A New Hydrosol of Gold Clusters

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Reduction of gold(III) ions by tetrakis(hydroxymethyl)phosphonium chloride gives a hydrosol of gold clusters with mean diameter 1.5 nm (average nuclearity about Au_{170}) and smaller.

The synthesis of ultrafine particles, or clusters, of metal has been the subject of considerable interest in the realms of chemistry,[1,2] physics[3] and biology.[4] One route to their preparation is the chemical reduction of metal ions in solution to give aggregates of atoms dispersed in the solvent. At nuclearities greater than those of molecular clusters, the dispersed species are termed colloids and are characterized by a distribution of particle diameters. Colloidal solutions (sols) of gold normally form at much greater particle diameters than reported here,[5] but small size is essential for effective gold catalysts,[6] as well as for high-resolution labelling of biological samples for transmission electron microscopic (TEM) examination.[4] Recently, hydrosols (aqueous sols) of gold clusters down to 2 nm have been reported to be formed by reduction of gold(III) ions with potassium thiocyanate,[7] but their optical properties (the dispersions are described as yellow) appear to differ markedly from those predicted—and indeed previously observed—for ultrafine elemental gold of these dimensions.[8] Here, we report a safe and efficient chemical route to tiny gold particles (large gold clusters).

The preparation of the standard hydrosol involves reduction by partially hydrolysed tetrakis(hydroxymethyl)phosphonium chloride (THPC) of chloroaurate(III) ions in aqueous solution. Successive charging of a vessel with water (44 ml), sodium hydroxide (3 ml of a 0.1 mol dm^{-3} aqueous solution), THPC (1 ml of a fresh 50 mmol dm^{-3} aqueous solution) and hydrogen tetrachloroaurate (2 ml of an aged 25 mmol dm^{-3} aqueous solution) results in the rapid formation of a clear, dark orange–brown solution. Five minutes is allowed between addition of THPC and that of the hydrogen tetrachloroaurate. Rapid stirring and, as usual with colloidal metal preparations, rigorous experimental cleanliness[9] are required.

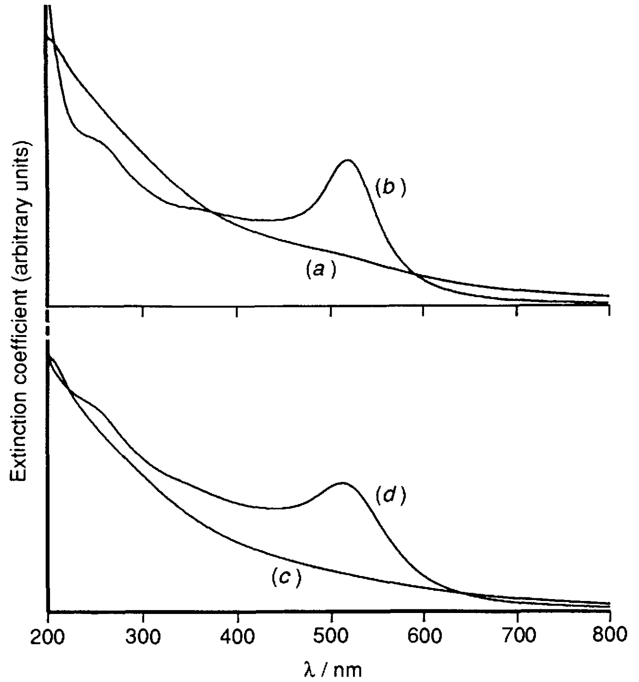

Fig. 1 UV–VIS extinction spectra of gold hydrosols. (*a*) The standard THPC gold sol; (*b*) a conventional gold colloid ($\langle d \rangle$ *ca.* 17 nm) prepared by the sodium citrate method;[5] (*c*) a THPC gold sol prepared using freshly dissolved (2 min) chloroauric acid; (*d*) a sol prepared by evaporative boiling for 2 h of a standard THPC gold hydrosol with dissolved sodium citrate.

Estimation of particle size was carried out using a variety of techniques, including TEM, analytical ultracentrifugation, X-ray diffraction line broadening and crystal-growth experiments. TEM of particles deposited from the standard sol yielded an average diameter $\langle d \rangle = 1.5$ nm, and a coefficient of variation (standard deviation divided by the mean), c.v. = 38%, but some cluster coalescence within the specimen was observed.[10] This particle size distribution (psd) corresponded to an average cluster nuclearity of about 170, but this is a very approximate (merely illustrative) figure—difficulties in image interpretation of these ultrafine clusters will be discussed in a further publication.[10] The optical extinction in the UV–VIS spectrum is illustrated in Fig. 1(*a*). The broad shoulder at *ca.* 500 nm seems to be a weak surface plasmon extinction, which is very much less pronounced than in a conventional colloidal gold of $\langle d \rangle$ = *ca.* 17 nm prepared by the sodium citrate method[5] [Fig. 1(*b*)], and which arises from excitement of a collective oscillation of the conduction electron gas.[3] The THPC gold hydrosol spectrum, with this plasmon feature suppressed owing to finite-size effects,[11] strongly resembles that of gold clusters in glass estimated at about 2 nm mean diameter,[8] that described for 1–2 nm gold clusters vapour-deposited into solvent[12] and also that of the putative Au_{55} cluster,[13] mean diameter about 1.2 nm, the monodispersity of which has been the subject of much debate.[14] Following extensive dialysis to remove solution species from the sol, chemical analysis of a dehydrated colloid showed that 7.0% by mass P, 6.3% C and 1.2% H remained in the colloid. Although it is impossible to say at present to what extent these elements are located entirely on the cluster surfaces or penetrate the interior, the optical extinction discussed above is compatible with the presence of elemental gold cores. Sedimentation velocity measurements of the standard sol in the ultracentrifuge gave a minimum value of (weighted) average diameter of 1.4 nm. Powder X-ray spectra of the gold particles both in sol and dispersed on alumina support produced an amorphous-like peak at $2\theta = 40.0°$ (from which a Scherrer treatment would give a nominal value of weighted-mean crystallite diameter at about 1.3 nm). Growth of the clusters to a size more easily measurable by TEM, employing the reducing agent hydroxylamine hydrochloride, allowed a limiting maximum value of mean diameter of 2.4 nm for the original THPC gold sol to be deduced from TEM measurements of the grown colloids. Coalescence of the primary nucleus particles during this growth process is indicated by the observation that the calculated nucleus diameter is larger for higher concentration of these 'seed' clusters.

