

Novel one-step synthesis of amine-stabilized aqueous colloidal gold nanoparticles†

M. Aslam,^a Lei Fu,^a Ming Su,^a K. Vijayamohan^b and Vinayak P. Dravid*^a

^aDepartment of Materials Science and Engineering, Institute for Nanotechnology, Northwestern University, Evanston, Illinois, 60208, USA.

E-mail: v-dravid@northwestern.edu

^bPhysical and Materials Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

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We demonstrate a simple one-step process for the synthesis of water-dispersed spherical gold nanoparticles using the multifunctional molecule oleyl amine (OLA) that electrostatically complexes with aqueous chloroaurate ions, reduces them, and subsequently caps the nanoparticles thus formed. The gold particles thus formed were of the fcc phase and were fairly monodisperse with particular concentrations of capping molecules.

After Brust *et al.*¹ demonstrated alkanethiol capped Au nanoparticles formation in a biphasic mixture, there has been an enormous effort to functionalize these particles with terminally functionalized alkanethiols or arenethiolates.² However, these gold nanoparticles are prepared in organic solvents and they were redispersible in nonpolar and weakly polar organic solvents.³ Gold particles are also prepared by chemical reduction of a chloride precursor under aqueous conditions: for example, the well-known Turkevich method⁴ involves reduction of HAuCl₄ by sodium citrate in water while Schmid has demonstrated that the reduction of AuCl(PR₃)₃ by B₂H₆ leads to Au₅₅ nanoclusters.⁵ However, a study of the recent literature reveals the need for new preparative methods leading to monodisperse particles of adjustable size and shape.⁶ Development of synthesis protocols for realizing monolayer-protected *water-dispersible* gold nanoparticles, on the other hand, has received considerably less attention and would have immediate applications in catalysis, sensors, molecular markers, and in particular, biological applications such as biolabeling and drug delivery. Recognizing that the solubility of gold, and in some instances silver, monolayer-protected nanoclusters (MPCs) in water/strongly polar organic solvents would be dominated by the terminal functionality of the capping monolayer,⁷ a number of different thiol-coordinated functional groups such as tiopronin,⁸ glutathione,⁹ succinic acid,¹⁰ sulfonic acid¹¹ and ammonium ions¹² have been shown to result in MPCs that are readily dispersible in water.

Recently there have been several reports where tertiary amine/amine adducts were used to form Ag nanoparticles using organometallic Ag complexes in organic medium.¹³ A similar approach was also undertaken for Au amine supramolecular complexes in toluene which leads to Au particles after decomposition.¹⁴ In addition, there is the demonstration that amine derivatives complex with gold nanoparticles in a manner similar to that of thiol derivatives and recently tryptophan has been used to synthesize Au nanoparticles.¹⁵ In a very recent development, Au nanoclusters were also synthesized using

aminophenoxyethylether as a reducing agent at an aqueous–chloroform interface, where the pH was controlled to transfer the organic molecule from chloroform to the aqueous phase. In sharp contrast to our system which indicates very precise particle size control with amine concentration, the reported method has much less control over the particle size and they are highly polydispersed and interlinked (particle size ≥ 100 nm) and reveals the phase transfer to chloroform with long term stirring.^{15f} Using amine chemistry for reduction as well as surface modification, we have shown for the first time that gold nanoparticles can be prepared in *water directly* by complexation with alkylamine molecules where it acts as reducing agent and then subsequently stabilizes the gold particles. Preparation of gold nanoparticles was carried out in a simple one-pot process. The typical procedure is addressed in the references section.¹⁶ This new approach opens up the exciting possibility of surface modification of gold nanoparticles with amino acids where binding with the gold nanoparticles surface may be accomplished through the amine functionality. In this communication, we report our finding that capping aqueous gold nanoparticles with the amine molecules stabilizes the particles in solution nearly covalently and also renders them water-dispersible. The amine-capped nanoparticles may be obtained in the form of a dry powder after evaporation of the aqueous component, this powder being extremely stable in air and readily redispersible in water as well as nonaqueous solvents. Development of protocols for the synthesis of water-dispersible nanoparticles has immense applications in a variety of fields, but clearly more so in biorelated areas such as biolabeling and biosensing. We use in this study primary amines containing long alkyl chains since these compounds are known to self-assemble and have been used as templating agents for the synthesis of mesoporous materials.¹⁷ The gold nanoparticles isolated as a powder (2.45 g, 94% yield based on gold) were also readily redispersed in nonpolar solvents such as toluene and hexane as well as aqueous media, showing no sign of precipitation for months while as-prepared particles were stable for months in water as well.

