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A simple one phase preparation of organically capped gold nanocrystals

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A simple reproducible one-phase preparation of highly monodispersed organically passivated gold nanoparticles is described. The effect of the capping ligand on the particle size is discussed along with the manipulation of the nanoparticles into colloidal crystals and 2D arrays.

Recently, Brust *et al.* reported a simple two phase method for the preparation of high quality thiol passivated gold nanoparticles which were soluble in many organic solvents.[1,2] These nanoparticles have subsequently been used in the preparation of superlattices and electroactive materials.[3,4] Other applications of nanoparticles of gold include biomarkers in TEM experiments,[5] and more recently in single-electron transistors.[6]

One popular method for the preparation of (II/VI) or III/V) semiconductor quantum dots is the use of tri-*n*-octylphosphine oxide (TOPO) as both a reaction medium and passivating ligand.[7,8] Recent developments include the preparation of other compound semiconductors,[9] the use of single-molecular precursors such as dithio- or diseleno-carbamates, and the incorporation of nanoparticles into devices.[10–12] Sun and Murray have recently reported the preparation of cobalt nanoparticles using a similar methodology.[13]

We now report that the reduction of gold(IV) chloride by sodium borohydride in hot TOPO or a mixture of polar Lewis base solvents results in gold nanoparticles.§ The reduction of gold chloride (added as a solution in 4-*tert*-butylpyridine) in TOPO at *ca.* 190 °C resulted in relatively uncontrolled growth to particles with a wide range of shapes and sizes. Fig. 1(a) shows a typical TEM image in which square, triangular and spherical particles ranging in size from 10 to 100 nm in diameter can be seen. The isolated re-suspended nanoparticles were stable in toluene for only a matter of hours. In contrast, growth in a mixture of TOPO and octadecylamine (1 : 0.57 molar ratio) at 190 °C resulted in the controlled growth of spherical nanoparticulate gold particles (8.59 ± 1.09 nm), which have proved stable in toluene for months [Fig. 1(b)].

The morphology of the gold nanoparticle is controlled by various properties of the capping ligands. The Lewis basicity must be sufficient for significant interaction to occur and the bond formed has to be sufficiently labile to allow controlled growth. The length of the alkyl group on the capping ligand further affects the tuning of the size. Longer chain ligands tend to favour slower growth and hence the formation of, relatively, smaller nanoparticles. Hence, a balance must be achieved between the growth rate and ligand stability to facilitate growth of nanoparticle of a uniform size. A similar discussion of the role of organic capping agents in controlling particle size has been presented by Murray *et al.*, in describing processes in the growth of organically passivated cadmium chalcogenides[7] or cobalt nanoparticles.[13] The effect of capping group on particle size is being investigated further.

Evidence for the presence of the capping groups was obtained using IR spectroscopy, mass spectrometry and NMR. IR spectroscopy of the gold nanoparticles capped with octadecylamine and TOPO showed the bands associated with both ligands. There is a weak, broad feature not seen in the free amine spectrum at *ca.* 500 cm^{-1}, possibly a ν(Au–N) stretch.[14] TOPO also binds to the surface gold sites and a feature at *ca.* 1130 cm^{-1} is consistent with the shifted ν(P=O) bond deformation observed in other TOPO capped nanoparticles.[15] It is assumed that both TOPO and octadecylamine bind through the electron rich O or N atoms respectively.

