Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

High temperature nucleation and growth of glutathione protected ~Ag_{75} clusters

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Supplementary information

Experimental section

Materials

All the chemicals were commercially available and were used without further purification. Silver nitrate (AgNO3, 99%), glutathione (GSH, 97%), and formic acid (HCOOH, 99%) were purchased from Aldrich.

Instrumentation

UV/Vis spectra were measured with a Perkin Elmer Lambda 25 instrument in the range of 200- 1100 nm. Luminescence measurements were carried out on a Jobin Yvon NanoLog instrument. The band passes for excitation and emission were set as 2 nm. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an Omicron ESCA Probe spectrometer with polychromatic MgKα X-rays (hυ=1253.6 eV). The samples were spotted as drop-cast films on a sample stub. Constant analyzer energy of 20 eV was used for the measurements. High resolution transmission electron microscopy of clusters was carried out with a JEOL 3010 instrument. The samples were drop casted on carbon-coated copper grids and allowed to dry under ambient conditions. Matrix-assisted desorption ionization mass spectrometry (MALDI MS) studies were conducted using a Voyager-DE PRO Bio-spectrometry Workstation from Applied Bio-systems. A pulsed nitrogen laser of 337 nm was used for the MALDI MS studies. Mass spectra were collected in negative ion mode and were averaged for 100 shots ^{1}H NMR were measured with a 500 MHz Bruker Advance III spectrometer operating at 500.13 MHz and equipped with a 5 mm triple-resonance PFG probe. Solutions were made in 99.98 % D_2O (Aldrich) and sealed immediately. The signal of the solvent served as the reference for the field frequency lock. All experiments were performed at a temperature of 25 °C. Standard Bruker pulse programs (Topspin 2.1) were employed throughout. Scanning electron microscopic (SEM) and energy dispersive X-ray (EDAX) analyses were done in a FEI QUANTA-200 SEM. For measurements, samples were drop casted on an indium tin oxide coated conducting glass and dried in vacuum.

S1. Supplementary information 1

Photographs during synthesis

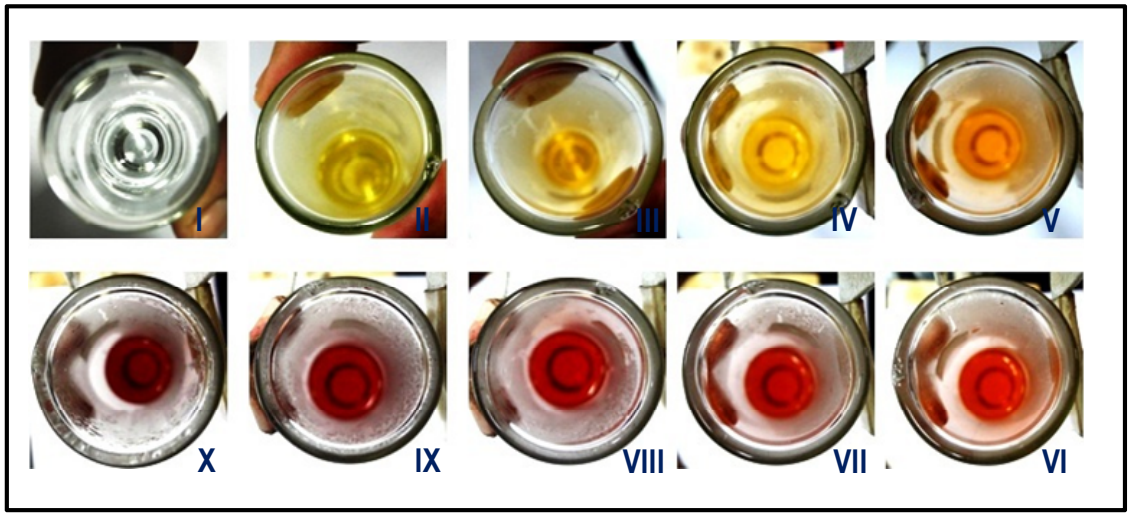

Fig. S1. Top views of the sample tubes during the synthesis of the cluster in different intervals of time, starting from 0 min to 3 hrs. Time was counted after the addition of formic acid.