Fig. 1a and b show the UV-vis spectra and the XRD pattern of gold nanoparticles prepared under aqueous conditions with amine at 0.1 M concentration respectively. The maximum at around 520 nm is a peculiar characteristic of the gold surface plasmon band.^{18a} For the highest concentration of amine as reducing/stabilizing agent the surface plasmon band appears at 522 nm and remains at the same maximum for the OLA concentration of 0.05 M. A further decrease in the amine concentration shifts the band at 529 nm suggesting an increase in the particle size. The plasmon band shifts to 544 nm (OLA; 5×10^{-3} M) and gradually broadens and shifts to 571 nm

† Electronic supplementary information (ESI) available: FTIR, TEM, UV-vis and XRD results. See <http://www.rsc.org/suppdata/jm/b4/b402823f/>

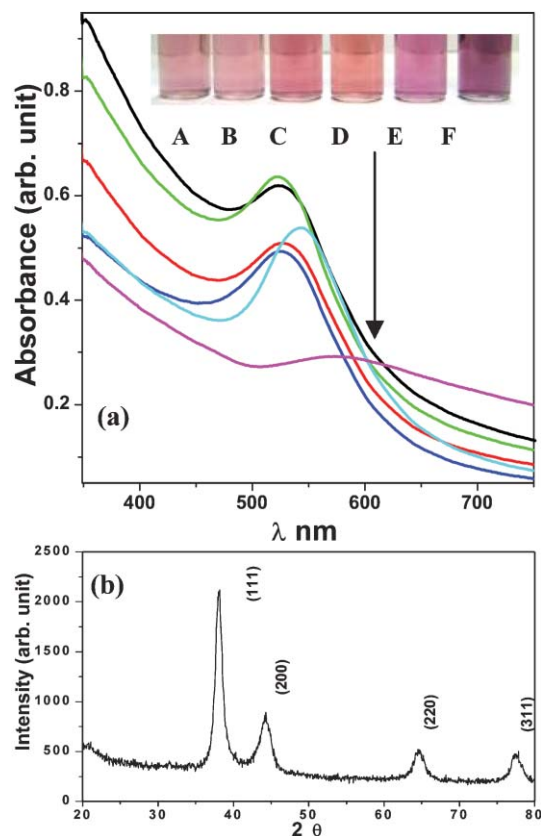


Fig. 1 (a) UV-vis absorption spectra recorded from the aqueous Au colloidal suspension after heating mixtures of 5×10^{-1} , 1×10^{-1} , 5×10^{-2} , 1×10^{-2} , 5×10^{-3} and 1×10^{-3} M oleyl amine (curves A–F, respectively) with 10^{-3} M aqueous chloroauric acid. The inset shows pictures of the water phase containing the Au particles and corresponds directly to spectra A–F. (b) XRD pattern of the ~ 14 nm size OLA-Au (0.01 M OLA; N4-Au) nanoparticles powder collected after drying the sample under ambient conditions.

suggesting the agglomeration and increase in the particle size which supports the issue that amine is playing an important dual role as reducing as well as stabilizing agent. The formation of gold metallic particles was also confirmed by the XRD pattern. It showed broad peaks assigned to the 111, 200, 220 and 311 planes of a face centered cubic (fcc) lattice of gold (Fig. 1b). The selected area electron diffraction pattern has also confirmed the fcc crystalline nanoparticles. The corresponding lattice constant is $a = 0.403$ nm, which is within the error of the reported data (JCPDS File No. 4-0784; $a = 0.4078$ nm). The average particle size of the metal nuclei (13.7 nm) calculated by the Scherrer equation, using the half width of the intense (111) reflection, was comparable with the value obtained from TEM images (N4-Au; ESI† OLA: 1×10^{-2} M). According to XPS measurements, Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks observed at 83.9 and 87.6 eV, respectively, were also identified with zero valent gold.^{18b} The N 1s peak for OLA-Au nanoparticles appears at 401.1 eV with a small shoulder at lower binding energy (399.2 eV) revealing the $-\text{NH}_2$ group gets oxidized itself when it reduces the AuCl ions.^{18b} Fourier transform infrared spectroscopy is a powerful tool for structure and composition studies of surface-adsorbed and coordinated materials.¹⁹ FTIR of OLA-Au MPCs is especially valuable to confirm the expected presence of distinctive vibrations due to its amine functionalities. FTIR spectra of the OLA precursor and OLA-Au MPC nanoparticles are shown in ESI† (Fig. S1), with selected band assignments. The spectrum of OLA is similar to the standard one.²⁰ The small peak at 3325 cm^{-1} , which corresponds to the N–H stretching vibration mode, disappears when the C18-amine molecules adsorb on the gold particle surface (Fig. S1), giving strong evidence that C18-amine

