Direct synthesis of gold nanodispersions in sol–gel derived silicate sols, gels and films

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A simple method for the preparation of stable colloidal suspensions of gold nanoparticles in silicate sols, silicate based films and monoliths is presented; organically modified sol–gel monomers containing amine functional groups are used for the stabilisation of Au ions and the metal nanocrystalline sol.

Several methods to produce metallic nanodispersions in aqueous and organic solvents have been recently reported.[1–4] In aqueous solutions colloids are stabilised by polymeric stabilisers [*e.g.* poly(vinyl pyrrolidine)][1] or buffer electrolytes such as *e.g.* citrate ions.[2] Long chain surfactants (*e.g.* quaternary ammonium compounds)[3] or specific ligands[4] are used to increase particle stability in organic solvents. In all these cases the removal of the stabilising agent causes immediate destabilisation of the sol. Encapsulation of metallic nanodispersions in sol–gel matrices is beset by additional complications. First, care should be taken to avoid aggregation or precipitation of the metal salts in the organic sol–gel precursors and additional means are required to prevent coalescence or precipitation of the metallic particles during sol–gel polymerisation. Two general schemes have been proposed for the encapsulation of metallic nanoparticles in sol–gel matrices. Silicate coated gold nanoparticles have been produced by preparing a gold sol by the citrate route and subsequent stabilisation by a 3-aminopropyltrimethoxysilane derived aminosilicate.[5] A second approach is based on sol–gel processing in inverse micelles.[6] Other methods to prepare highly dispersed metal particles in a porous support of silica or alumina were devised by hydrogen reduction or thermal decomposition of metal oxides or salts that were previously deposited on the support.[7] The method is simple to perform but gives a rather wide particle size distribution. Schubert and coworkers[8] developed a general methodology in which the metal ions are first attached to a silane monomer containing a chelating organofunctional group and then sol–gel polymerisation is initiated. The resulting gel is subsequently subjected to thermal oxidation giving a dispersion of metal oxide, which can then be reduced by treatment with hydrogen gas. Highly homogeneous monodispersions of nanocrystalline metals in sol–gel materials were produced by this method.

For practical reasons it is highly desirable that a single stabiliser should be employed for the stabilisation of the metal salt and the nanocrystalline sol. Additionally it is preferable that the sol will be stable for at least several weeks and that there should be no leaching of organic moieties or chelating agents from the supported catalysts. Sol–gel monomers containing amine functional chelating groups are very promising for this purpose. Alkylamines have been reported to form stable monolayers on bare gold substrates in the vapour phase[9] (although the stability of monolayers that were prepared from solvents was rather limited[10]). Furthermore, a recent report,[11] demonstrated that alkylamine can cap gold nanoparticles in a similar manner to that of thiols.[12]

Here, we use the precursors *N*-[3-(trimethoxysilyl)propyl]-ethylene diamine (EDAS) and aminopropyltrimethoxysilane (APS), which are capable of coordinating $\mathrm{AuCl_4^-}$, stabilising the Au nanoparticles in the sol–gel solution, and becoming an integral and unleachable part of the supporting matrix after gelation. Gold colloid formation (*e.g.* by reduction with $\mathrm{NaBH_4}$) can be initiated either before or after the polycondensation step. The preparation procedure involved the addition of the required amount of $\mathrm{HAuCl_4}$ to EDAS or APS giving clear yellow solutions and subsequent sonication for 10 min. No phase separation or increased turbidity was noted, indicating a uniform dispersion of the gold salt in the silane precursor. The hydrolysis and condensation of the materials were then initiated by addition of a fixed quantity (3–5% by volume) of 0.1 M HCl and water (1–3% by volume) to the homogeneous solution. Formation of gold nanoparticles was achieved by subsequent dropwise addition of 0.4 M $\mathrm{NaBH_4}$ solution (3–5% by volume) to the sol, causing an instantaneous purple coloration indicative of gold colloid formation.