S2. Supplementary information 2

Plot of absorbance with respect to energy

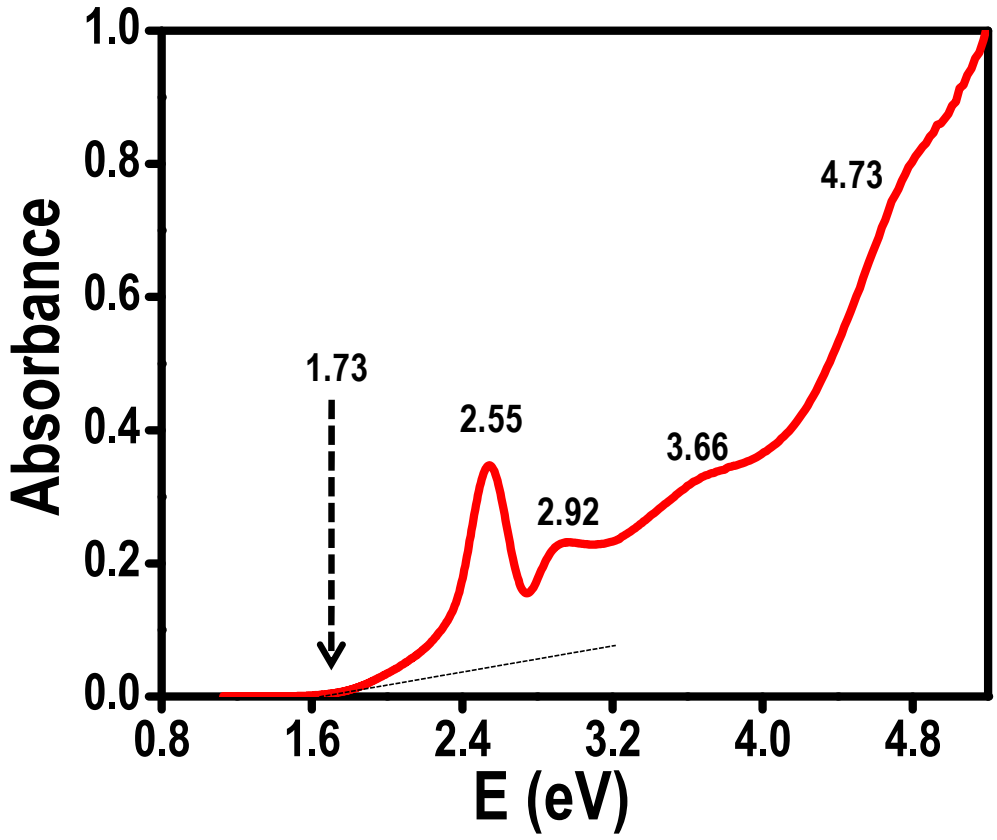

Fig. S2. The absorption spectrum is plotted in energy (eV) axis. Peaks are labeled. The spectrum shows a band gap of 1.73 eV on extrapolation.