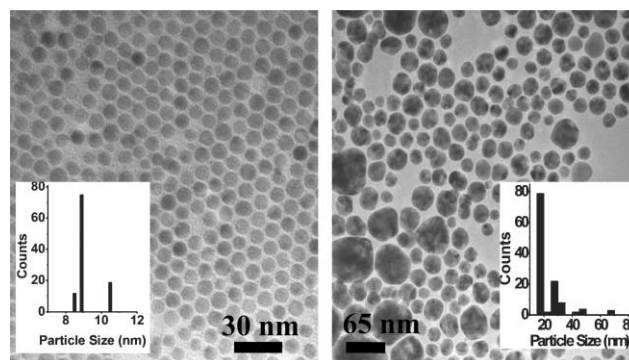


Fig. 2 Representative TEM images from the aqueous Au colloidal suspension after dropcasting them on a carbon coated copper grid. The left and right images correspond to the data from 5×10^{-1} M OLA and 5×10^{-3} M OLA amine capped gold nanoparticles, respectively.

anchors on the gold surface through the N atom in the amine group.

The core size and size distribution of the amine-stabilized Au nanoparticles were examined by transmission electron microscopy (Fig. 2). In general, the present Au nanoparticles have a narrow size distribution similar to those of the previously known alkanethiolate- or arylthiolate-stabilized gold nanoparticles.²¹ For example, N2-Au (OLA: 1×10^{-1} M), having an average core size of 10 ± 0.6 nm, shows a narrower size distribution compared with the gold nanoparticles (N3-Au; OLA = 5×10^{-2} M) prepared with lower OLA concentration (ESI†). Most remarkably, the histogram of the particle diameters plotted in Fig. 2, left (OLA: 5×10^{-1} M; N1-Au) indicates a nearly monodispersed state with an average core size of 9.2 ± 0.3 nm. The edge–edge separation between particles cores (3.2–3.4 nm) is nearly double the extended chain length of the oleyl amine moiety.^{21c,d} On the other hand, N4-Au has a larger and less narrow disperse core (14.0 ± 0.6 nm) compared with N1-Au and N2-Au. The larger core size of N4-Au over those of N1-Au and N2-Au is in agreement with the earlier observation that the cores of thiol-stabilized Au nanoparticles decrease in size and dispersity with increasing thiol concentration. Further decrease in the amine concentration gives N5-Au which is polydispersed with large irregularly shaped particles (Fig. 2, right) with a broad statistical distribution. At present, we understand that there is apparently a simple correlation between the amine concentration and particle size, *i.e.* the particle size increases with the decrease in the concentration of the amine molecules. The irregular shape of gold nanoparticles indicates the inappropriate molar ratio of Au : OLA to fully passivate the particle core so the partial covering by the amine molecule causes the further growth and agglomeration of the particles.

The particle size and distribution were affected by the molar concentration of the amine molecule. For instance, N1-Au (Fig. 2, left) afforded smaller nanoparticles (9.5 ± 0.5 nm) with a narrow distribution, ranging from 9.5 to 11.5 nm. In the case of the particles derived from N4-Au, the particle size distribution was relatively broad, ranging from 14 to 18 nm (average diameter 14 ± 2.5 nm). Furthermore, in the reaction of N5-Au, the particle size became very large (average diameter 50 ± 10.5 nm), and the size distribution was also broader, the range of which was from 10 to 75 nm. Thus, the particle size and distribution of gold nanoparticles prepared in this work was strongly controlled by the amine : gold ion molar ratio.

