Supplementary information for the paper:

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

L. Dhanalakshmi, T. Udayabhaskararao, Thalappil Pradeep *

DST Unit of Nanoscience (DST-UNS), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

*E-mail: pradeep@iitm.ac.in

Table of contents

S1. Supplementary information 1

Experimental Section

Synthesis of Ag@citrate nanoparticles

Silver nanoparticles were prepared by the well-known Turkevich method. 5 mM solution of silver nitrate in 50 mL deionized water was heated until it began to boil. 75 mg of sodium citrate dissolved in 1 mL deionized water was added drop-wise to the boiling silver nitrate solution and the boiling was continued. The color of the solution slowly turned into pale yellow, indicating the reduction of the Ag^+ ions. Heating was continued for an additional 10 min. These nanoparticles show surface plasmon resonance peak at 420 nm which is characteristic of silver nanoparticles.

Synthesis of MSA protected silver quantum clusters

As prepared silver nanoparticle suspension was kept in ice cold water. 73.5 mg of MSA in powder form was added to this solution and kept for stirring at 70 ^oC for 24 h. The color of the solution changes from golden yellow to orange. Solution was freeze dried to yield a sticky paste which upon addition of water gave a concentrated solution. The cluster was precipitated from it by the addition of methanol. The precipitate was repeatedly washed by 90% methanol to remove unbound MSA and citrate ions. The product was dried under vacuum and was stored in the laboratory atmosphere. Yield of crude Ag_{QC}@MSA was 25 mg, starting from the above method, corresponding to 44% in terms of silver.

Purification by polyacrylamide gel electrophoresis (PAGE): PAGE separation of the clusters was performed as per the procedure given below.

A gel electrophoresis unit with 1 mm thick spacer (Bio-rad, Mini-protein Tetra cell) was used to process the PAGE. Total contents of the acrylamide monomers were 28% (bis(acrylamide:acrylamide) = 7:93) and 3% (bis(acrylamide:acrylamide) = 6:94) for the separation and condensation gels, respectively. The eluting buffer consisted of 192 mM glycine and 25 mM tris(hydroxymethylamine). The crude mixture of Ag_{QC}@MSA clusters, as a orange powder, obtained from the reaction was dissolved in 5% (v/v) glycerol-water solution (1 mL) at a concentration of 60 mg/mL. The sample solution (1.0 mL) was loaded onto a 1 mm gel and eluted for 4 h at a constant voltage of 100 V to achieve separation shown in Fig. 1A (f, f_1). The gel fractions containing the clusters were cut out, ground, and dipped in distilled water (2 mL) for 10 min. Subsequently, the solutions were centrifuged at 15,000 rpm for 15 min at -10 °C, followed by filtering with filter paper having 0.22 μm pores to remove the gel lumps suspended in the solution. The samples were freeze dried to get the Ag_{QC}@MSA powder. This was dispersed in water and UV spectrum was collected (Fig. S3).

Even without PAGE, the clusters are rather pure, the excess MSA was removed by washing with methanol many times.

Procedure for phase transfer

Clusters were phase transferred to toluene layer by using tetraoctlyammonium bromide as phase transfer agent. Procedure is as follows: 2 mL of cluster in water was phase transferred to 2 mL of toluene by using 5 mg of tetraoctylammonium bromide

Synthesis of Ag_{QC}@SG

Citrate capped silver nanoparticles were prepared by taking 1mM silver nitrate in 50 ml deionized water in a synthesizer tube and was heated until it began to boil (100 ^oC). 1 mL of 47 mM sodium citrate was added dropwise to the silver nitrate solution and boiling was continued for 15 min to get the nanoparticle. Synthesizer tube containing nanoparticle suspension was kept in ice-cold water. Cluster formation was preferable at basic conditions obtained by the addition of 1 mL of 0.15 M NaOH. To get the clusters 30.7 mg of glutathione in solid form was added and the solution was kept for stirring at 70 ^{0}C for 48 h. The color of the solution changes from yellow to orange. The Ag_{QC}@SG powder was obtained by following the same procedure used for Ag_{QC}@MSA. Powder in visible light appears as orange and it can be stored at laboratory conditions.

Method of Jacobian correction

To amplify the less-intense absorption features, the data have been corrected with the Jacobian factor. For this, the experimentally obtained absorbance values as a function of wavelength [I(ω)], were converted to energy-dependent numbers [I(E)], using the expression,

$$I(E) = \frac{I(\omega)}{\partial E/\partial\, \omega} \propto I(\omega)^{*}\, \omega^{2}$$

where ∂E/∂ω represents the Jacobian factor.

Analytical procedures

A. UV-vis spectroscopy

UV-vis spectra were recorded using Perkin Elmer Lambda 25 UV-vis spectrometer. Spectra were typically measured in the range of 190-1100 nm.

B. Fourier-transform infrared (FT-IR) spectra

Perkin Elmer Spectrum One instrument were used for measuring FT-IR spectra. KBr crystals were used as the matrix for sample preparation.

C. Luminescence spectroscopy

The photoexcitation and luminescence studies were carried out using HORIBA JOBIN VYON Nano Log spectrofluorimeter with 100-W xenon lamp as excitation source. The band pass for both excitation and emission was set as 5 nm.