The ^{1}H NMR spectrum of gold nanoparticles passivated with TOPO/octadecylamine displayed resonances associated with

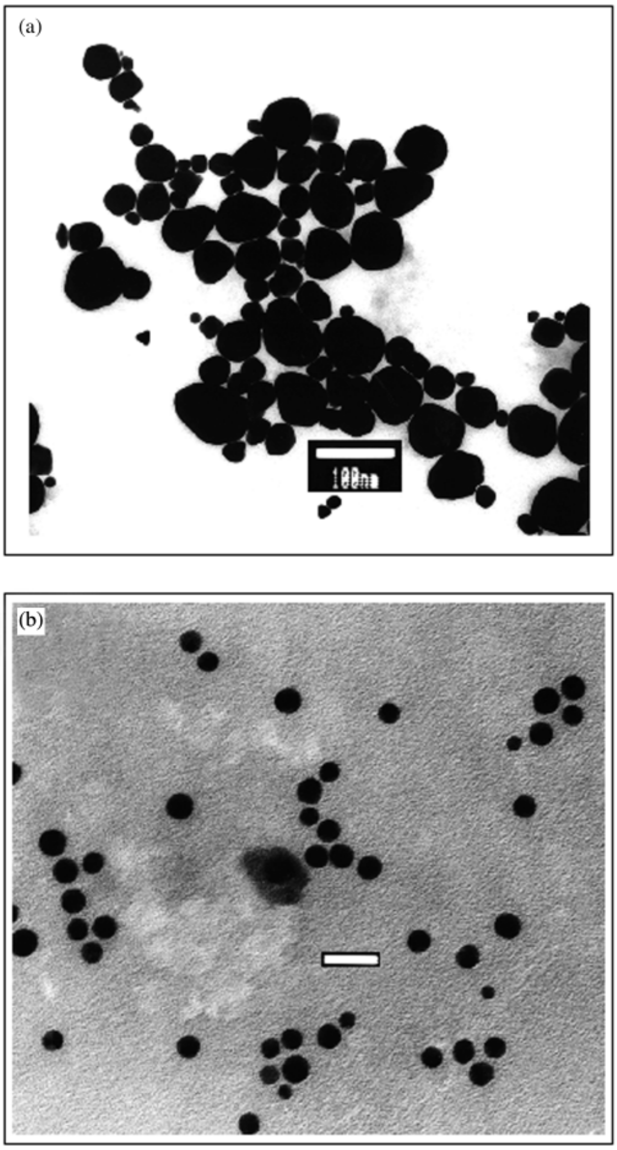

Fig. 1 (a) TEM of TOPO capped Q–Au (190 °C, 30 min), bar = 100 nm; (b) TEM of TOPO/octadecylamine capped Q–Au (190 °C, 30 min), bar = 20 nm.

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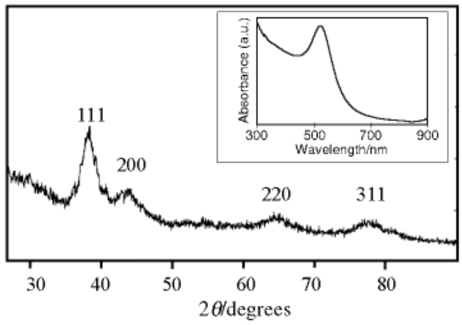

Fig. 2 XRD pattern of TOPO/octadecylamine capped Q–Au (190 °C, 30 min). Inset, electronic spectrum of TOPO/octadecylamine capped Q–Au (190 °C, 30 min).

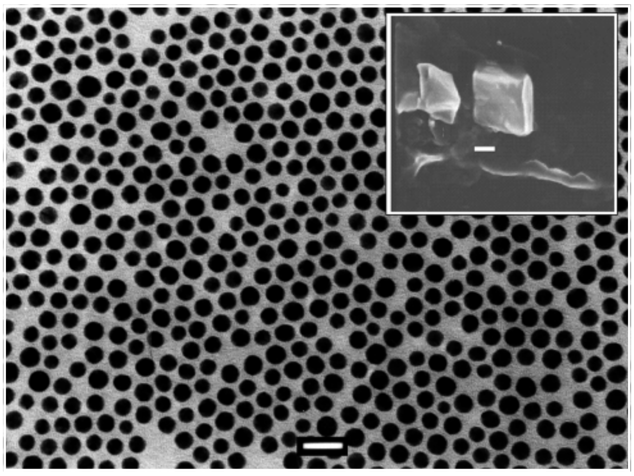

Fig. 3 2D lattice of octadecylamine/TOPO capped gold, bar = 20 nm. Inset; SEM of cubic colloidal crystal prepared from octadecylamine/TOPO capped gold nanoparticles (190 °C), bar = 80 μm.