S3. Supplementary information 3

Time dependent emission spectra

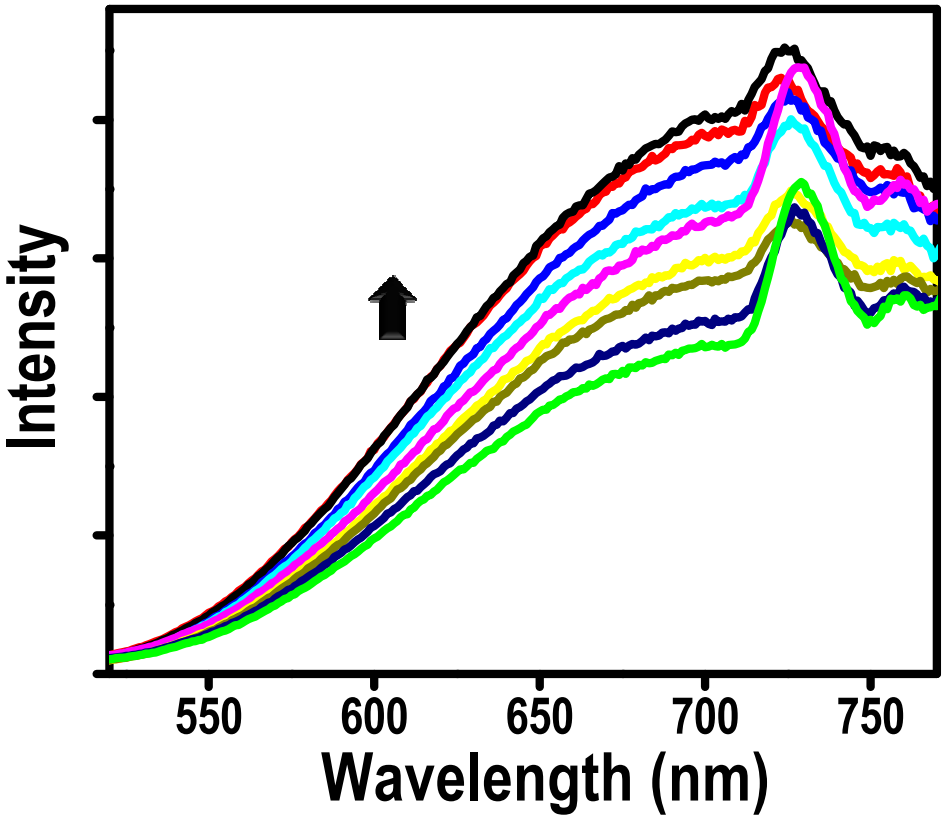

Fig. S3. The time dependent luminescence spectra of as-synthesized Ag@SG cluster that shows gradual increase in emission intensity with time till complete nucleation. It was excited with 400 nm wavelength.

S4. Supplementary information 4

Control experiment with different concentration of GSH

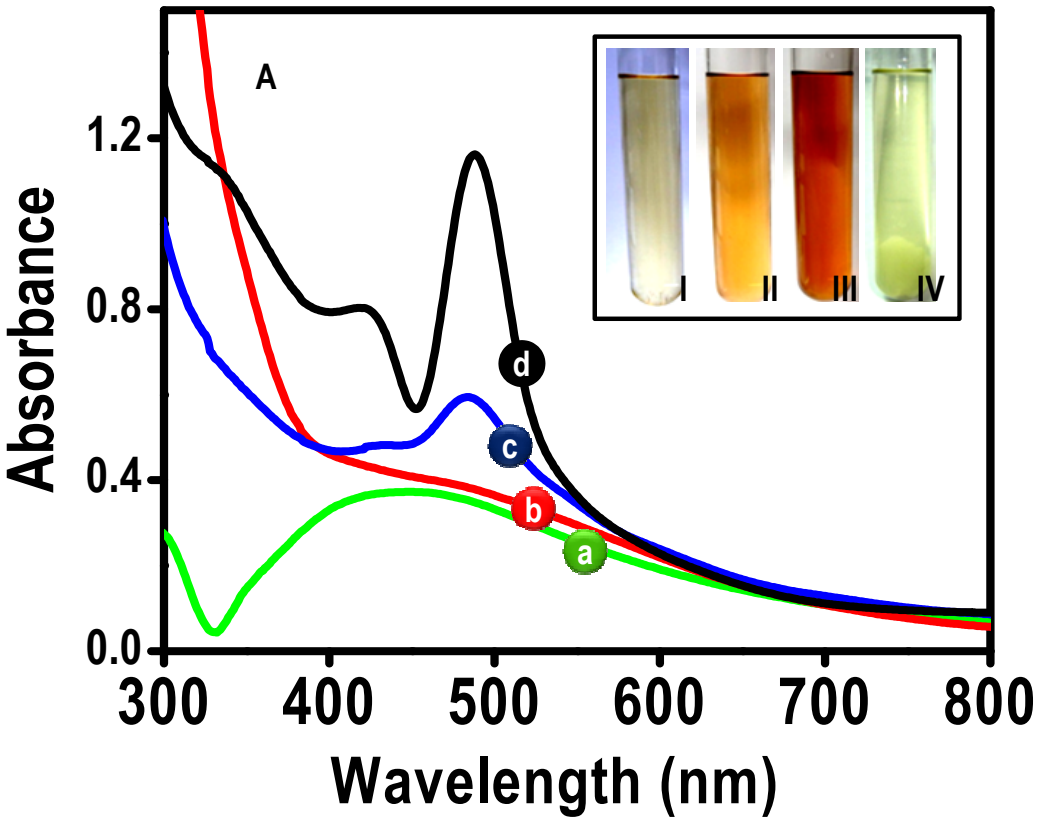

Fig. S4. UV-vis spectra of materials obtained at different concentrations of glutathione keeping the silver nitrate concentration fixed. Traces a, b, c, and d are the spectra associated with 0, 0.1, 0.275 and 0.675 mM of glutathione. Insets are the photographs of the materials formed with 0 (I), 0.1 (II), 0.675 (III) and 1 (IV) mM, respectively.