D. Transmission electron microscopy (TEM)

TEM images were collected using a JEOL 3010 microscope. A diluted solution of phase transferred cluster was spotted on carbon coated copper grid and was dried in laboratory ambience.

E. ESI MS

Mass spectrometric studies were conducted using an electrospray system, MDX Sciex 3200 QTRAP MS/MS instrument having a mass range of m/z 50-1700. As prepared clusters were dissolv3d in 1:1 water/methanol mixture in ppm concentration. The samples were electrosprayed at a flow rate of 10 μL/min and ion spray voltage of 5 kV.

F. Matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI TOF MS)

The mass spectrometric studies were also conducted using a Voyager DE PRO Biospectrometry Workstation (Applied Biosystems) MALDI TOF MS instrument. A pulsed nitrogen laser of 337 nm was used (maximum firing rate: 20 Hz, maximum pulse energy: 300 mJ) for desorption ionization and TOF was operated in the delayed extraction mode. The mass spectra were collected in negative mode and were averaged for 100 shots. The spectra were simulated using the Data explorer version 4.0.0.0 software provided by Applied Biosystems Inc. which uses the isotope database of IUPAC.

G. SEM and EDAX analyses

Scanning electron microscopic (SEM) and energy dispersive X-ray (EDAX) analyses were done in a FEI QUANTA-200 SEM. For measurements, clusters were drop-casted on an indium tin oxide coated conducting glass and dried in vacuum.

H. X-ray photoelectron spectroscopy

XPS measurement was done using an Omicron Nanotechnology spectrometer with polychromatic Al Kα X-rays. As prepared clusters in water were spotted on a Mo plate and allowed to dry in vacuum. The X-ray flux was adjusted to reduce beam induced damage of the sample. The spectrometer was operated in the constant analyzer energy mode. Survey and high-resolution spectra were collected using pass energies of 50 and 20 eV, respectively. The binding energy was calibrated with respect to C 1s at 285.0 eV.

I. X-ray powder diffraction

Powder XRD patterns of the samples were recorded using PANalytical X'pertPro diffractometer. The powder samples of parent silver nanoparticles and clusters were taken on a glass plate and the X-ray diffractogram was collected in the 2Θ range of 5 to 100 degrees.

J. Thermogravimetry (TG)

TG analyses of the as-prepared clusters were carried out with a Perkin Elmer TGA 7 at a heating rate of 20 °C per min in N_2 atmosphere.

K. NMR

^{1}H NMR spectra were measured with 500 MHz Bruker AVANCE III spectrometer. 20 mg/ 0.5 mL D_2O was used for ^{1}H NMR analyses.

L. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

ICP-OES measurements were done using Perkin Elmer Optima 5300 DV. As prepared cluster was dissolved in distilled water in ppm concentrations.

