

Cite this: *Chem. Commun.*, 2012, **48**, 859–861

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COMMUNICATION

Conversion of double layer charge-stabilized Ag@citrate colloids to thiol passivated luminescent quantum clusters†

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Received 9th September 2011, Accepted 10th November 2011

DOI: 10.1039/c1cc15604g

A red luminescent silver cluster was synthesized in milligram quantities by the direct core reduction of the most widely studied class of large silver nanoparticles, namely silver@citrate of tens of nanometres diameter. No byproducts such as thiolates were detected, unlike in the case of typical methods of making such clusters. The route provides nearly pure clusters. The possibility to make diverse clusters from large nanoparticles expands the scope of cluster research.

One of the most studied families of nanomaterials is noble metal nanoparticles (NPs)¹ or colloids. A well known synthetic methodology to make noble metal nanoparticles is the citrate route, originally proposed by Turkevich *et al.* in 1951.² These charge stabilized nanoparticles, commonly described as M@citrate (M = Au, Ag) and their variants, exhibiting intense surface plasmon resonance (SPR) have been the most extensively used materials on which several unusual phenomena at the nanoscale have been explored. Typical Ag@citrate NPs are 30–70 nm in diameter while the gold analogues made under identical conditions are smaller, 15–20 nm in diameter. Diverse applications of such materials in catalysis,³ spectroscopy,⁴ water purification⁵ and a number of other areas became possible with various forms of these NPs. Such NPs are different from the more recent thiol and phosphine monolayer protected NPs in terms of their stability. In the former case, stability is based on the electrical double layer and in the latter, it is due to ligand passivation. The most recent addition to noble metal nanoparticles is their sub-nanometre size analogues, known as quantum clusters (QCs) composed of a few metal atoms in the core and a protecting ligand shell. Quantum clusters exhibit intense luminescence and associated physicochemical properties. Diverse methodologies have been employed to create clusters such as Au₂₅,⁶ Au₁₅,⁷ Au₂₃,⁸ Ag₉,⁹ Ag₇,¹⁰ *etc.* Typically, many clusters are formed together and versatile synthetic routes to create specific clusters in pure form are desired. While smaller monolayer protected nanoparticles of 2–3 nm or smaller diameter have been converted to clusters, particularly Au₂₅, by a core etching protocol,^{6c,e} the conversion of large, plasmonic NPs to clusters has not

been demonstrated. In this communication, we show that luminescent silver clusters can be made in one step from the most extensively studied family of nanomaterials, namely citrate protected nanoparticles. The formation of few atom clusters starting from M@citrate may enable the exploration of properties of a range of nanomaterials, from the largest to the smallest.

The process of synthesis involves making Ag@citrate NPs of average diameter 30–70 nm by boiling 5 mM, 50 mL AgNO₃ and adding aqueous sodium citrate (75 mg in 1 mL water) to it and continuing boiling for 10 min. Reduction in core dimension occurs by adding excess mercaptosuccinic acid (MSA, in solid form; 73.5 mg, details are in S1, ESI†) and maintaining a temperature of 70 °C, the temperature being critical. The as-synthesized Ag@citrate NPs show a SPR at 420 nm (Fig. 1Aa). During the reaction, there is a disappearance of the plasmon feature at 420 nm (Fig. 1Ab) implying that no

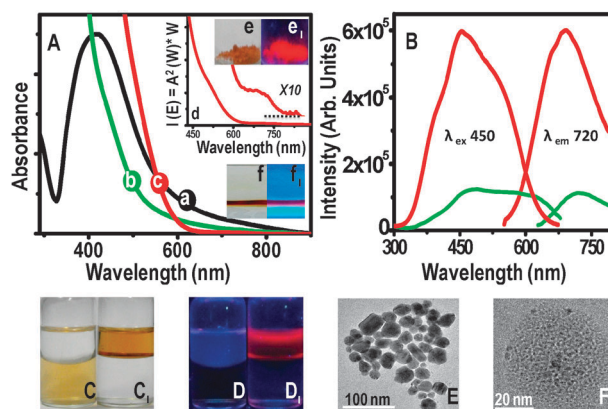


Fig. 1 (A) Spectral variation during the conversion of silver nanoparticles to quantum clusters. (a), (b) and (c) Spectra of parent Ag@citrate nanoparticles, that after 1 h and 24 h after adding MSA, respectively. Inset: (d) Jacobian corrected spectrum of the red trace as described in S1 (ESI†), (e) photograph of the crude cluster in visible light, (e₁) the same in UV light, (f) photograph of PAGE separated cluster in visible and (f₁) the same in UV light. (B) Luminescence spectra of the cluster before (green trace) and after (red trace) phase transfer. Excitation and emission wavelengths are marked. C and C₁ are the photographs before and after phase transfer in visible light and D and D₁ are in UV light. TEM images of (E) Ag@citrate and (F) phase transferred cluster protected with tetraoctylammonium bromide. Clusters are faintly visible. The larger particles are due to electron beam induced aggregation.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1cc15604g

