

One-step synthesis of hydrophobized gold nanoparticles of controllable size by the reduction of aqueous chloroaurate ions by hexadecylaniline at the liquid–liquid interface

PR. Selvakannan, Saikat Mandal, Renu Pasricha, S. D. Adyanthaya and Murali Sastry*

Materials Chemistry Division, National Chemical Laboratory, Pune-411 008, India.

E-mail: sastry@ems.ncl.res.in

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Vigorous stirring of a biphasic mixture containing hexadecylaniline in chloroform and aqueous chloroauric acid results in the formation of gold nanoparticles of controllable size in the organic phase.

Development of synthesis protocols for nanostructured materials with tunable physicochemical properties is an important goal in nanotechnology. Gold nanoparticles, in particular, have received considerable attention and interesting applications of the nanoparticles in single electron tunneling¹ and non-linear optical devices² as well as in DNA sequencing³ have been demonstrated. It is not surprising, therefore, that there are a number of synthesis procedures for obtaining gold nanoparticles over a range of sizes⁴ and shapes.⁵ Most reports on the synthesis of gold nanoparticles in non-polar organic solvents have followed the Brust protocol^{6a,b} wherein aqueous chloroaurate ions are transferred into the organic solvent using phase-transfer molecules (tetraalkylammonium salts). The chloroaurate ions in the organic phase are then reduced and capped with alkanethiol^{6a,b}/alkylamine⁷ molecules resulting in stable gold nanoparticles that may be stored as a powder, readily redispersed in a range of non-polar to weakly polar organic solvents for use as novel reagents.⁸ In this communication, we show that the Brust protocol may be considerably simplified to yield in one step reduction of aqueous chloroaurate ions, capping of the gold nanoparticles thus formed and their phase transfer into non-polar organic solvents. This is accomplished in a biphasic setup consisting of aqueous chloroauric acid solution and hexadecylaniline (HDA) in chloroform which, under vigorous stirring, results in the formation of gold nanoparticles in the organic phase. The size of the nanoparticles may be controlled by simple variation in the chloroaurate ion:HDA molar ratio.

In typical experiments, 50 ml of 10^{-3} M aqueous solutions of HAuCl_4 were taken in beakers along with 50 ml solutions of 1×10^{-2} , 5×10^{-3} , 1×10^{-3} , 5×10^{-4} and 1×10^{-4} M HDA in chloroform. The biphasic mixtures were stirred vigorously on a magnetic stirrer for 12 h following which the appearance of reddish colours in the organic phase could be discerned. The inset of Fig. 1 shows test-tubes of the organic phase after the

reaction, A–E corresponding to 1×10^{-2} , 5×10^{-3} , 1×10^{-3} , 5×10^{-4} and 1×10^{-4} M HDA in the organic phase, respectively. A clear variation in colour is observed that ranges from orange in A and B to brownish-red in E. Fig. 1 shows UV–vis spectra[†] recorded from the organic solutions A–E shown in the inset.⁹ This experiment demonstrates that not only are the gold nanoparticles present in the organic phase, but also that there is a large variation in size of the particles in chloroform.⁹ These solutions were rotovapped, washed repeatedly with acetone and the particles obtained as a dry powder. The HDA-capped gold nanoparticles could be readily redispersed in hexane, toluene and ethanol.

Fig. 2A shows data obtained from a thermogravimetric analysis (TGA)[†] of purified powders of gold nanoparticles obtained by the reaction of 10^{-3} M HAuCl_4 with 10^{-2} M HDA in the organic phase. It is observed that there is a *ca.* 40% weight loss at 250 °C which is followed by almost complete loss of the powder in the heating crucible by 600 °C. The weight loss at 250 °C is attributed to desorption of surface-bound HDA molecules and a small percentage of gold nanoparticles.¹⁰ This instability temperature is close to that observed by Leff *et al.*⁷ and Sastry *et al.*¹¹ in gold nanoparticles capped with alkylamines and suggests that the binding of HDA to the nanoparticle surface occurs through the amine functionality. The complete weight loss at 600 °C is puzzling and has been observed by us in alkylamine-capped gold nanoparticles.¹¹ In a separate experiment, heating of the gold nano-HDA powder in vacuum (10^{-6} Torr) at 200 °C resulted in films of gold nanoparticles on different substrates placed in the vacuum chamber and suggests desorption of gold nanoparticles as the likely mechanism for the weight loss in the TGA studies.