S2. Supplementary information 2

Time dependent UV-Vis spectra

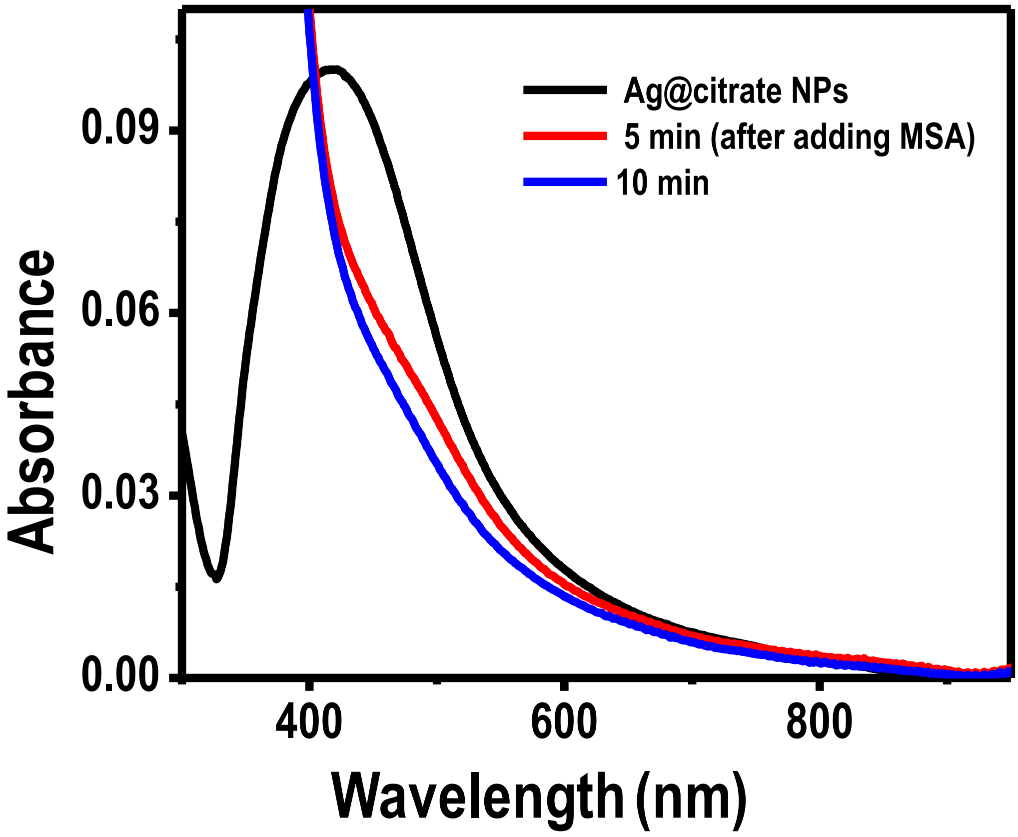


Fig S2. Spectral variation of Ag@citrate NPs after the addition of MSA followed by heating at 70 ºC. After adding MSA, SPR peak of Ag@citrate NPs disappears after 10 minutes. The data at 5 and 10 minutes show a weakening shoulder due to the plasmon resonance.

S3. Supplementary information 3

UV-Vis of Ag_{QC}@MSA after PAGE

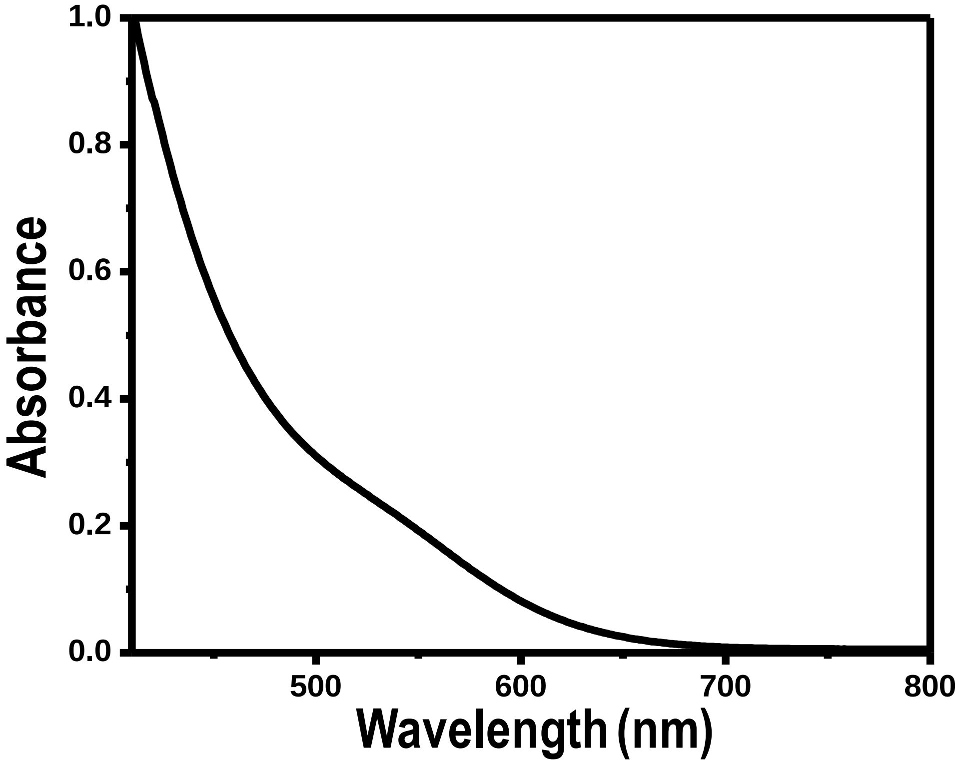


Fig S3. UV spectrum of Ag_{QC}@MSA cluster after PAGE separation, showing the similar feature corresponding to as-synthesized cluster.