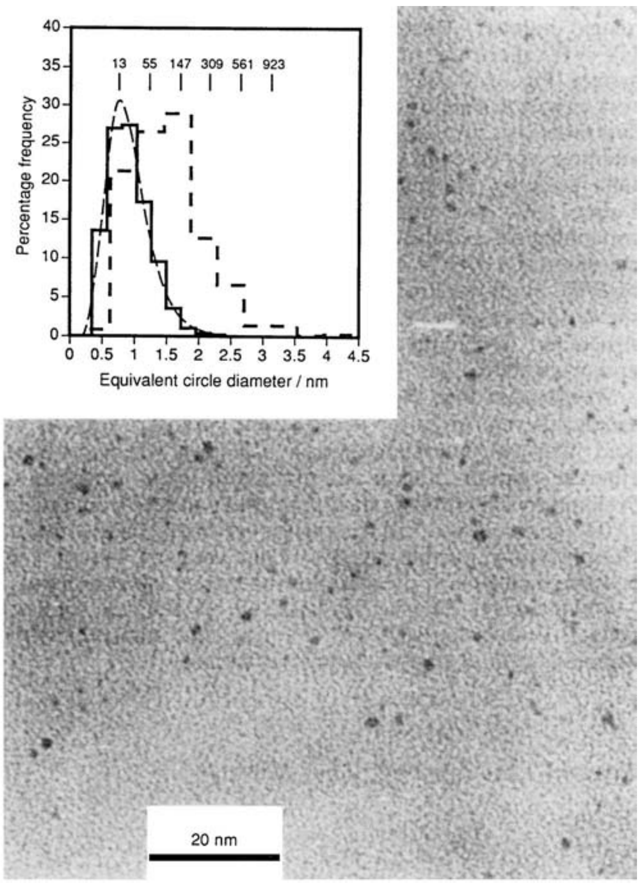

Fig. 2 TEM image of gold clusters from the THPC gold hydrosol prepared using freshly dissolved (for 2 min) chloroauric acid crystals instead of an aged solution. Inset: psd (solid histogram) of this sol. The lognormal fit[13] (dashed curve) employs the parameters: statistical median = 0.87 nm, geometric standard deviation = 1.43. The psd of the standard sol (dashed histogram) is shown for comparison. The calculated diameters of the first six 'magic number' closed shell cuboctahedral clusters of gold are indicated and labelled according to nuclearity.

In structural studies using high resolution TEM the particles either appeared to be face-centred cubic-based (with relatively few multiply twinned structures, MTPs[2]) for the larger particles in the size distribution, or to show no lattice detail, in the case of the majority of the smaller particles. This suggests that the latter species are either highly fluxional or amorphous.

According to both TEM and UV–VIS measurements, even finer hydrosols can be formed either by adding less hydrogen tetrachloroaurate to the reducing mixture (*e.g.* 1.8 ml of the 25 mmol dm^{-3} solution instead of 2 ml), or by employing the usual volume (2 ml) of a freshly made up solution, added within 2 min of dissolution of the crystals. In the latter case, the psd determined from TEM micrographs (Fig. 2) yielded a mean diameter of 0.9 nm, coefficient of variation of 36% and nominal mean nuclearity of 34. The good fit of this and all the other psd histograms to lognormal frequency distribution curves suggest that coalescence plays a major role in colloid genesis.[15] Calculated diameters for geometric closed-shell 'magic number' clusters are indicated on the psd. The UV–VIS spectrum of this exceptionally finely dispersed system [Fig. 1(*c*)] displays no obvious plasmon feature, being very nearly a smooth exponential. The synthesis of coarser hydrosols is easily accomplished by boiling the sol in air after addition of trisodium citrate (or alternatively other sodium salts such as phosphate, oxalate or carbonate) to *e.g.* 1 mmol dm^{-3} concentration. One thus prepared red hydrosol containing trisodium citrate [optical extinction Fig. 1(*d*)] was measured at $<d>$ = 4.4 nm, c.v. = 20% and a mean nuclearity of 2900. High-resolution electron microscopy of this system showed lattice detail ({111} and {200} fringes) and particle structures (including MTPs[2]) typical of colloidal gold microcrystallites.

We propose that the synthesis may find application as a simple alternative to the widely used Faraday[16] method of gold hydrosol preparation ($<d> \geqslant 3$ nm), which employs ethereal solutions of toxic and pyrophoric white phosphorus. Preliminary experiments show that gold particles from boiled THPC-gold sols attached to supports are catalytically active in CO oxidation. Further studies on the catalytic activity and possible biological applications of the system are continuing.

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