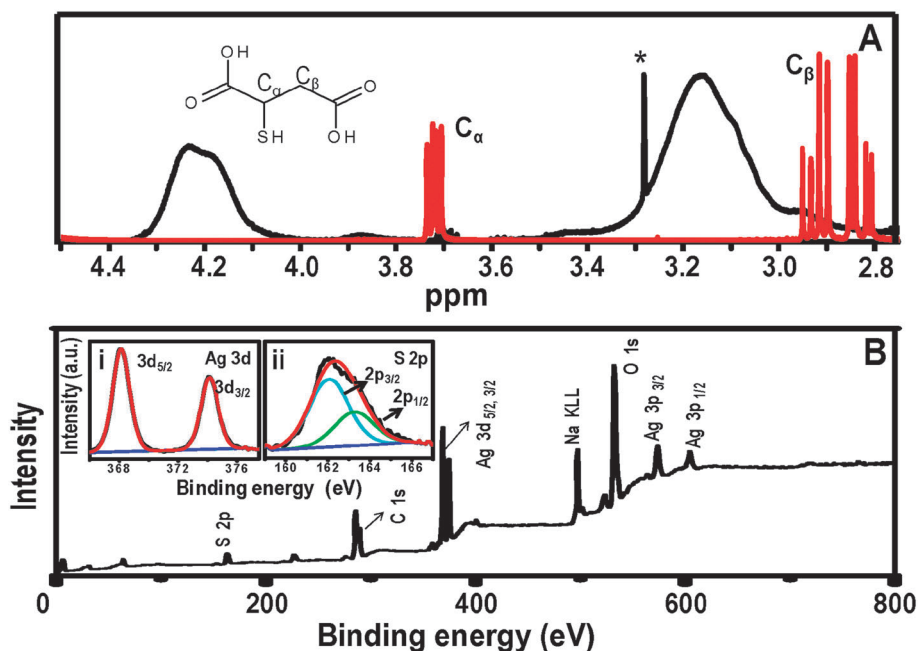


Fig. 2 (A) ^1H NMR spectrum of the $\text{Ag}_{\text{QC}}@\text{MSA}$ cluster in D_2O along with that of MSA. The peak labeled with * is due to methanol used in washing, which could not be removed despite freeze-drying. (B) XPS survey spectrum of $\text{Ag}_{\text{QC}}@\text{MSA}$ cluster. Inset (i) and (ii) are corresponding to Ag 3d and S 2p. Their components are fitted.

gradual but direct core reduction happens, unlike in the core-etching methods where the conversion is slower, taking hours.^{6c,e} Spectra collected at various times such as 5 and 10 minutes after adding MSA show this drastic decrease in plasmon features (Fig. S2, ESI†). The cluster formed has no apparent optical absorption features (Fig. 1Ac). The step-like behavior and specific features are clear after the Jacobian correction (Fig. 1A inset, trace d). During the reaction, the color of the solution changes from golden yellow to orange with no observable precipitation due to thiolates or nanoparticles, unlike in the case of core etching. The solution upon precipitation and washing gave an orange powder (Fig. 1A, inset e) which shows red luminescence in the solid state (Fig. 1A, inset e₁). Extensive literature on quantum clusters¹¹ suggest that this luminescence is indicative of their formation. To know the monodispersity of the clusters, we separated the crude clusters by polyacrylamide gel electrophoresis (details are in S1, ESI†) which shows the presence of a single band. The photograph of the gel with this band was collected at room temperature in visible light and at 5 °C in UV light (Fig. 1A, inset (f and f₁)). The pink luminescence of the clusters is evident from the image. The band upon extraction gives an optical absorption spectrum resembling the crude (details in Fig. S3, ESI†) indicating that the parent material has no visible impurities. As a result, subsequent measurements were done with the crude. The luminescence spectrum of the as-prepared $\text{Ag}_{\text{QC}}@\text{MSA}$ shows excitation at 450 nm and emission at 720 nm. The quantum yield of the as-prepared cluster in water at 10 °C was found to be 6×10^{-3} using rodamine6G. The cluster can be easily phase transferred (details are in S1, ESI†) and luminescence shows an increase in intensity in the organic medium as shown in Fig. 1B. Photographs of the cluster before and after phase transfer in visible light (Fig. 1C and C₁) and the same in UV light

(D and D₁) show the expected characteristics. The cluster is not visibly luminescent at room temperature in water (Fig. 1D). From our previous studies of silver and gold QCs, it is known that water quenches luminescence.¹⁰ However, a toluene solution is visibly luminescent at room temperature (RT, 23 °C). The parent citrate NPs are polydisperse with a size in the range of 30–70 nm (Fig. 1E) while the clusters are too tiny (~ 1 nm) to be seen under the electron beam (Fig. 1F) and are also extremely beam sensitive, resulting in large particles upon longer term irradiation (Fig. S4, ESI†).¹² The yield of the cluster is 44%, in terms of the metal used.