With respect to the preparation of amine capped gold nanoparticles, the amine plays an important role in the reaction process. Amine did not dissolve in water at room temperature, but the reaction proceeded at 80°C , affording a highly disperse liquid of gold nanoparticles in a short time. On the other hand, the amine molecules did not react with silver, Co and Cu

chlorides at even around 80 °C, but at the same time gold nanoparticles could be prepared with secondary and tertiary amines and dodecylamine, respectively. This suggests that the intermediate, *i.e.* the gold–amine complex, is formed in the reaction procedure and its reactivity strongly depends on the nature of the amine indicating that the gold nanoparticles are produced *via* the Au–amine complex; the first step and the second step is its thermal decomposition. Thus, thermal decomposition of the gold amine complex formed in water was so rapid that the gold nanoparticles were subsequently strongly protected by the amine molecule to avoid further aggregation of nanoparticles. In practice, the particle size was scarcely affected by the reaction time. Therefore, particle size is determined by thermal decomposition of the gold amine complex formed under aqueous conditions and is affected by changing the amine concentration. A similar result was reported for the preparation of silver nanoparticles by the reduction of Ag-benzoate by tertiary amine in the presence of thiol and similarly decomposition of Au thiol (amine) complexes^{13a,b} but none of them were water dispersible, importantly when amine is a backbone of all biological molecules and may play an important role for catalyzing certain reactions in biosensors, catalysts *etc.* Therefore, this is a novel reaction, affording monodispersed gold nanoparticles capped by amine ligands from an Au–amine water-soluble complex which renders amine-capped Au particles water dispersible. We are currently investigating these particles with DNA linkages as amine is a “backbone functional group” in biological molecules.

