

Supplementary information for paper

Sunlight mediated synthesis and antibacterial properties of monolayer protected silver clusters

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Supporting information 1.

Phase transfer of cluster

The silver cluster is protected with glutathione and is water soluble. This cluster can be transferred from the aqueous to the toluene phase by the phase-transfer reagent, tetraoctylammonium bromide (TOABr). For this, an aqueous solution of cluster (5 mg/mL) was mixed with 5 mM TOABr in toluene and stirred vigorously for 2 min. Silver clusters underwent immediate and complete phase transfer from the aqueous to the toluene layer. The phase transfer can be monitored visually by the color changes in the aqueous and toluene layers. The colorless toluene layer turned reddish brown and the aqueous layer, which was originally reddish brown, turned colorless after stirring. The phase transfer occurred by the electrostatic attraction between the hydrophilic carboxylate anion of the glutathione ligand on the cluster in the aqueous phase and the hydrophobic tetraoctylammonium cation in the toluene phase.

Supporting information 2

Large scale synthesis of Ag@SG clusters

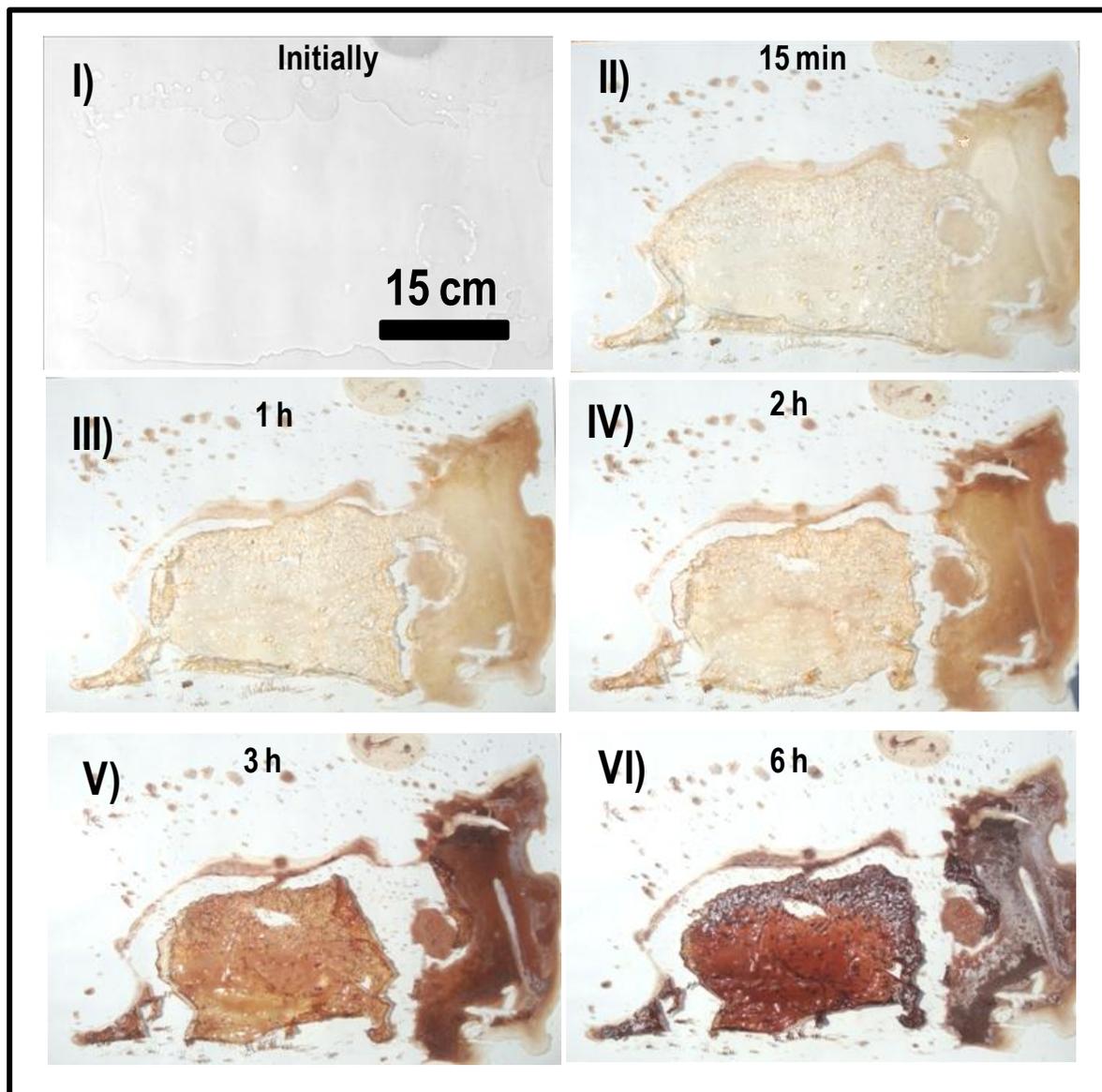


Fig. S2. Polyacrylamide solution along with Ag (I) SG was spread on a glass plate and kept under sunlight for six hours to complete the reaction. I) to VI) show the progress of the reaction with time.

Supporting information 3

Extraction of the cluster

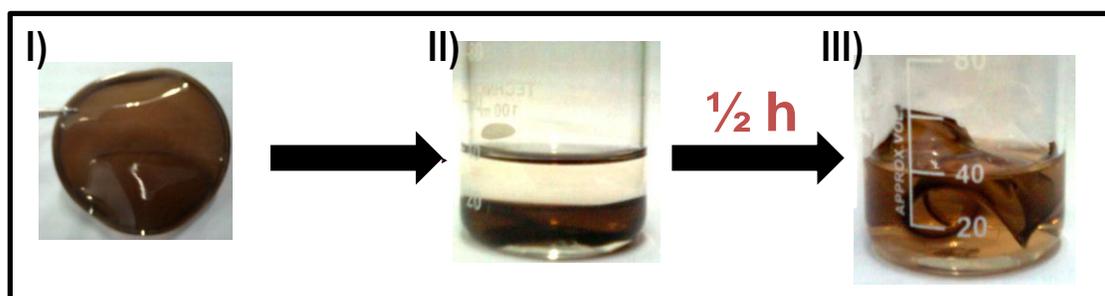


Fig. S3. I) Photograph of the gel template containing Ag@SG clusters. II) These templates were soaked in water for 30 min. III) The clusters were dispersed and the gel remained insoluble.