Fig. 2B shows XRD patterns in the region of the (111) Bragg reflection recorded from drop-cast films of gold nanoparticles synthesized in the 10^{-3} M HAuCl_4 – 10^{-2} M HDA (upper curve) and 10^{-3} M HAuCl_4 – 10^{-4} M HDA experiments (lower curve).[†] The gold nanoparticles grown in the presence of higher HDA concentration present a broader (111) Bragg reflection indicating smaller gold nanoparticles than in the 10^{-4} M HDA experiment. An exact estimate of the particle size was obtained from TEM analysis (see below). It is thus clear that the size of the gold nanoparticles formed in the organic phase may be

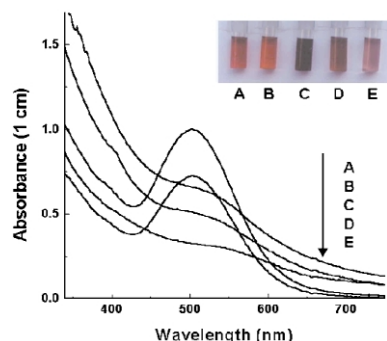


Fig. 1 UV–vis absorption spectra recorded from the chloroform phase after reaction of 1×10^{-2} , 5×10^{-3} , 1×10^{-3} , 5×10^{-4} and 1×10^{-4} M HDA (curves A–E, respectively) with 10^{-3} M aqueous chloroauric acid (see text for details). The inset shows pictures of the chloroform phase and correspond directly to spectra A–E.

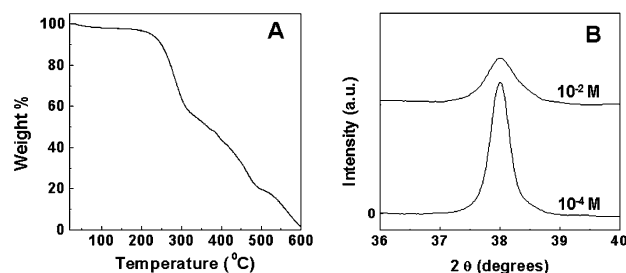


Fig. 2 A) TGA data recorded from gold nanoparticles capped with HDA in the 10^{-3} M HAuCl_4 – 10^{-2} M HDA experiment (see text for details). B) XRD patterns from films of gold nanoparticles prepared in the 10^{-3} M HAuCl_4 – 10^{-2} M HDA (upper curve) and HAuCl_4 – 10^{-4} M HDA (lower curve) experiments (see text for details).

controlled by varying the chloroaurate:HDA molar ratio as has been demonstrated using the Brust protocol with alkanethiols.¹²

Transmission electron microscopy (TEM) measurements† were carried out on gold nanoparticle films deposited on carbon-coated and holey TEM grids from the 10^{-3} M HAuCl_4 – 10^{-4} M HDA (Fig. 3A) and 10^{-3} M HAuCl_4 – 10^{-2} M HDA (Fig. 3B) experiments. In the former case, the gold nanoparticles are seen to be extremely uniform in size (Fig. 3A, diameter = 18.0 ± 1.4 nm). A large percentage of the particles were observed to populate linear superstructures that extended over $10 \mu\text{m}$ in length (Fig. 3A). This aspect will be addressed in a separate publication. The gold particles in the 10^{-3} M HAuCl_4 – 10^{-2} M HDA experiment were much smaller (Fig. 3B, diameter = 4.2 ± 0.6 nm) and are faintly visible in Fig. 3B populating the periphery of the holes in TEM grid. Thus, the size control that can be exercised in the protocol of this communication indicated by the UV–vis and XRD measurements is corroborated by the more direct TEM analysis. The particles in both experiments are well-separated with little indication of physical contact and sintering. This indicates steric stabilization of the gold nanoparticles via a monolayer of HDA molecules on the nanoparticle surface.

The above results suggest the following mechanism for the formation of gold nanoparticles in the organic phase. During stirring of the biphasic mixture, the solution turns turbid indicating formation of microdroplets that facilitate the electrostatic binding of the aqueous chloroaurate ions with the protonated amine groups of HDA. Thereafter, the ions are reduced by HDA to yield Au^0 and thus, results in the formation of gold nanoparticles. The fact that the particles are transferred to the chloroform phase clearly shows that the HDA molecules also bind to the surface of the gold nanoparticles, rendering them sufficiently hydrophobic. Binding of primary amines to gold nanoparticles is known, albeit relatively unexplored.^{7,11} The multiple role of HDA in complexing with aqueous chloroaurate ions, spontaneously reducing them and capping the gold nanoparticles thus formed to effect their phase transfer is a salient feature of our work and considerably simplifies the Brust protocol wherein different reagents/molecules are used to accomplish these actions. While the exact mechanism for the reduction of the chloroaurate ions by HDA molecules is to be elucidated, we would like to mention that reduction of Au^+ ions in complexes of the form $\text{AuCl}(\text{RNH}_2)$ has been observed previously.¹³

In conclusion, the one-step synthesis of organically soluble gold nanoparticles in a biphasic phase transfer experiment has

