semiconductor quantum dots cannot always be used to effectively passivate metal structures, and a dual surfactant system was chosen. Long chain amines, usually weakly binding to a bulk silver surface, were found to be effective passivating agents. The steric properties of weakly bound trialkylphosphine oxides also appear to affect the particle stability. The choice of capping agents highlight the importance of both the Lewis base functionality and steric factors and these may play a key part in the design of future nanostructured materials. It also emphasizes that effective capping agents for nanodispersed metals are not necessarily the optimum ligands for other systems such as semiconductors, metal oxides, *etc*.

Metal colloids have been known since 1857, but only recently realised in devices such as single electron transistors and nanoscale electronic switches.[1–3] Key papers by Brust *et al.* describe the preparation of high quality nanometer sized gold particles.[4,5] This work has been advanced by other groups, notably Heath and Whetten.[6,7] Other nanometer sized metal particles such as silver,[8] platinum,[9] iridium[10] and palladium[10] have been prepared by analogous routes. Recent work worthy of note includes the tuning of silver quantum dots through a metal-insulator transition, and investigations into the emission properties of small gold nanoclusters.[11,12] There are also many applications emerging for nanosized metal particles such as biotagging, which makes use of the large surface plasmon resonance effects, especially in the case of gold and silver.[13,14]

In 1993, Murray and co-workers reported an elegant route to II-VI quantum dots capped with tri-*n*-octylphosphine oxide (TOPO).[15] These quantum dots were crystalline, monodispersed and highly luminescent. This method has been adapted for the preparation of other semiconductors, notably the III-V's.[16] Various adaptations of the TOPO routes have been reported, including the preparation of core/shell structures and the use of single source precursors.[17] Sun and Murray, and Dinega and Bawendi have utilised the TOPO route for the preparation of cobalt nanocrystals, giving high quality magnetic materials that exist in a new crystalline phase (designated ε-cobalt).[18,19] This was followed by the preparation of iron/platinum alloys,[20] iron,[21] gold[22] and lead[23] nanocrystals passivated with organic ligands based on the TOPO system. These cases are of interest due to the novel capping ligands employed. Polar Lewis bases such as phosphine oxides are not normally employed as capping agents for metals, nor are carboxylic acids, and amines have only recently been used. It appears however that such ligands make excellent passivating agents. Long chain thiols are normally utilised as passivating agents initially based on sulfur's affinity for gold.[24,25] The adsorption of amines and trialkylphosphines on bulk gold surfaces has previously been investigated and found to be inferior to thiols.[25,26] Here we report the preparation of trialkylphosphine oxide/amine passivated silver nanoparticles by reduction of silver(I) nitrate in various coordinating solvents by sodium borohydride.

Experimental

Tri-*n*-octylphosphine oxide (TOPO) (90%), tri-*n*-butylphosphine oxide (TBPO) (95%), octadecylamine (97%), silver nitrate (99%), 4-*tert*-butylpyridine (99%), sodium borohydride (99%) were all obtained from Aldrich. Methanol and toluene (analysis grade) were obtained from Fisher Scientific. All reagents were used as received. Reactions were carried out under nitrogen using standard Schlenk line techniques unless otherwise stated.

Instrumentation

NMR spectra were obtained using a Varian Mercury-VX 300 MHz NMR spectrometer operating at 299.98 MHz for ^{1}H and 121.44 for ^{31}P. Electron microscope images were obtained using a JEOL 4000EX operating at 400 kV with samples deposited on a carbon coated copper grid. FTIR spectra were obtained using a Perkin-Elmer Spectrum 1 spectrophotometer with universal ATR sampling accessory. Absorption spectra were obtained using a Hitachi U-4100 spectrophotometer. XRD pattern reflections were obtained using a Philips 1830 generator, an MPD goniometer, PW/710 controller and APD software.