Supporting information 4

Evaluation of cluster growth monitored by UV

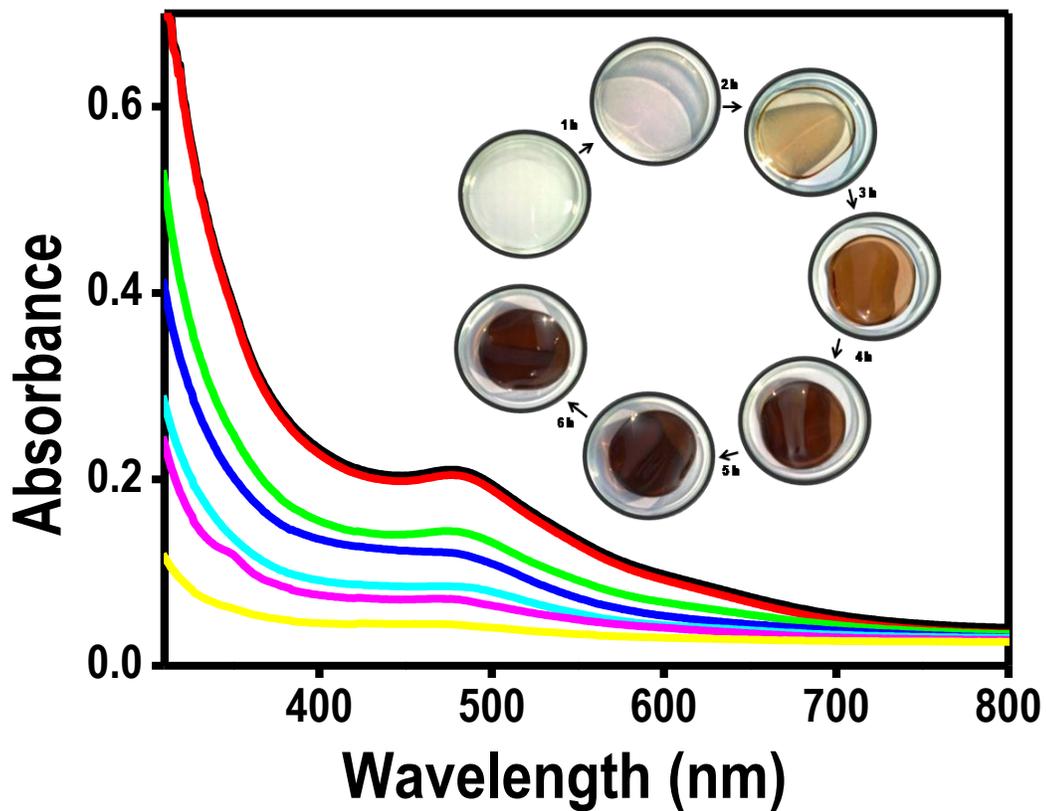


Fig. S4. Time dependent UV/Vis spectra during Ag@SG cluster evaluation. Corresponding photographs are shown in inset.