S5. Supplementary information 5

UV-visible spectrum of the Au@SG cluster

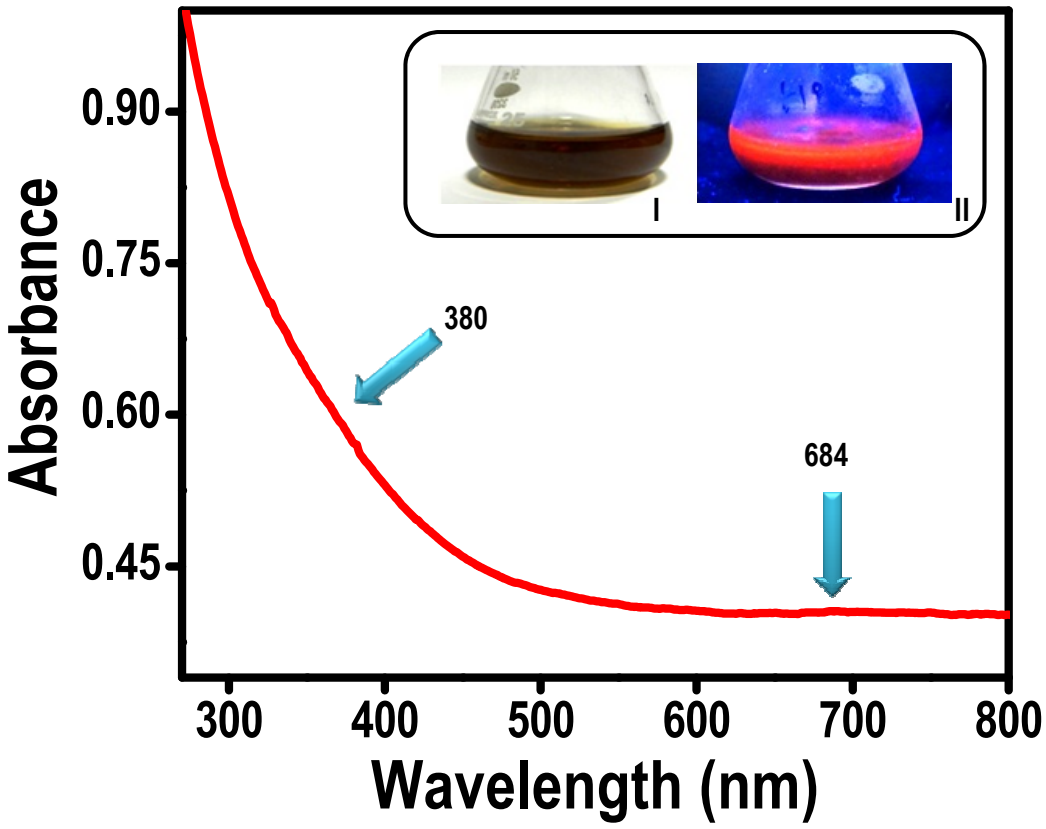

Fig. S5. The absorption spectrum of the Au@SG cluster synthesized using the same reducing agent. Two characteristics humps were observed at 684 nm and 380 nm. Inset is showing photographs under visible and UV light.