Growth of nanoparticles

In a typical reaction, $AgNO_3$ (0.15 g, 9.4×10^{-4} M) was mixed in 3 ml of 4-*tert*-butylpyridine in air and stirred until cloudy and well dispersed. In a separate flask, the solvent(s) (TOPO, 9.98 g, 0.0258 M, and octadecylamine, 2.96 g, 0.0109 M *or* TOPO, 14.19 g, 0.0367 M *or* TBPO, 5.65 g, 0.0258 M and octadecylamine, 2.97 g, 0.0109 M) was/were mixed with $NaBH_4$ (0.0448 g, 1.2×10^{-3} M), flushed three times with nitrogen then heated under vacuum for 1 hour up to 200 °C.

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The system was flushed with nitrogen and the temperature stabilised at 200 °C. The silver salt was then rapidly injected into the hot solvents, causing an immediate dark colouration and a temperature drop of *ca.* 10 °C. The solution was stabilised at *ca.* 200 °C and left for 30 minutes. The reaction flask was then removed from the heat and allowed to cool to 60 °C. Approx. 50 ml of CH_3OH was then added and the resulting precipitate isolated by centrifugation. The solid was then dispersed in approx. 100 ml toluene and centrifuged further to remove solid waste products, giving an optically clear brown/yellow solution of capped silver nanocrystals. Size fractionation was achieved by the addition of methanol to the toluene solution until the solution turned slightly turbid. Centrifugation resulted in the isolation of the larger particles, leaving the smaller crystals in solution.

Discussion

The reduction of silver nitrate (added as a dispersion in 4-*tert*-butylpyridine) at *ca.* 200 °C in various polar Lewis base solvents resulted in the immediate reduction of the silver salt and the growth of silver nanoparticles. The silver salt : solvent molar ratio was 1 : 39 for reactions in TOPO. Where two solvents were used, the silver : trialkylphosphine oxide : octadecylamine molar ratio was 1 : 27.4 : 11.6.

The effect of the capping agent with respect to particle growth and stability was investigated. The particles were prepared in a range of solvents; TOPO, TOPO/octadecylamine or TBPO/octadecylamine and hence materials with different capping groups were obtained.

Nanoparticulate silver prepared in TOPO alone exhibited controlled growth in solution with only a small amount of bulk waste product. When precipitated with methanol, the majority of the resulting solid was found to be insoluble in toluene, indicating the TOPO had been removed from the surface by the non-solvent. Once dispersed in toluene, the weak solution was found to be unstable, flocculating over a matter of days. The small amount of TOPO capped silver that was soluble in toluene could readily undergo ligand exchange with thiols and amines, and therefore were easily phase-transferred to an aqueous system by exchanging the organically soluble ligands for aqueous-soluble ones. These results will be reported fully elsewhere. These results suggest that TOPO is only weakly bound to the surface, and is much more labile than TOPO bound to a semiconductor surface such as CdSe. This is somewhat surprising as TOPO has been utilised as an effective capping agent for cobalt nanoparticles prepared in a similar manner.[18]

Preparation of silver nanoparticles using a mixture of octadecylamine and TOPO also exhibited controlled growth in solution. The nanoparticles could be precipitated with methanol and easily re-dispersed in toluene, with only a small amount of insoluble material resulting. The toluene solution was relatively stable (small amount of precipitation after 3 months) in ambient conditions and appeared resistant to bleaching. Attempts to undergo a phase transfer to water using water-soluble ligands such as thiols, amines and other phosphine oxides were unsuccessful, suggesting the amine was relatively strongly bound to the metal surface and essential for a stable colloid. It is conceivable that the TOPO ligands were removed and replaced with different water-soluble ligands, however, the amine appears to be the dominant capping agent and could not be removed. Further precipitation with methanol resulted in a powder with a slightly decreased solubility in toluene, suggesting that more surface capping ligands had been removed. This was confirmed by FTIR on samples isolated by non-solvent precipitation, where no evidence was found of TOPO.

Synthesis of the quantum dots in octadecylamine and the shorter chained TBPO resulted in uncontrolled growth, with material precipitating out of the reaction mixture within minutes of injection of the silver salt. Only a small amount of nanoparticles could be isolated into toluene using precipitation techniques. The material was found to be unstable over a matter of hours.