Supporting information 5

HRTEM images

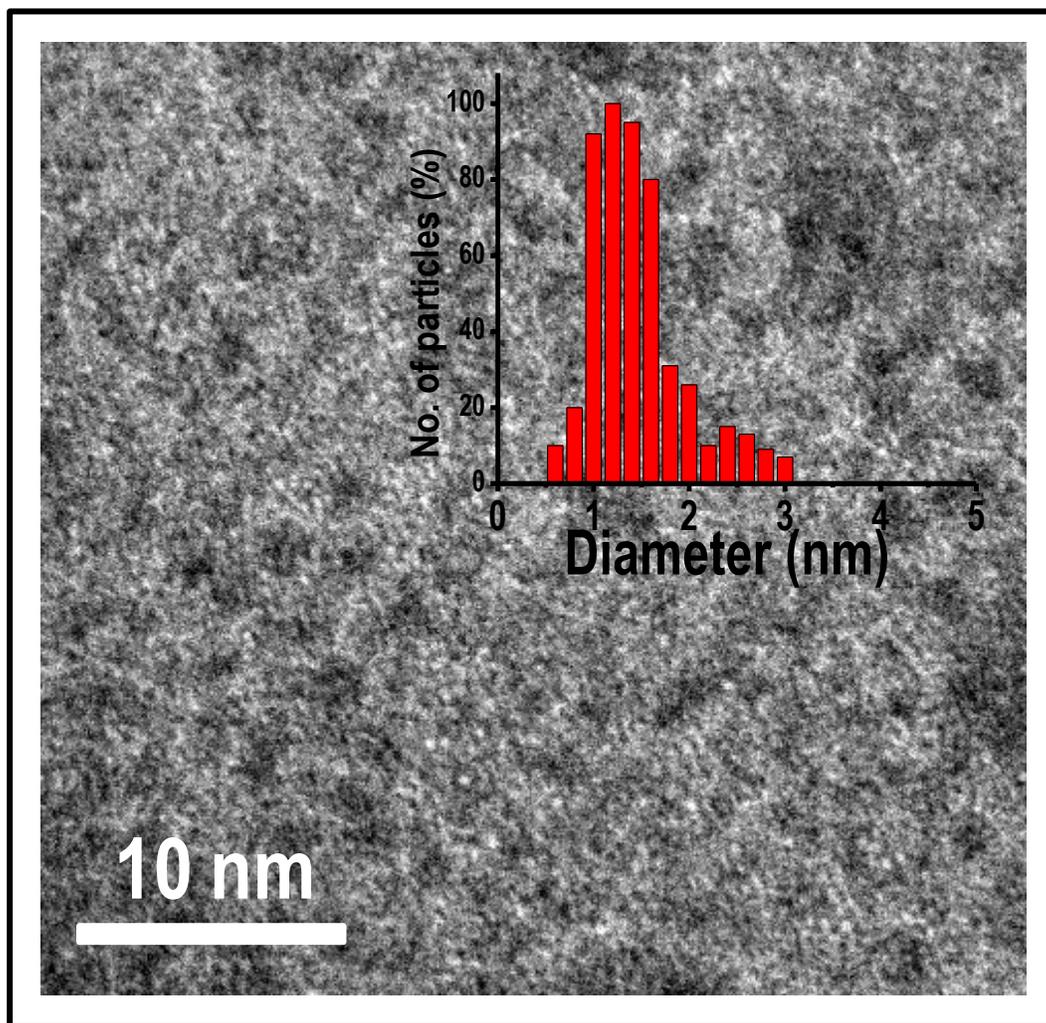


Fig. S5. HRTEM image of Ag@SG clusters. Inset shows the size distribution of clusters indicating an average size of 1.6 nm.

Supporting information 6.

XPS survey spectrum

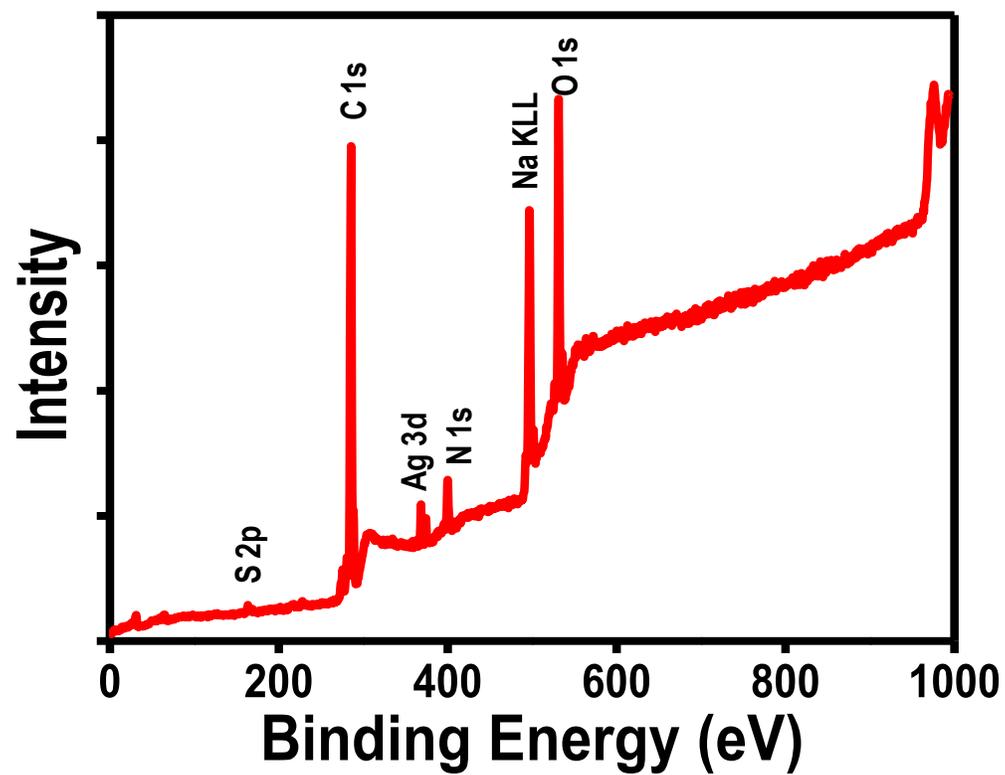


Fig. S6. XPS survey spectrum of the as-synthesized cluster. Individual peaks are labeled.