S4. Supplementary information 4

TEM, effect of electron beam irradiation

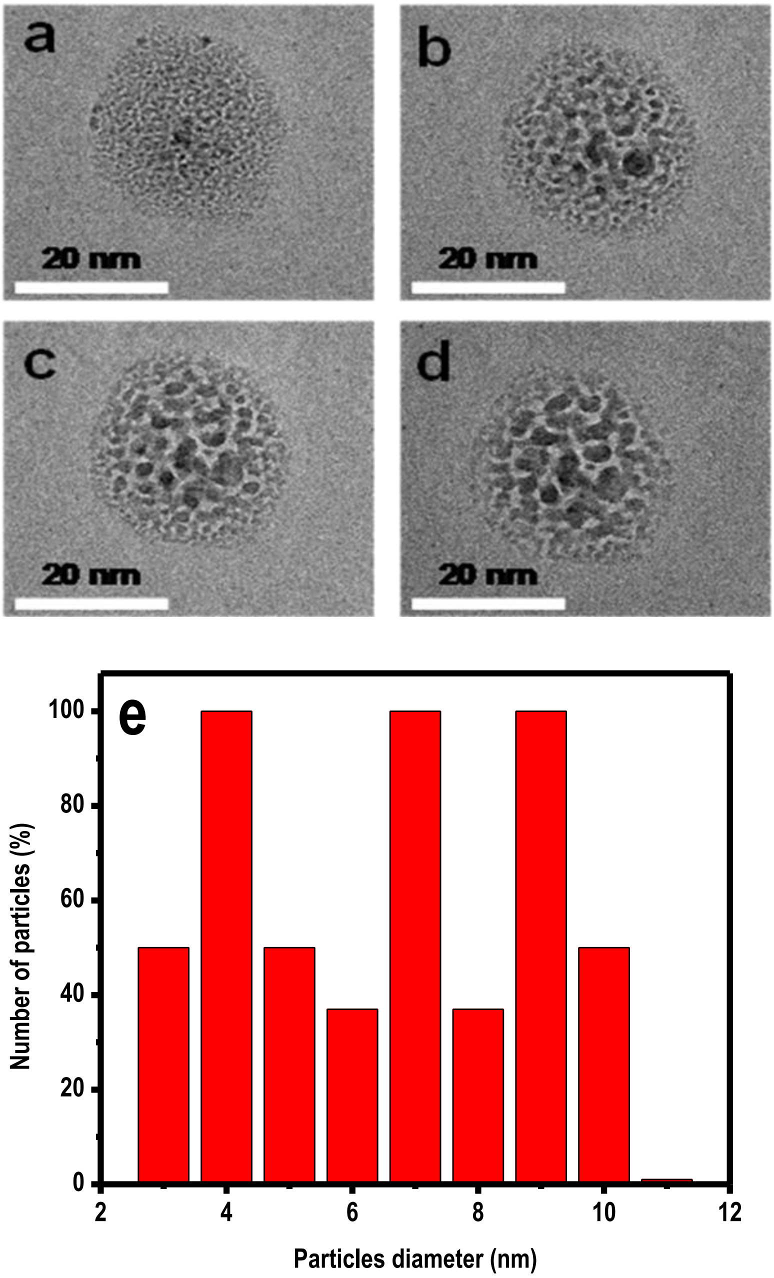


Fig S4. TEM image of phase transferred Ag_{QC}@MSA cluster aggregates upon continuous electron beam irradiation. The same regions of the grid are shown in images a, b, c and d. Image ‘a’ is at the start of the irradiation showing small clusters, image ‘b’ is after 30 sec. In ‘c’ the irradiation time was 60 sec. It was 90 sec in ‘d’. Diagram ‘e’ is the particle size distribution corresponding to the TEM image ‘d’. Various size distributions from 3 to 11.5 nm are due to Ag_{QC}@MSA cluster aggregates, upon electron beam irradiation.

S5. Supplementary information 5

ESI MS of as-prepared Ag$_{QC}$@MSA cluster

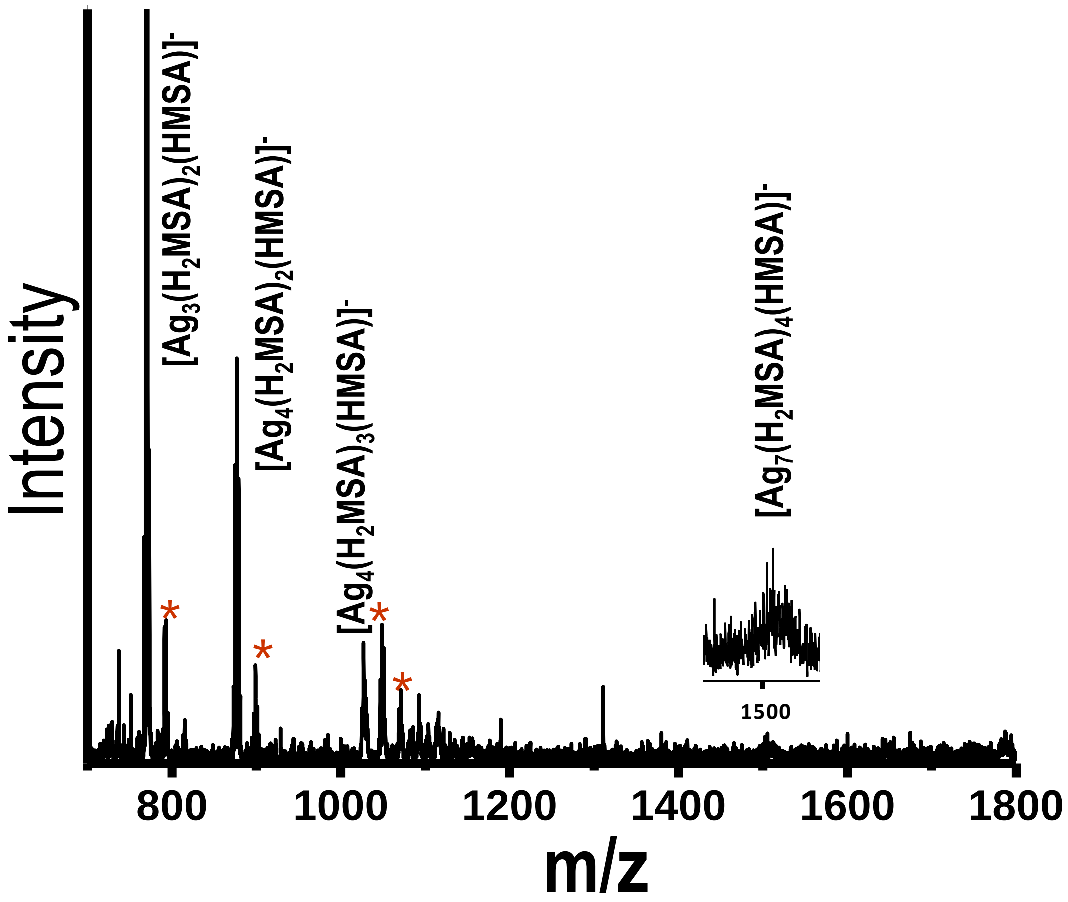


Fig S5. ESI MS of the Ag$_{QC}$@MSA cluster collected in the negative mode. Peaks with * show the Na adducts of the preceding formula. These appear to be decomposition products.