It can be concluded that the strongly binding long chain amine acts as a stabilising ligand, similar to the long chain acids used in the work of Sun and Murray on cobalt quantum dots.[19] This is unusual, as it has been reported that the analogous Au^0/amine interactions are much weaker than Au^0/thiol interactions, and that amines bind to inert metal surfaces such as gold through a charge-neutral weak covalent bond. The stability of amine capped gold nanoparticles has been discussed in some depth by Leff *et al.*, suggesting that the Au–N bond has a size effect as amines adsorbed onto bulk gold surfaces are normally unstable.[27]

The difference in Lewis base character of the ligands obviously dictates the particle stability, requiring a firmly bound moiety to stabilise quantum dot growth and the weakly bound phosphine oxide to fine tune growth. Whilst the amine is not necessary for controlled growth, it appears essential in this case for long-term stability. The chain length of the trialkylphosphine oxide appears to dictate the growth of the particles, with shorter alkyl chains resulting in uncontrolled growth resulting in bulk material. Similar results were previously reported with TOPO and TOPO/amine capped gold nanoparticles, where using TOPO alone resulted in a wide size range and distribution, whilst preparation in TOPO/amine resulted in controlled growth and nanoparticles with a relatively narrow size distribution.[22] Some in-depth investigations into capping agents and their effect on particle size, *etc.*, were reported by Sun and Murray[19] on long chain acid/phosphine oxide capped cobalt, and more recently by Alivisatos and co-workers.[28]

Further evidence of the capping groups was obtained by Fourier transform infrared (FTIR) spectroscopy. Analysis of TOPO/octadecylamine capped silver nanoparticles (200 °C, 30 min) showed the presence of both capping agents (Fig. 1). The υ(P=O) stretch in TOPO, observed at *ca.* 1145 cm^{-1}, is also present in the passivated silver nanoparticles. The feature is normally shifted when TOPO is bound to a surface, however, no such shift occurs and remains at *ca.* 1145 cm^{-1}. We attribute this to the TOPO being only weakly coordinated to the nanoparticle surface. The υ(N–H) bond deformations present in octadecylamine at *ca.* 1565, 1614 and 1645 wavenumbers were also present in the passivated silver nanoparticles. The features, slightly weaker and broadened in the nanoparticle samples, were present at *ca.* 1560 cm^{-1} and 1640 cm^{-1}. The $\upsilon(CH_3)$ bend at *ca.* 1465 cm^{-1}, present in both octadecylamine and TOPO, was present in the capped nanoparticles and attributed to both passivating ligands. FTIR experiments on the smaller dots,

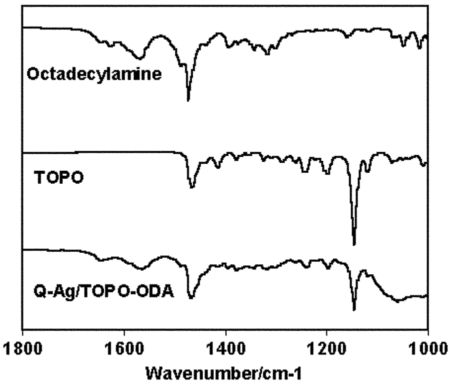

Fig. 1 FTIR data for tri-*n*-octylphosphine oxide, octadecylamine and Q-Ag capped with TOPO/octadecylamine.

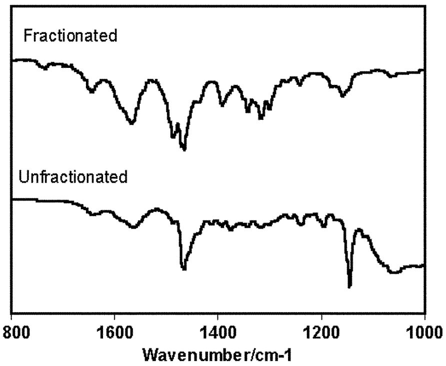

Fig. 2 FTIR data for fractionated and unfractionated samples of Q-Ag capped with TOPO/octadecylamine.

isolated by selective precipitation, confirm the presence of both TOPO and the amine. However, individual fractions of dots isolated by addition of a non-solvent (methanol) showed FTIR spectra consistent with larger amounts of amine, which confirms our hypothesis that TOPO is only weakly bound and can be removed easily (see Fig. 2).