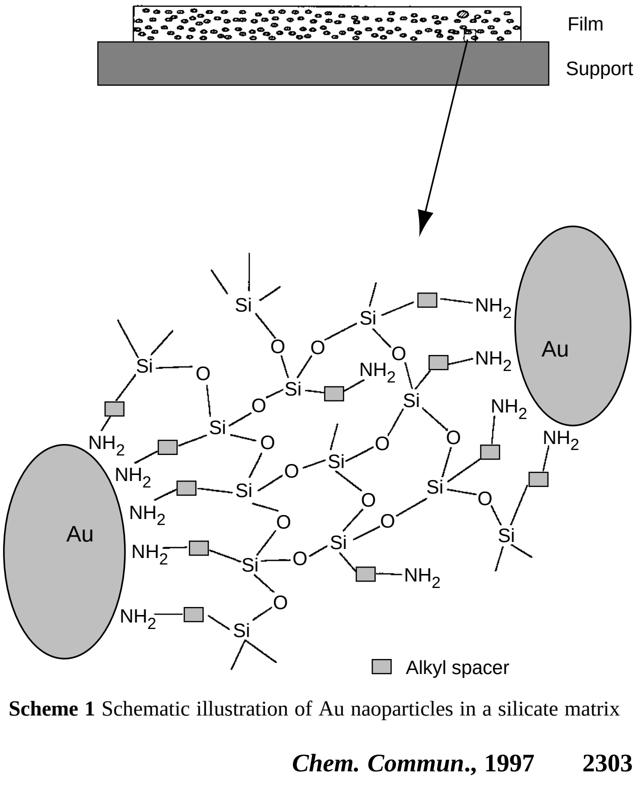
The general reaction can be represented by eqns. (1) and (2)

$$(\mathrm{MeO})_3\mathrm{Si{-}X{-}NH_2} + \mathrm{HAuCl_4}^- \rightarrow (\mathrm{MeO})_3\mathrm{Si{-}X{-}NH_3}^+\mathrm{AuCl_4}^- \tag{1}$$

$$(\mathrm{MeO})_3\mathrm{Si{-}X{-}NH_3}^+\mathrm{AuCl_4}^- \xrightarrow{\mathrm{NaBH_4}} (\mathrm{MeO})_3\mathrm{Si{-}X{-}NH_2Au}_m \tag{2}$$

where X is an alkyl spacer. Thus, the tetrachloroaurate anions are bound to silane precursors, which assures good homogenisation, and after reduction of $\mathrm{AuCl_4^-}$ the amine groups attach to and stabilize the metal nanoparticles. A schematic illustration of the gold nanoparticles in the aminosilicate network is shown in Scheme 1.

Absorbance spectra of typical sols are shown in Fig. 1. A surface plasmon peak at *ca.* 500–540 nm, characteristic of a



Scheme 1 Schematic illustration of Au naoparticles in a silicate matrix

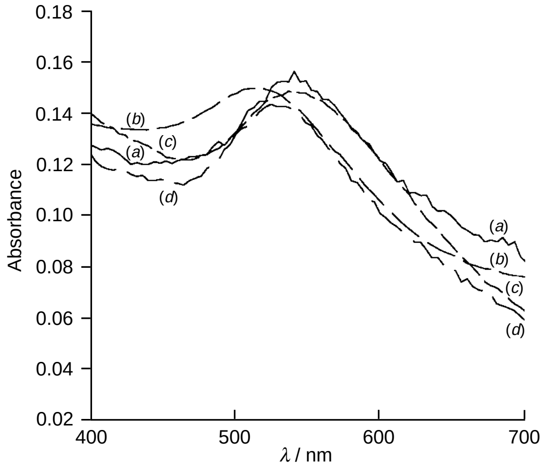


Fig. 1 Visible spectra of different sols (*a*) EDAS : Au ratio 5 : 1 (*b*) EDAS : Au ratio 100 : 1, (*c*) the sol of (*a*) after a month and (*d*) thin film produced from sol (*a*)

gold sol, confirms the presence of Au nanoparticles. The surface plasmon absorbance of colloidal gold particles is affected by particle size as well as by the refractive index of the medium and thus it is impossible to determine the average particle size based on the optical characteristics alone.[13]