S6. Supplementary information 6

MALDI MS

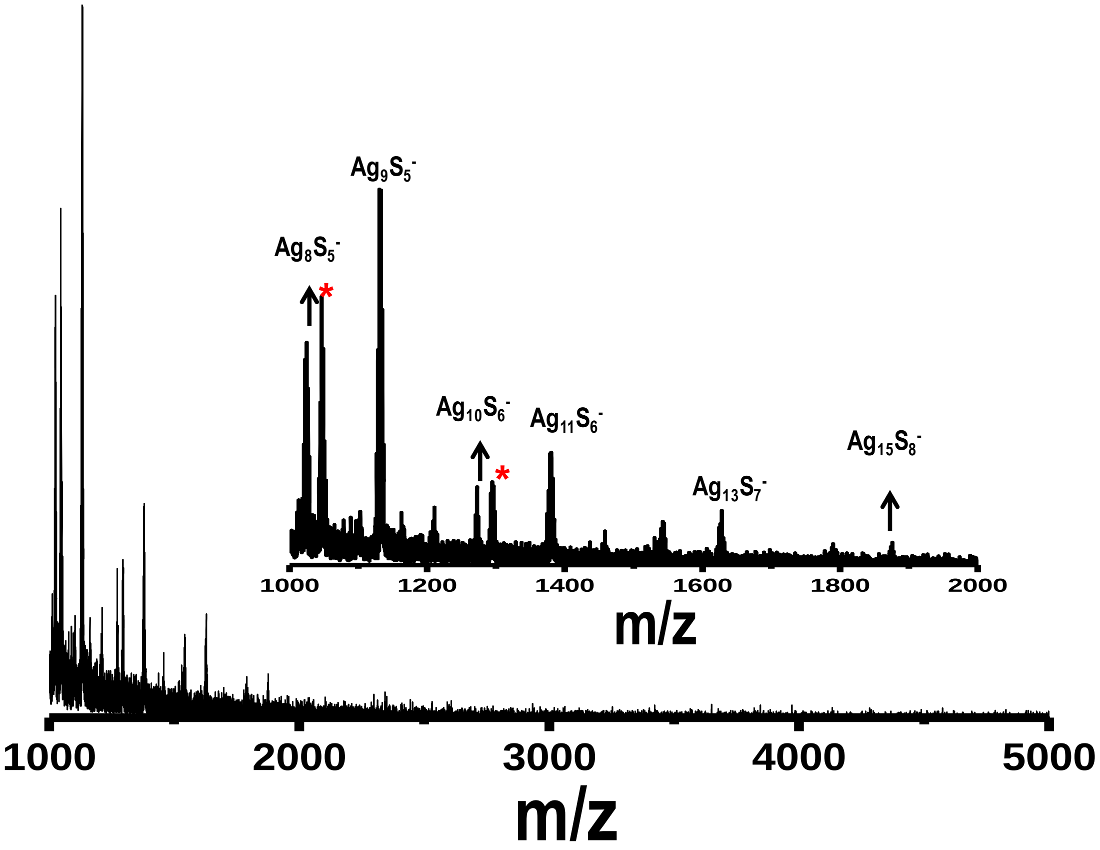


Fig S6*.* MALDI MS of Ag$_{QC}$@MSA cluster in negative mode. The Ag$_n$S$_m^-$ series is labeled with their corresponding molecular formulae. Peaks with * show the Na adducts of the preceding formula. Inset shows expanded view of the MALDI MS.