The ^1H NMR spectra of MSA and $\text{Ag}_{\text{QC}}@\text{MSA}$ clusters were measured in D_2O and are shown in Fig. 2A. Two strong multiplets at 2.8 and 3.7 ppm in the ^1H NMR spectrum are from CH_2 and CH protons of MSA, respectively. These multiplets are broadened in the QC due to fast relaxation. Both CH and CH_2 protons are shifted downfield, but CH protons are shifted more because of the proximity to the silver core. The data presented suggest the formation of MSA protected silver clusters. Although detailed mass spectrometry (MS) was attempted both by electrospray ionization (ESI) and by matrix assisted laser desorption ionization (MALDI), no characteristic features were obtained; however, the presence of silver, sulfur and some Ag–MSA complexes was seen due to the decomposition of the cluster at higher capillary temperatures (Fig. S5 and S6, ESI†). This is not surprising as many clusters are not stable even under soft ionization conditions. Therefore, in the absence of MS, a detailed elemental analysis was performed to arrive at the cluster composition. The total organic fraction estimated was 47.1% (15.3% C, 20.4% O, 10.2% S, 1.2% H) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) gave 53.2% weight of silver. All the results were checked for reproducibility. These suggest a cluster compound

composed of ~ 38 Ag atoms and ~ 24 MSA ligands. The calculated silver and organic fraction for $\text{Ag}_{38}(\text{MSA})_{24}$ is 53.4% Ag and 46.6% MSA. Slight changes are attributed to water included in such a dicarboxylic acid incorporated structure, despite long freeze-drying as suggested by infrared spectroscopy (see below). Thermogravimetric (TG) analysis of the as-prepared cluster (Fig. S7, ESI†) gives 38% of the organic fraction as the remaining material was largely silver with some sulfur. This is in agreement with Ag–S and S–C bond cleavages in such clusters.¹⁰ Further support for the structure was obtained from energy dispersive analysis of X-rays (EDAX) and X-ray photoelectron spectroscopy (XPS). The silver to sulfur atomic ratio in EDAX was 0.62 (calculated 0.63). The EDAX spectrum and images of Ag, S, and C are shown in Fig. S8, ESI†. XPS gave a silver to sulfur atomic ratio of 0.65. All these quantitative analyses support the tentative formula of $\text{Ag}_{38}(\text{MSA})_{24}$. We are, however, continuing our efforts on the MS analysis to confirm the composition.

The XPS survey spectrum shows all the expected elements (Ag, C, O and S). High resolution XPS of silver shows Ag in the Ag(0) state (Fig. 2B, i). A binding energy (BE) of 368.0 eV for Ag $3d_{5/2}$ is similar to those of other silver clusters.^{10,13} S $2p_{3/2}$ appears at 162.0 eV due to S^- (Fig. 2B, ii). Both these are characteristic of thiolate protected silver quantum clusters. Expanded XPS spectra in the C 1s and O 1s regions are shown in Fig. S9 (ESI†). The MSA protection is confirmed by the IR spectrum which shows features corresponding to MSA ($\text{C}=\text{O}_{\text{str}} \sim 1579 \text{ cm}^{-1}$, $\text{C}-\text{O}_{\text{str}} \sim 1388 \text{ cm}^{-1}$, $\text{C}-\text{H}_{\text{str}} \sim 2929 \text{ cm}^{-1}$) and the disappearance of the S–H proton (Fig. S10, ESI†) in the cluster is due to thiolate binding. The presence of water is also clear from the IR data. X-Ray diffraction for Ag@citrate gives features at 38° , 44° , 64° , 77° and 80° , but a broad peak around $2\theta \approx 37^\circ$ was obtained for $\text{Ag}_{\text{QC}}@\text{MSA}$ clusters (Fig. S11, ESI†). This kind of large broadening of the peaks is seen in gold¹⁴ and silver¹⁵ QCs.

The same method was tried with glutathione (SG) by changing some experimental conditions (details are in S1, ESI†). $\text{Ag}_{\text{QC}}@\text{SG}$ clusters in powder form as well as in organic phase show red luminescence. Absorption profiles of Ag@citrate and $\text{Ag}_{\text{QC}}@\text{SG}$ clusters upon reaction and the luminescence spectrum of the phase transferred $\text{Ag}_{\text{QC}}@\text{SG}$ cluster are shown in Fig. S12, ESI†.

In conclusion, we report direct conversion of the most studied class of nanoparticles to the most emerging category

of sub-nano materials by a simple one step route. This methodology with various ligands and experimental conditions may give diverse clusters with varying properties. Access to a range of cluster sizes from tens of nanometres to sub-nanometres, as in clusters, allows diverse properties to be examined.

We thank the Department of Science and Technology, Government of India for financial support. Thanks to SAIF, IIT Madras for NMR and ICP-OES.

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