S6. Supplementary information 6

HRTEM images of the cluster

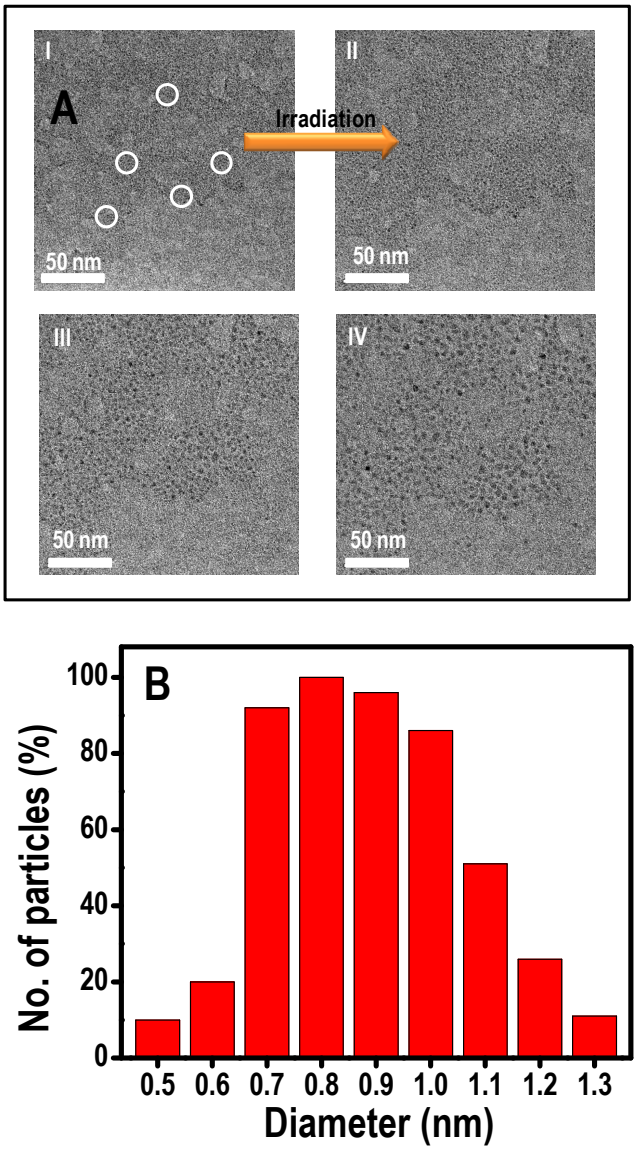

Fig. S6. A (I) HRTEM images of Ag@SG cluster, some areas are marked. II, III and IV are the effect of electron beam irradiation of the same area at a definite time interval (60 sec). It shows gradual increase in cluster size as time progresses. B is the size distribution plot for Ag@SG cluster which is ranging from 0.5 to 1.3 nm with an average diameter of 0.85 nm.