S7. Supplementary information 7

TG analysis

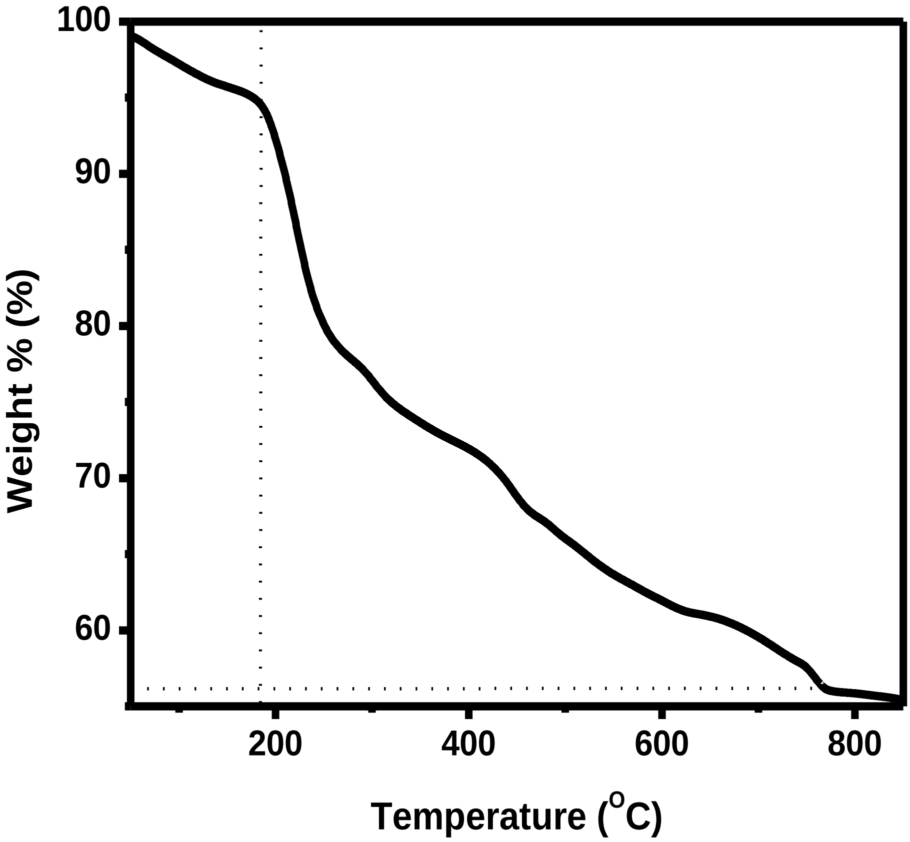
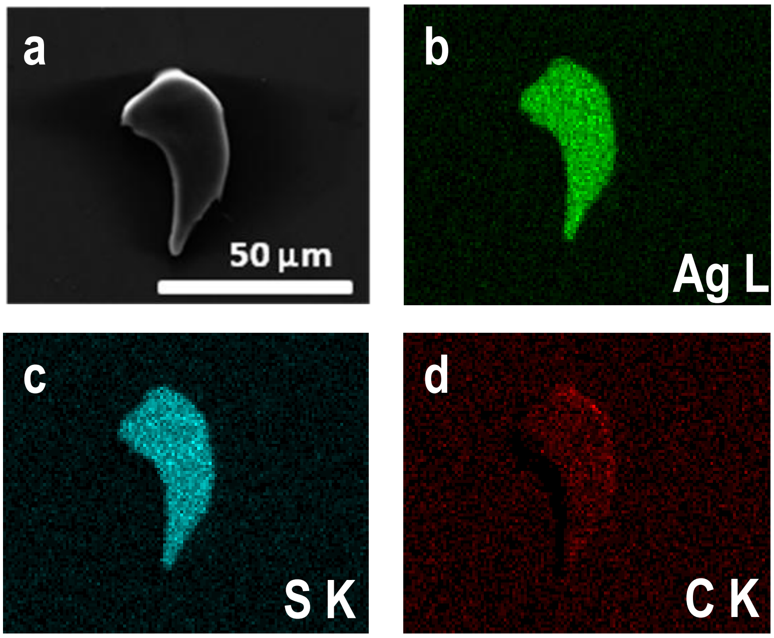


Fig S7. Thermogravimetric (TG) analysis of Ag_{QC}@MSA clusters performed under N_2. A detailed analysis of the data was not attempted as such clusters decompose leaving Ag_2S as well as Ag. Several organic species are observed in thermal decomposition of such clusters. Both Ag-S and S-C bond cleavages are observed (unpublished data).

S8. Supplementary information 8

SEM/EDAX

A)



B)

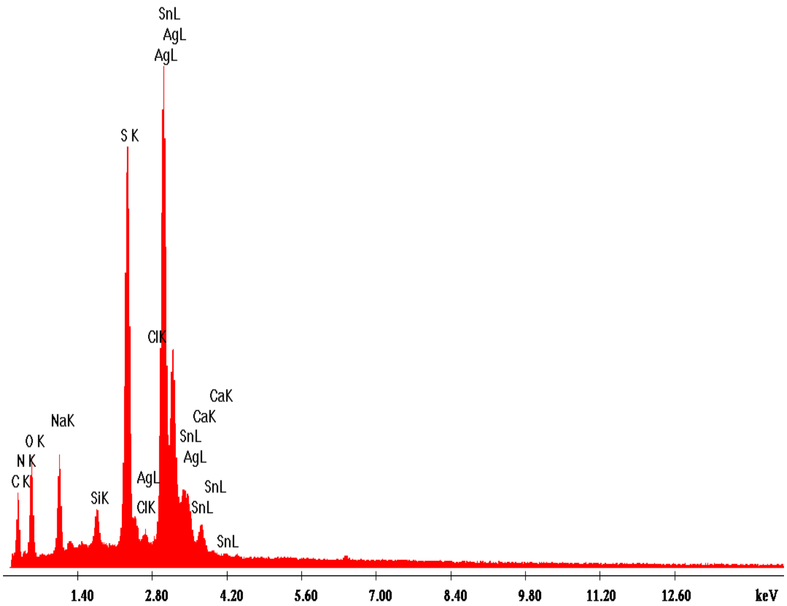


Fig S8. A) SEM and EDAX images of the cluster. EDAX maps using C **K**$_{\alpha}$, Ag **L**$_{\alpha}$, and S **K**$_{\alpha}$ are shown. B) EDAX spectrum of Ag$_{QC}$@MSA cluster.