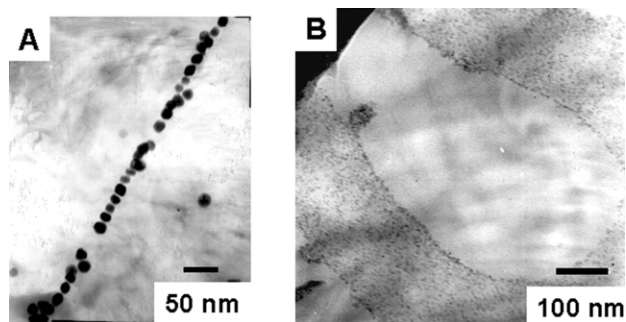


Fig. 3 TEM pictures recorded from gold nanoparticles grown in the 10^{-3} M HAuCl_4 – 10^{-4} M HDA (A) and 10^{-3} M HAuCl_4 – 10^{-2} M HDA (B) experiments.

been described. The use of HDA molecules to accomplish complexation with aqueous chloroaurate ions, their reduction to form gold nanoparticles and capping (to render them hydrophobic and soluble in the organic solvent) is the highlight of this work that considerably simplifies the Brust protocol currently used. Size control over the gold nanoparticles synthesized in this manner may be exercised by varying the HDA: AuCl_4^- molar ratio.

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Notes and references

† UV–vis spectra of the gold colloidal solutions were recorded on a Hewlett–Packard HP 8452 diode array spectrophotometer at a resolution of 2 nm. TGA profiles of carefully weighed quantities of purified powders of HDA-capped gold nanoparticles were recorded on a Seiko Instruments model TG/DTA 32 instrument at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. XRD patterns of the gold nanoparticle films deposited on glass substrates by solvent evaporation were recorded on a Phillips PW 1830 instrument operating at the voltage of 40 kV and a current of 30 mA with Cu-K α radiation. TEM measurements on the gold nanoparticle films cast onto carbon-coated TEM grids were carried out on a JEOL model 1200EX instrument at an accelerating voltage of 120 kV.

- R. P. Andres, T. Bein, M. Dorogi, S. Feng, J. J. Henderson, C. P. Kubiak, W. Mahoney, R. G. Osifchin and R. Reifengerger, *Science*, 1996, **272**, 1323.
- P. Galletto, P. F. Brevet, H. H. Girault, R. Antoine and M. Broyer, *J. Phys. Chem. B*, 1999, **103**, 8706.
- C. A. Mirkin, R. L. Letsinger, R. C. Mucic and J. J. Storhoff, *Nature*, 1996, **382**, 607.
- (a) *Colloidal Gold*, ed. M. A. Hayat, Academic Press, San Diego, CA, 1991; (b) J. S. Bradley in *Clusters and Colloids*: ed. G. Schmid, VCH, Weinheim, 1994, pp. 459–544.
- (a) N. R. Jana, C. Gearheart and C. J. Murphy, *J. Phys. Chem. B*, 2001, **105**, 4065; (b) E. Dujardin, S. Mann, L. B. Hsin and C. R. C. Wang, *Chem. Commun.*, 2001, 1264.
- (a) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801; (b) J. Fink, C. J. Kiely, D. Bethell and D. J. Schiffrin, *Chem. Mater.*, 1998, **10**, 922.
- D. V. Leff, L. Brandt and J. R. Heath, *Langmuir*, 1996, **12**, 4723.
- A. C. Templeton, M. J. Hostetler, E. K. Warmoth, S. Chen, C. M. Hartshorn, V. M. Krishnamurthy, D. E. Forbes and R. W. Murray, *J. Am. Chem. Soc.*, 1998, **120**, 4845.
- The striking colour of gold colloidal solutions is a consequence of excitation of surface plasmon vibrations in the gold nanoparticles that occur in the range 515–530 nm. The range of colours and nature of UV–vis spectra in Fig. 1 are similar to that reported for gold hydrosols synthesized by the reduction of HAuCl_4 with alkaline tetrakis(hydroxymethyl)phosphonium chloride (D. G. Duff, A. Baiker and P. P. Edwards, *Langmuir*, 1993, **9**, 2301).
- Energy dispersive analysis of X-rays measurements of the gold nanoparticle powder yielded a nitrogen:gold molar ratio consistent with close-packed monolayers of HDA on 18 nm size gold particles. The contribution of the HDA coating to the overall weight of the powder is ca. 5%. Since the weight loss measured at $250 \text{ }^\circ\text{C}$ is ca. 40%, some desorption of the gold particles appears likely.
- M. Sastry, A. Kumar and P. Mukherjee, *Colloid Surf. A*, 2001, **181**, 255.
- D. V. Leff, P. C. Ohara, J. R. Heath and W. M. Gelbart, *J. Phys. Chem.*, 1995, **99**, 7036.
- S. Gomez, K. Philippot, C. Colliere, B. Chaudret, F. Senocq and P. Lecante, *Chem. Commun.*, 2000, 1945.