S7. Supplementary information 7

HRTEM images of the ligand exchanged cluster

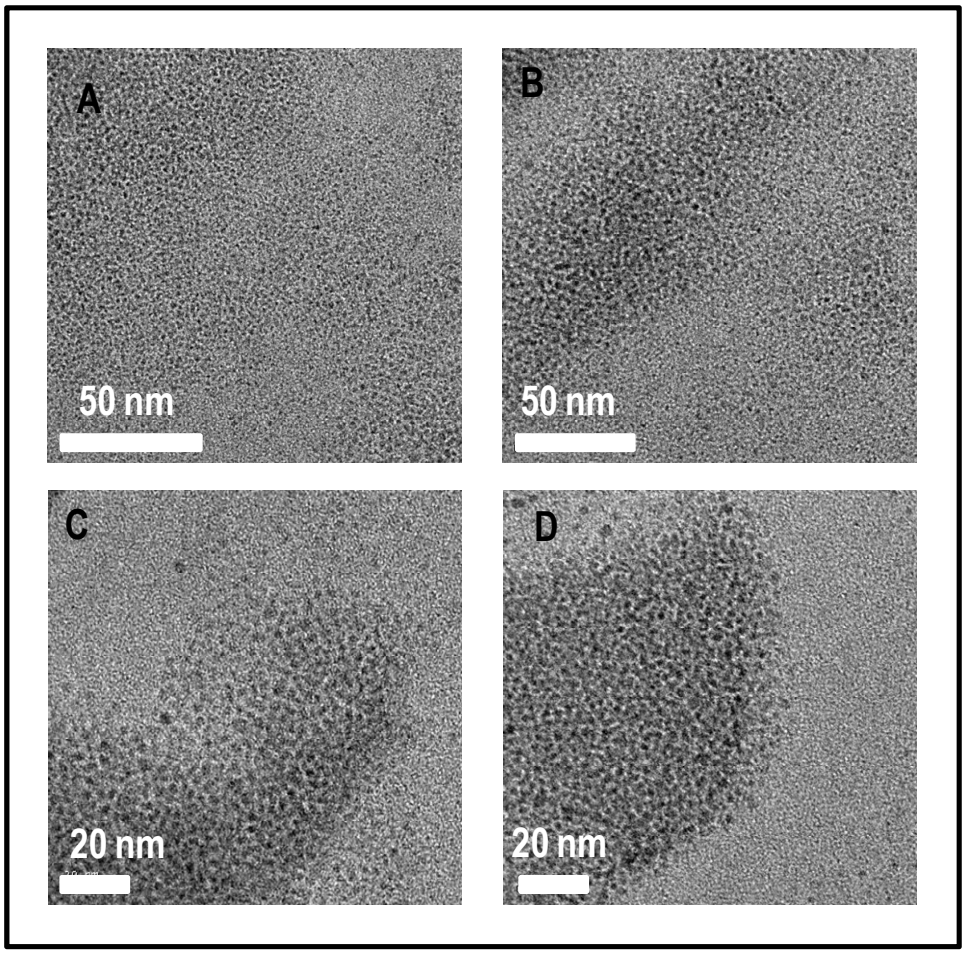

Fig. S7. HRTEM images of Ag@PET clusters. Average diameter of the clusters is almost the same. A, B, C, and D are the different regions taken from the grid.

S8. Supplementary information 8

XPS spectrum of Ag@SG

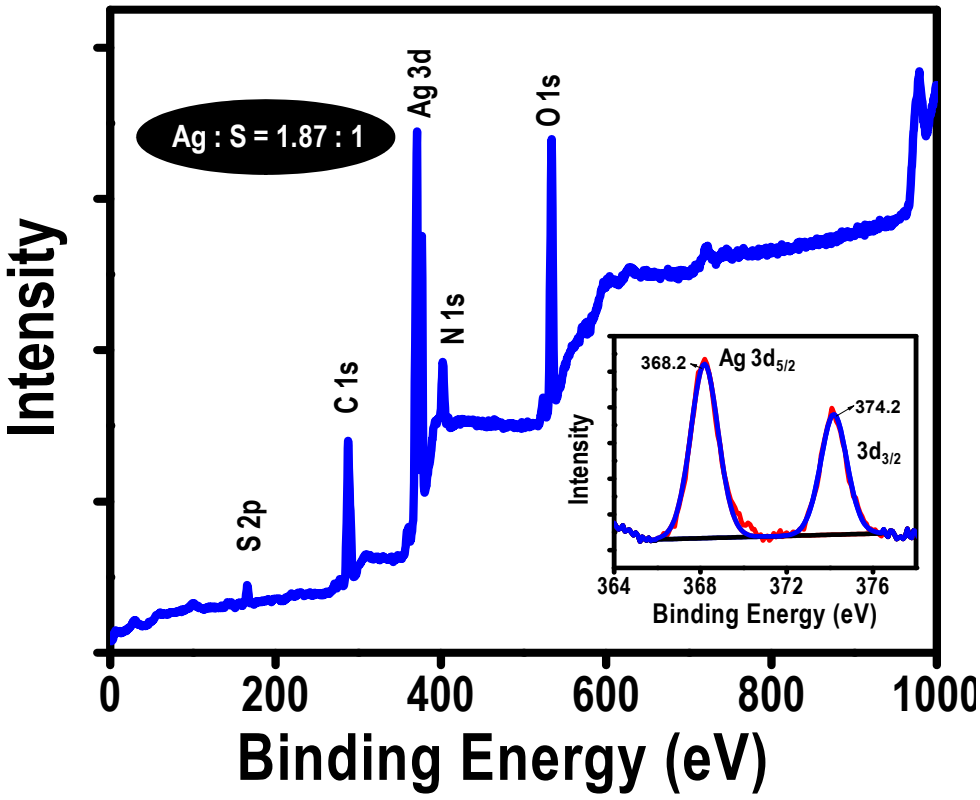

Fig. S8. The XPS survey spectrum of Ag@SG cluster. Individual elements are assigned in the spectrum. Inset is showing the expanded spectrum of Ag 3d. All peaks are labeled.