organic ligands anchored to the nanoparticulate surface. Broad singlets at δ 0.9 and between δ 1.2 and 1.5 cannot be assigned as either TOPO or octadecylamine; broadening effects render resonances indistinguishable. The broadening of ^{1}H resonances of nanoparticle capping agents has previously been observed and attributed to either a reduction in rotational freedom at the surface site, or the inhomogeneous distribution of magnetic environments found on the nanocrystalline surface.[16,17] The ^{31}P NMR of capped gold nanoparticles show a single resonance at δ *ca.* 45; free TOPO displays a single resonance at δ 50. The upfield shift of 5 ppm is consistent with the surface metal shielding the phosphorus nuclei. This evidence again infers that the TOPO ligand bonds through the lone pair on the oxygen atom. FAB mass spectrometry of dots prepared in the mixed solvent system revealed the presence of not only TOPO (*m/z* 387) and octadecylamine (*m/z* 270), but also 4-*tert*-butylpyridine (*m/z* 136). It is assumed that only small amounts of 4-*tert*-butylpyridine are attached to the nanoparticle as no evidence for the ligand is found in either the ^{1}H NMR or the IR spectra. Powder X-ray diffraction data for the TOPO/octadecylamine capped dots showed broad peaks for the 111, 220, 200 and 311 planes of fcc gold (Fig. 2). Electronic spectroscopy of TOPO/octadecylamine gold dots showed the well documented plasmon resonance associated with colloidal gold at *ca.* 540 nm (2.29 eV).[18]

Murray *et al.* previously reported the controlled evaporation of solutions of TOPO capped CdSe and organically passivated Co, resulting in the preparation of superlattices and films.[13,19] Samples of as prepared octadecylamine/TOPO capped gold nanoparticles were washed with methanol removing all excess capping ligands and redispersed in the minimum amount of toluene. Aliquots of the toluene solutions were then placed either in a glass flask or on a glass slide and left to dry slowly (over *ca.* 3 days). Optical and electron microscopy revealed the presence of small cubic colloidal crystals with dimensions of the order of micrometers (Fig. 3, inset). XRD experiments on these colloidal crystals are currently in progress.

The as prepared octadecylamine/TOPO capped gold dots were found to spontaneously self assemble when deposited on a copper grid, forming ordered hexagonal close packed two-dimensional lattices (Fig. 3). Spontaneous self assembly has been observed before for highly monodispersed TOPO capped semiconductor nanoparticles.[20] We are at present developing this novel approach in the preparation of nanometric particles of different metals.

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Notes and references

§ Nanoparticles were prepared using two different solvent systems. (1) In a typical synthesis, 0.07 g (23 mmol) $AuCl_4$ was dissolved in 7 ml 4-*tert*-butylpyridine. The solution was injected into a reaction flask containing 15 g TOPO and 0.0325 g $NaBH_4$ stabilised at 190 °C, left for 30 min, then removed from the heat source. The nanoparticles were isolated by solvent–non-solvent interactions at 60 °C, 30 ml of dry methanol was added leading to a precipitate which was isolated by centrifugation. The precipitate was stable in toluene for *ca.* 10 h.

(2) As above, injecting gold chloride dissolved in 4-*tert*-butylpyridine into a mixture of 10 g octadecylamine, 25 g TOPO and 0.0325 g $NaBH_4$ at 190 °C, with a growth time of 30 min. Upon injection, the reactants turned deep red. The nanoparticles were isolated using methanol as described above, and were found to be indefinitely stable in toluene. Once isolated as a powder, the nanoparticles were washed several times with methanol to remove excess capping agent before analysis.

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