S9. Supplementary information 9

XPS

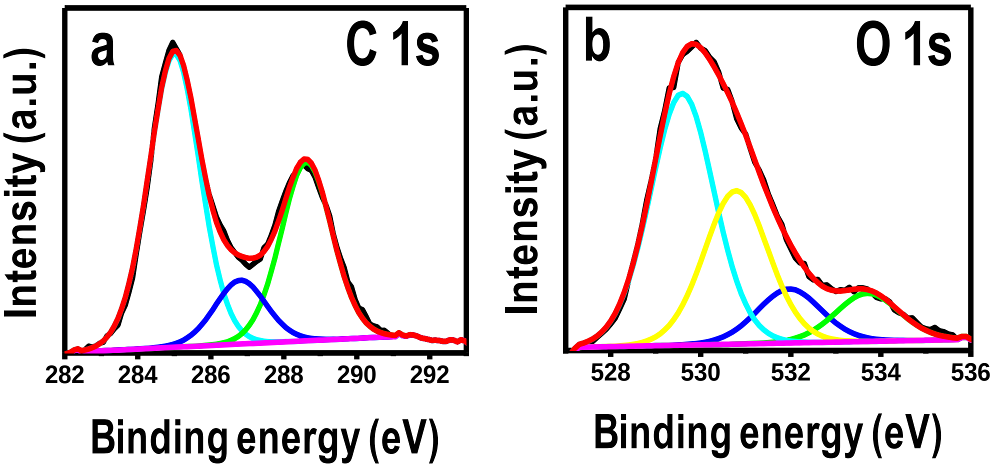


Fig S9. a) and b) C 1s and O 1s XPS spectra, respectively. C 1s region shows three peaks at 285.0, 286.8 and 288.3 eV, corresponding to the CH/CH2, C-S and COO^- groups respectively. O 1s shows peaks at 529.6, 530.8, 532.0 and 533.5 eV corresponding to various species such as hydroxyl group, carboxylate oxygens and adsorbed H_2O. The Ag:S atomic ratio is 1:0.65 whereas the expected value is 1:0.63. The C:O ratio is not reliable in view of potential surface contamination.

S10. Supplementary information 10

FT-IR

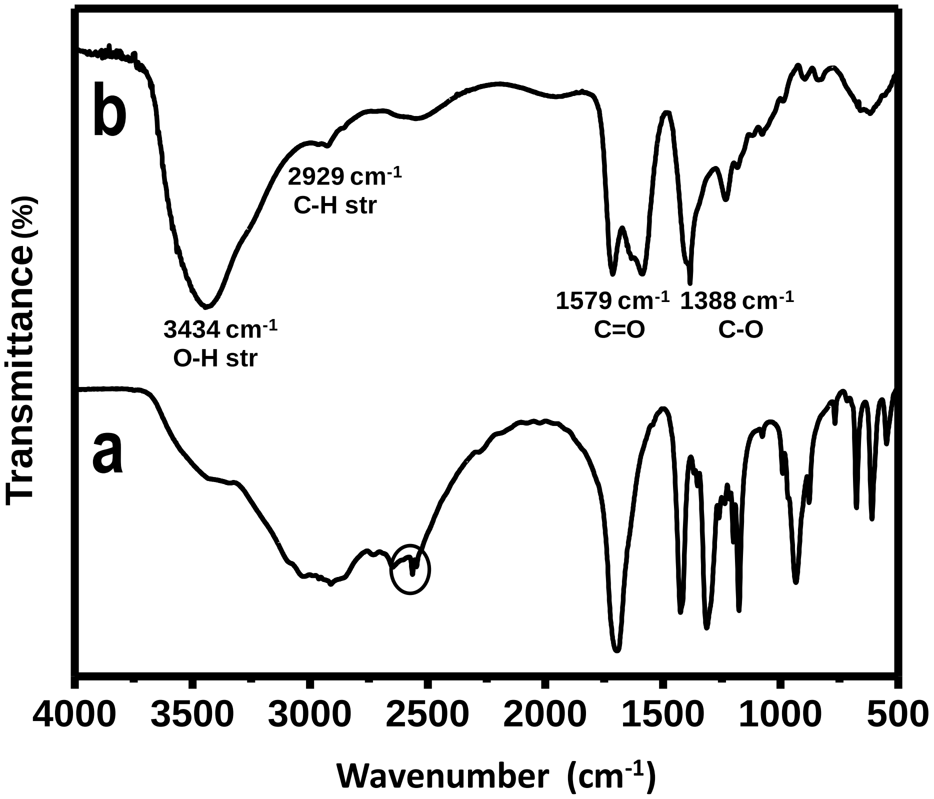


Fig S10. FT-IR spectra of (a) MSA (b) as-prepared Ag_{QC}@MSA. The -SH stretching feature at 2575 cm^{-1} in H_2MSA is marked by a circle in (a) which is absent in Ag_{QC}@MSA cluster. H_2MSA features in the region of 2000-500 cm^{-1} confirm the presence of MSA in the cluster. The strong band at 3434 cm^{-1} in FT-IR of Ag_{QC}@MSA is due to hydrated water.