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Expanded XPS of elements C 1s, S 2p, N 1s, and O 1s

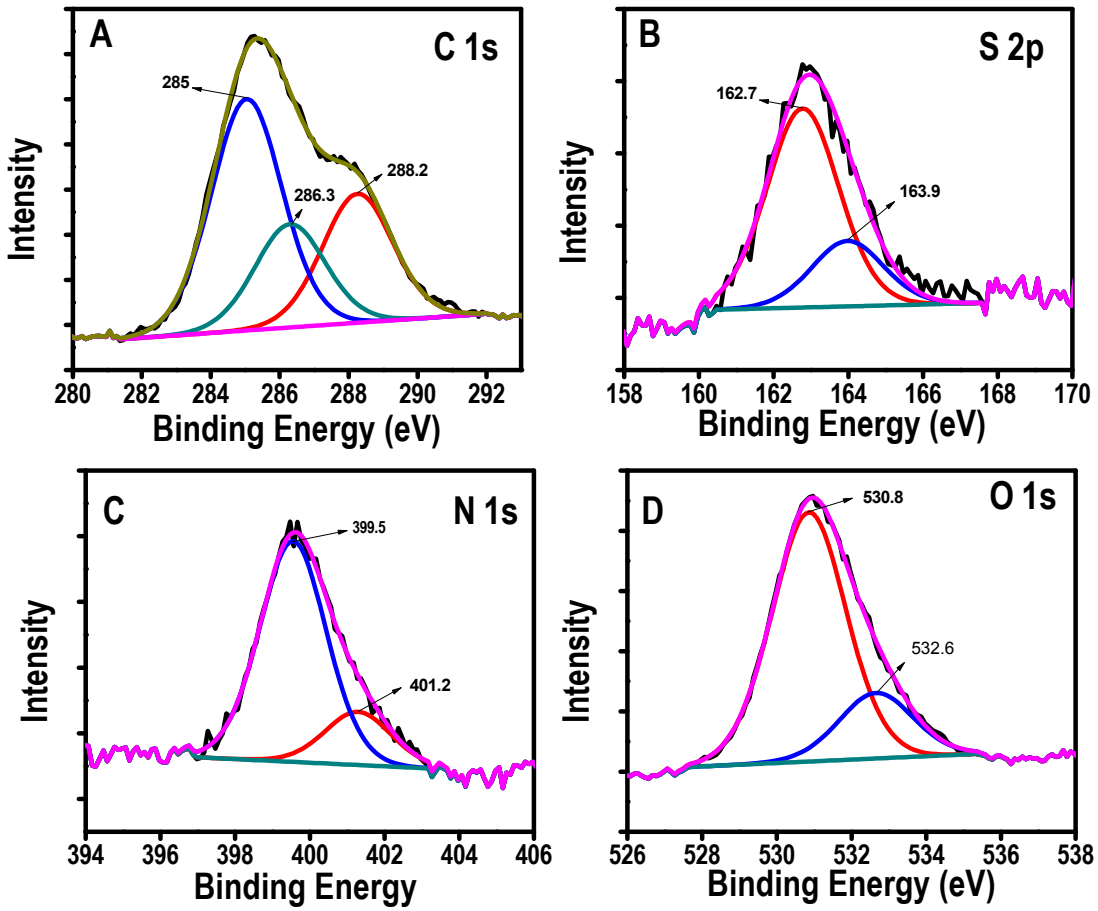

Fig. S9. A, B, C, and D are the expanded regions, C 1s, S 2p, N 1s, and O 1s, respectively. All the spectral features have been fitted into the different chemical species expected.

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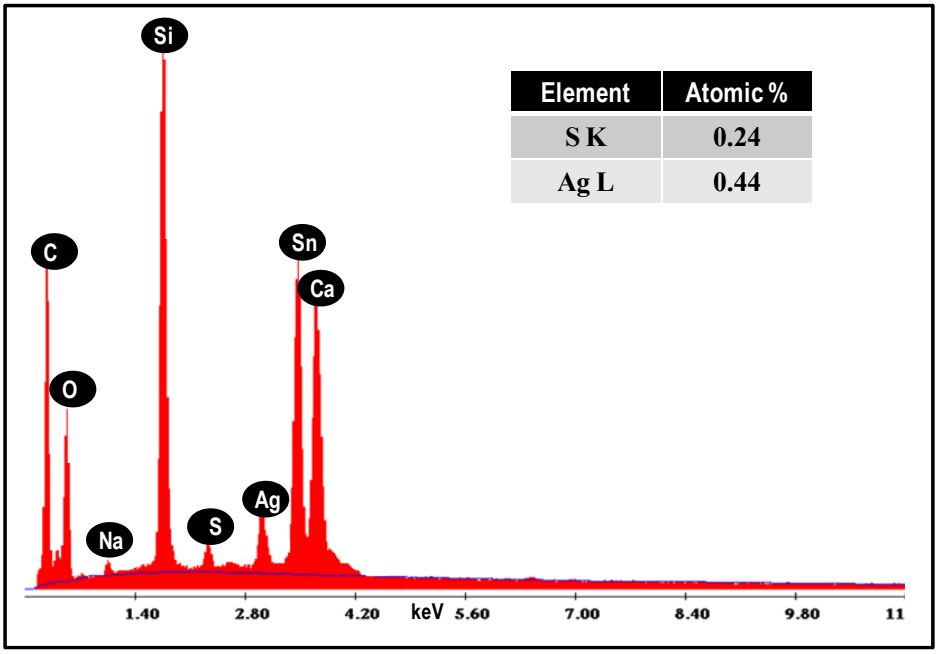
EDAX spectrum of the Ag@SG cluster