Gold sols were prepared with different EDAS : Au ratio, from < 1 : 1 to 100 : 1 in order to elucidate the sensitivity of particle size distribution to the gold loading. A stable gold sol was observed only for EDAS : Au ratio > 1. The absorbance spectra of the sols prepared using EDAS : Au = 5 : 1 and 100 : 1 are shown in Fig. 1(*a*) and (*b*). The absorbance maxima shifts from 540 to 514 nm as the Si : Au ratio is increased from 5 : 1 to 100 : 1. However, TEM investigations clearly showed that the particle size distribution was not affected by the Si : Au ratio, or by changing the aminosilane precursor. The small absorbance shift is probably caused by changes in the refractive index of the sol.[13] Fig. 1(*a*) and (*c*) show the absorbance spectra for a sol prepared with an Si : Au ratio of 5 : 1, taken 1 h after preparation and after a month. The time invariant spectra indicate good stability of the colloidal suspension. No visible aggregation of the particles took place over several months. Between the two silane precursors used, the EDAS–gold sols were stable for at least a few months as evidenced from the unchanged absorbance spectra. However gold sols prepared with APS were stable for only two weeks or so, after which slight deterioration of the sol homogeneity was observed. Attempts to prepare gold colloids using TEOS or methyltrimethoxysilane (MTMOS) without aminosilane precursors resulted in immediate aggregation of the gold particles during reduction with $NaBH_4$. This clearly establishes the role played by the aminosilanes in binding and dispersing the metal ions in addition to stabilising the Au nanoparticles.

The sol could be gelled to give monoliths of various shapes or films (1–10 μm thick) by dip or spin coating. A typical absorption spectrum of a thin silicate film containing a gold dispersion (prepared from a 5 : 1 EDAS : Au sol) is shown in Fig. 1(*d*). The resemblance of Fig. 1(*a*) and (*d*) indicates high stability of the dispersion which is maintained during sol–gel processing. Changes of sol–gel processing variables such as Si : HCl or Si : H_2O ratio altered the rate of hydrolysis and gelation time but had no measurable influence on the particle size distribution of the resulting sol.

Transmission electron micrographs of the gold dispersed silica films were taken with a Philips electron microscope. A typical TEM image of gold nanoparticles prepared with EDAS : Au = 5 : 1 dispersed in a silicate network is shown in Fig. 2. It can be seen that the shape of the gold particles is mostly spherical with an average diameter of 5–6 nm. TEM images of particles obtained from the two aminosilane precursors were very similar. A few cylindrical (tubular) particles can also be seen which appear to be formed by coalescence of two or three particles.

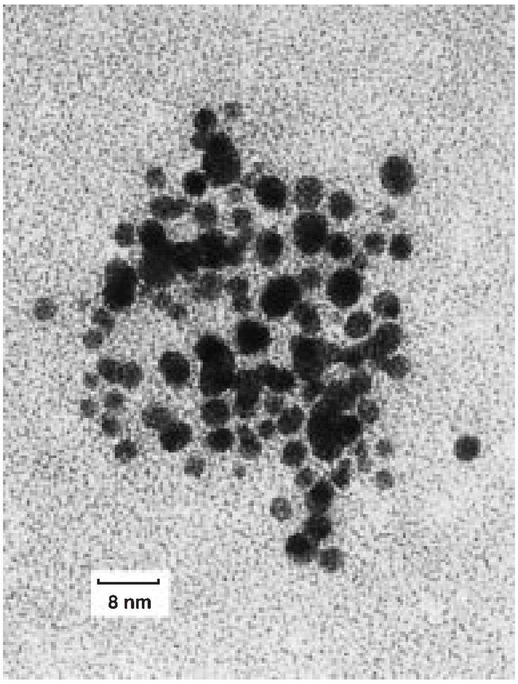


Fig. 2 TEM image of Au nanoparticles with EDAS : Au ratio 5 : 1

In conclusion, it has been shown that Au nanoparticles can be stabilized in an organically modified silica sol, without the aid of any external stabilizing agent. Judicial selection of a suitable organo-functionalised sol–gel monomer can play a dual role of dispersing the metal salt precursors and stabilising the nanoparticles.

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Footnote and References

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