S11. Supplementary information 11

XRD

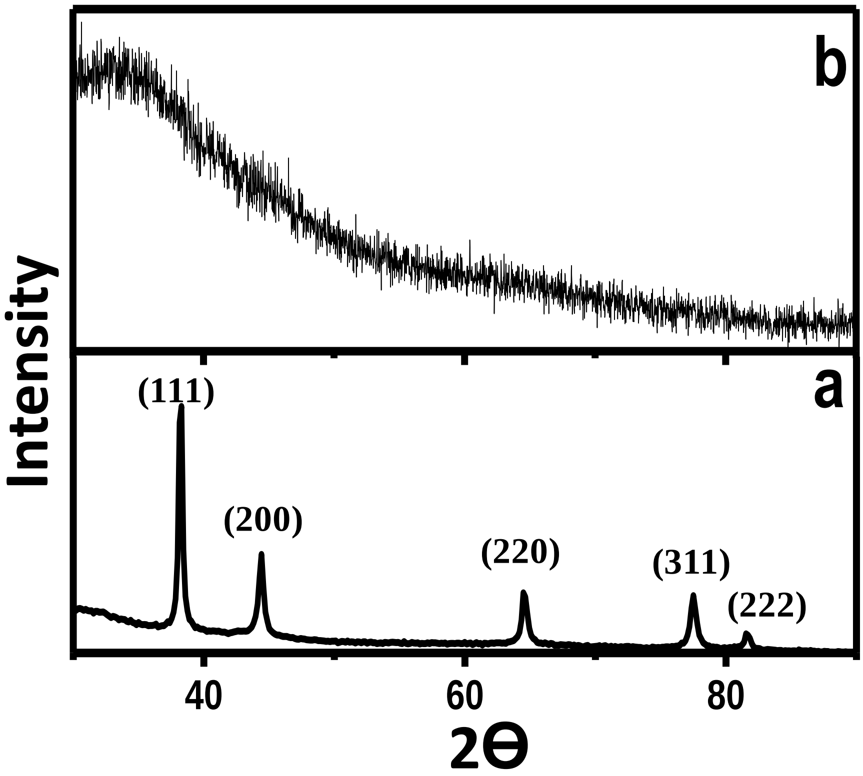


Fig S11. Comparing the X-ray diffraction patterns of (a) Ag@citrate (b) Ag_{QC}@MSA.

S12. Supplementary information 12

Ag_{QC}@SG quantum cluster

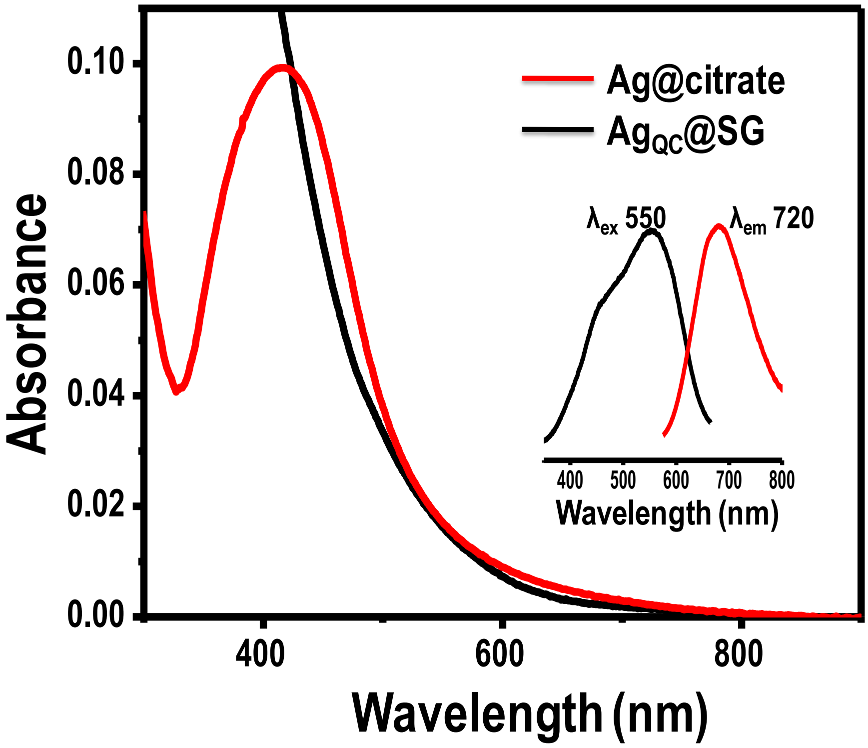


Fig S12. Absorption profile of Ag@citrate and Ag_{QC}@SG cluster upon reaction. Inset shows the luminescence spectrum of the phase transferred Ag_{QC}@SG cluster.