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Notes and references

- 1 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801.
- 2 (a) L. A. Porter, D. Ji, S. L. Westcott, M. Graupe, R. S. Czernuszewicz, N. J. Halas and T. R. Lee, *Langmuir*, 1998, **14**, 7378; (b) S. L. Logunov, T. S. Ahmadi, M. A. El-Sayed, J. T. Khoury and R. L. Whetten, *J. Phys. Chem. B*, 1997, **101**, 3713; (c) C. S. Weisbecker, M. V. Merritt and G. M. Whitesides, *Langmuir*, 1996, **12**, 3763; (d) A. C. Templeton, M. J. Hostetler, C. T. Kraft and R. W. Murray, *J. Am. Chem. Soc.*, 1998, **120**, 1906; (e) M. J. Hostetler, S. J. Green, J. J. Stokes and R. W. Murray, *J. Am. Chem. Soc.*, 1996, **118**, 4212; (f) M. Brust, J. Fink, D. J. Schiffrin and C. Kiely, *J. Chem. Soc., Chem. Commun.*, 1995, 1655; (g) S. R. Johnson, S. D. Evans and R. Brydson, *Langmuir*, 1998, **14**, 6639; (h) S. Chen and R. W. Murray, *Langmuir*, 1999, **15**, 682.
- 3 A. C. Templeton, M. J. Hostetler, E. K. Warmouth, S. Chen, C. M. Hartshorn, V. M. Krishnamurthy, M. E. D. Forbes and R. W. Murray, *J. Am. Chem. Soc.*, 1998, **120**, 4845 and references therein.
- 4 J. Turkevich, P. C. Stevenson and J. Hillier, *Discuss. Faraday Soc.*, 1951, **11**, 55.
- 5 G. Schmid, *Chem. Rev.*, 1992, **92**, 1709.
- 6 (a) G. Schmid and B. Corain, *Eur. J. Inorg. Chem.*, 2003, 3018; (b) M. A. El-Sayed, *Acc. Chem. Res.*, 2001, **34**(4), 257–264; (c) A. C. Templeton, M. P. Wuelfing and R. W. Murray, *Acc. Chem. Res.*, 2000, **33**, 27–36; (d) R. Shenhar and V. M. Rotello, *Acc. Chem. Res.*, 2003, **36**(7), 549–561; (e) C. N. R. Rao and A. K. Cheetham, *J. Mater. Chem.*, 2001, **11**, 2887; (f) A. N. Shipway and I. Willner, *Chem. Commun.*, 2001, 2035.
- 7 M. Faraday, *Philos. Trans. R. Soc. London*, 1857, **147**, 145.
- 8 C. K. Yee, R. Jordan, A. Ulman, H. White, A. King, M. Rafailovich and J. Sokolov, *Langmuir*, 1999, **15**, 3486.
- 9 G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyer, G. H. Calis and J. W. A. Van der Velden, *Chem. Ber.*, 1981, **114**, 3634.
- 10 F. Tian and K. J. Klabunde, *New J. Chem.*, 1998, **22**, 1275.
- 11 (a) M. Brust, J. Fink, D. Bethell, D. J. Schiffrin and C. Kiely, *J. Chem. Soc., Chem. Commun.*, 1995, 1655; (b) M. Brust, D. Bethell, D. J. Schiffrin and C. J. Kiely, *Adv. Mater.*, 1995, **7**, 795.
- 12 (a) M. J. Hostetler and R. W. Murray, *Curr. Opin. Colloid Interface Sci.*, 1997, **2**, 42; (b) M. J. Hostetler, C. J. Zhong, B. K. H. Yen, J. Andereeg, S. M. Gross, N. D. Evans, M. D. Porter and R. W. Murray, *J. Am. Chem. Soc.*, 1998, **120**, 9396; (c) J. Fink, C. J. Kiely, D. Bethell and D. J. Schiffrin, *Chem. Mater.*, 1998, **10**, 922.
- 13 (a) N. K. Chaki, S. G. Sudrik, H. R. Sonawane and K. Vijayamohan, *Chem. Commun.*, 2002, 76; (b) M. Yamamoto and M. Nakamoto, *J. Mater. Chem.*, 2003, **13**, 2064.
- 14 S. Gomez, K. Philippot, V. Collière, B. Chaudret, F. Senocq and P. Lecante, *Chem. Commun.*, 2000, 1945.
- 15 (a) M. Green and P. O'Brien, *Chem. Commun.*, 2000, 183; (b) D. V. Leff, L. Brandt and J. R. Heath, *Langmuir*, 1996, **12**, 4723; (c) L. O. Brown and J. E. Hutchison, *J. Phys. Chem. B*, 2001, **105**, 8911; (d) A. Kumar, S. Mandal, P. R. Selvakannan, R. Pasricha, A. B. Mandale and M. Sastry, *Langmuir*, 2003, **19**(15), 6277–6282; (e) P. R. Selvakannan, S. Mandal, S. Phadtare, A. Gole, R. Pasricha, S. D. Adyanthaya and M. Sastry, *J. Colloid Interface Sci.*, 2004, **269**(1), 97; (f) P. R. Selvakannan, P. S. Kumar, A. S. More, R. D. Shingte, P. P. Wadgaonkar and M. Sastry, *Langmuir*, 2004, **20**(2), 295–298.
- 16 A quantity of 90 ml of 10⁻³ M concentrated aqueous solution of chloroauric acid (HAuCl₄) was reduced by 1 ml of 10⁻³ M oleyl amine under mild heating at 50 °C to yield stable gold nanoparticles in water. While gold nanoparticles are also produced by the room temperature reaction of amine with chloroauric acid, we have observed that the rate of reduction of chloroaurate ions by amine is considerably enhanced at 50 °C and consequently, all gold nanoparticle syntheses were carried out at this temperature. The amine-reduced gold nanoparticle solution was subjected to ultracentrifugation and the resulting pellet was washed with copious amounts of deionized water to remove any uncoordinated amine molecules. The pellet was then redispersed in deionized water for UV-vis spectroscopy studies.
- 17 S. Biz and M. L. Occelli, *Catal. Rev. Sci. Eng.*, 1998, **40**, 329 and references therein.
- 18 (a) J. A. Creighton and G. D. Eadon, *J. Chem. Soc., Faraday Trans.*, 1991, **87**(24), 3881; (b) D. V. Leff, L. Brandt and J. R. Heath, *Langmuir*, 1996, **12**, 4723.
- 19 D. L. Allara and R. G. Nuzzo, *Langmuir*, 1985, **1**, 52.
- 20 *The Aldrich Library of FT-IR Spectra*, Edition II, Aldrich Chemical Co., Milwaukee, WI, 1997, **vol. 1**, p. 506.
- 21 (a) M. J. Hostetler, J. E. Wingate, C. J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, D. J. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans and R. W. Murray, *Langmuir*, 1998, **14**, 17; (b) S. Chen and R. W. Murray, *Langmuir*, 1999, **15**, 682; (c) L. Motte and M. P. Pileni, *J. Phys. Chem. B*, 1998, **102**, 4104; (d) O. I. Micic, S. P. Ahrenkiel and A. Z. Nozik, *Appl. Phys. Lett.*, 2001, **78**, 4022.