Element	Atomic %
S K	0.24
Ag L	0.44

Fig. S10. SEM EDAX spectra of the as-synthesized cluster. Inset is a table showing individual elemental percentages. Elements such as Si and Sn in the spectrum are from the substrate.

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CD spectra of the Ag@SG cluster

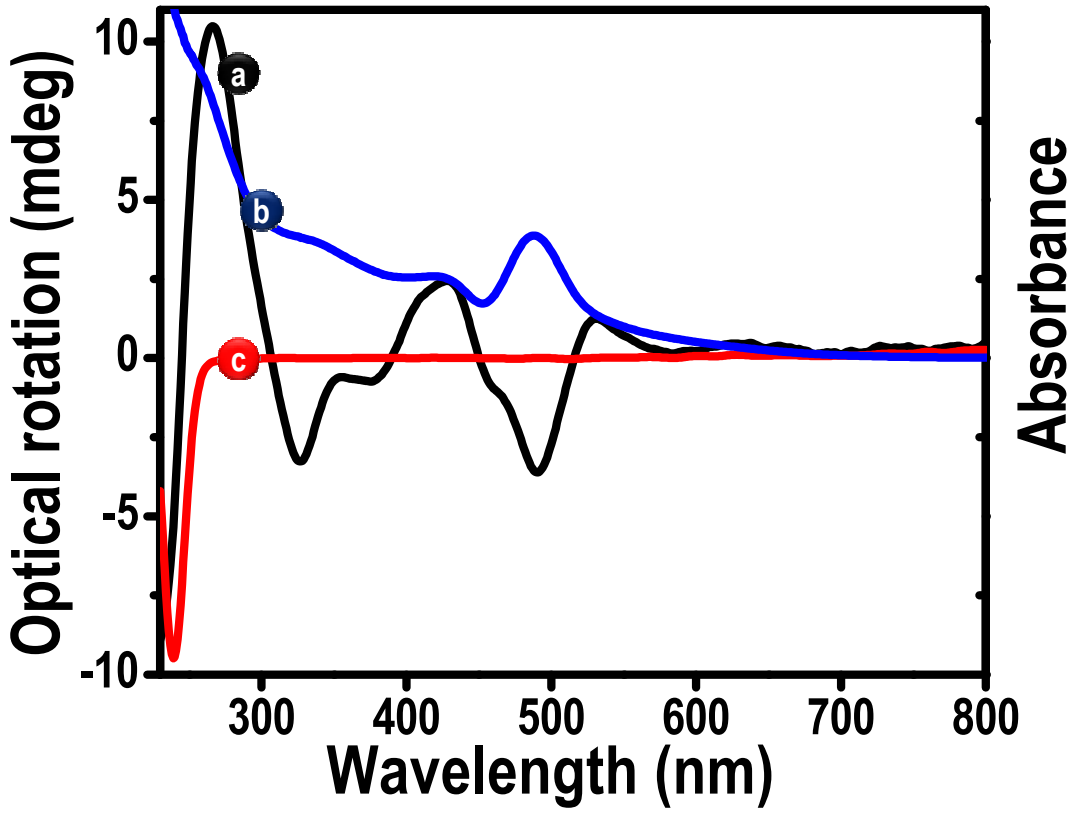

Fig. S11. CD spectra of as-synthesized Ag@SG cluster (a) and GSH ligand (c) which shows that the chirality of the cluster is from its silver core. For comparison, the absorption spectrum of the cluster is also plotted (b).