Solution ^{1}H NMR of TOPO/octadecylamine capped silver nanoparticles displayed typical broad resonances between 0.5 and 2.0 ppm, which makes assignment to either ligand difficult. Solution ^{31}P NMR displays a strong resonance at *ca.* 50 ppm, similar to the resonance observed in uncoordinated TOPO. This reinforces the hypothesis that TOPO is only weakly coordinated to the silver surface, as TOPO strongly bound to a quantum dot surface exhibits a shift in the ^{31}P resonance.[29]

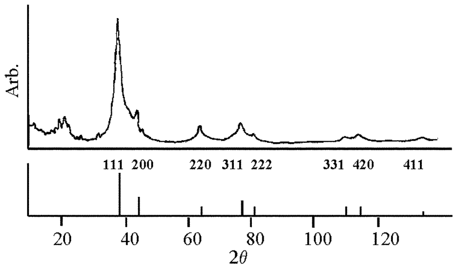

Fig. 3 XRD data for tri-*n*-octylphosphine oxide/octadecylamine capped Q-Ag, showing expected reflections and intensities for associated Miller indices.

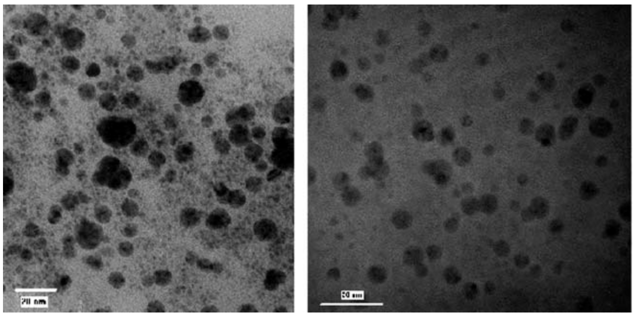

Fig. 5 TEM images of TOPO/octadecylamine capped Ag, scale bars = 20 nm.

X-Ray diffraction patterns obtained from TOPO/octadecylamine capped Q-Ag displayed reflections consistent with cubic silver (Fig. 3). The reflections were broadened, typical of nanostructured material but were easily assigned whilst referring to data from the bulk system.

The findings were supported by HRTEM, showing highly crystalline material, approximately spherical, with aspect ratios up to 1.7 in the larger particles. The nanoparticles appeared to exhibit a bimodal distribution — in the size ranges 2–3 nanometers for the smallest, with the largest particles in the size range 10–15 nanometers (Fig. 4 and 5). Small amounts of large particles, above 50 nm could also be observed. This is surprising as Au nanoparticles prepared by an analogous route exhibited a high degree of monodispersity.[22] This is not the first time that a bimodal distribution has been observed,[30] and can be attributed to the highly reactive surface of Ag nanoparticles relative to the analogous Au system. The size distribution could be narrowed further by size selective precipitation, similar to that of TOPO capped CdSe (*ca.* ±5% standard deviation) using methanol and toluene as a non-solvent/solvent pair. Obtaining a narrow size distribution is essential for most applications. It is interesting to note that after size fractionation,

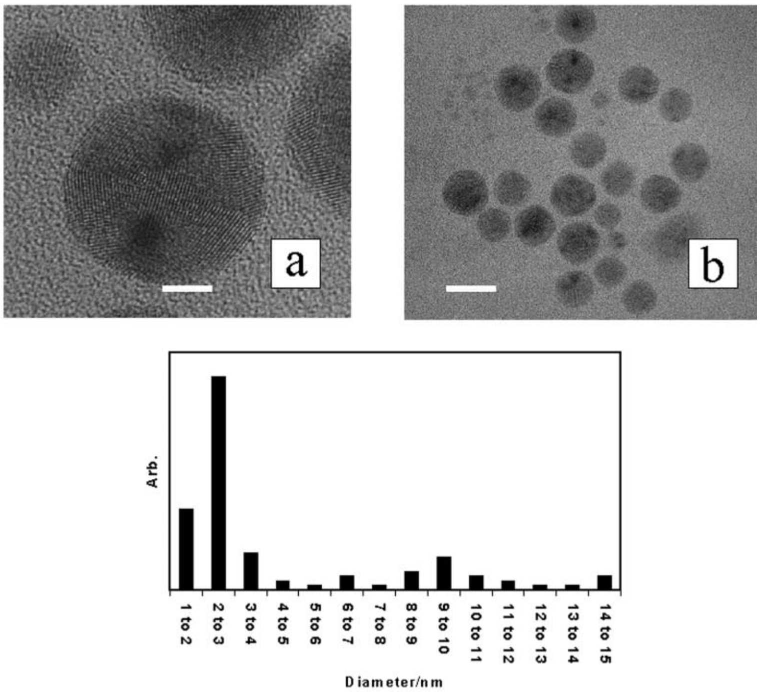

Fig. 4 HRTEM images of TOPO/octadecylamine capped Ag. Size bar, a = 2 nm, b = 10 nm, and size distribution of TOPO/octadecylamine capped Ag.

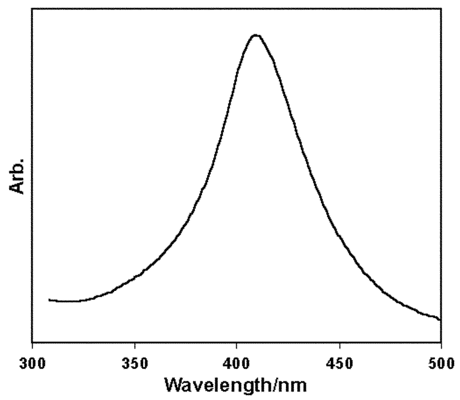

Fig. 6 Electronic spectrum of Q-Ag capped with TOPO/octadecylamine (200 °C, 30 min) displaying the surface plasmon resonance.

small amounts of large (> 10 nm) nanoparticle of silver can still be observed. The larger quantum dots (*ca.* 10 nm diameter) displayed distinct facets with some particles showing evidence of twinning. The HRTEM images suggest shapes and morphologies similar to those proposed by Henglein and Giersig, who use citrate groups as stabilisers.[31]

Many models have been proposed to describe the growth of nanoparticles, including mechanisms proposed by La Mer[32] (fast nucleation and slow growth) and Finke[33] (slow nucleation and fast growth), Zukoski[34] or Van Hyning[35] (aggregative) and more recently Buhro[36] (heterogeneous seeded growth). Growth of particles described here may not be by the usual route (La Mer type growth) used to described TOPO capped CdSe and is unlikely to be explained by the aggregative growth model of nanosized silver suggested recently by Van Hyning *et al.*[36] which describes small (5 nm diameter) particle growth by strong van der Waals attraction. Aggregative growth is usually eliminated by the use of a steric barrier (*i.e*, a capping agent) and therefore the growth mechanism is at present unknown. The bimodal size distribution corresponds with the XRD pattern (Fig. 3), which appears to exhibit broad based reflections (smaller particles) on top of narrower reflections (larger particles).

Silver nanoparticles have distinct optical properties, often displaying a surface plasmon resonance. The TOPO/amine capped silver nanoparticles (prepared at 200 °C, 30 min) had a distinct surface plasmon feature at *ca.* 409 nm (Fig. 6), consistent with other reports of Q-Ag.[31] The energy of the resonance is consistent with that expected for silver dispersed in toluene, $\varepsilon_{\mathrm{Ag}} = -2\varepsilon_{\mathrm{toluene}}$ using the bulk values of complex permittivity for silver.[37]

Conclusions

Highly crystalline silver nanoparticles have been prepared in a mixed solvent system. Investigation into the capping agents revealed that TOPO, a relatively effective capping agent in semiconductors quantum dots, is ineffective on its own. A second, stabilising ligand must be employed to obtain a stable dispersion. Long chain amines, such as octadecylamine, normally a weakly coordinating ligand on bulk surfaces is found be strongly bound to nanosized silver and hard to remove, even in ligand exchange reactions. Further investigations reveal that although TOPO is only weakly bound, its steric factors dictate the stability of the colloid and a long alkyl change is required. Whilst the long alkyl chain appears favourable in these studies, further work is needed to ascertain whether this is a general trend.

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