Supporting information 7.

Elaborated XPS spectra for individual regions

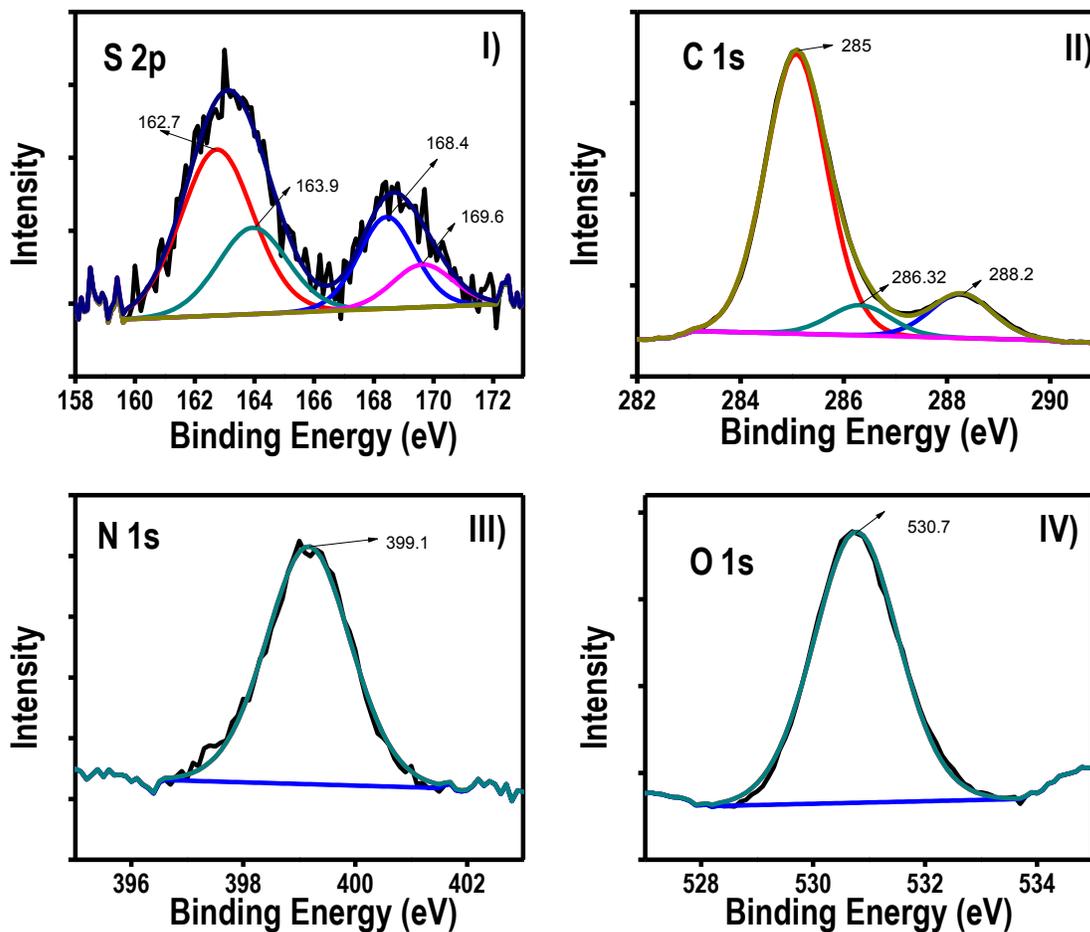


Fig. S7. XPS spectra for individual regions. Spectra were fitted using Casa XPS software.

Supporting information 8

IR spectra of GSH and AgQCs

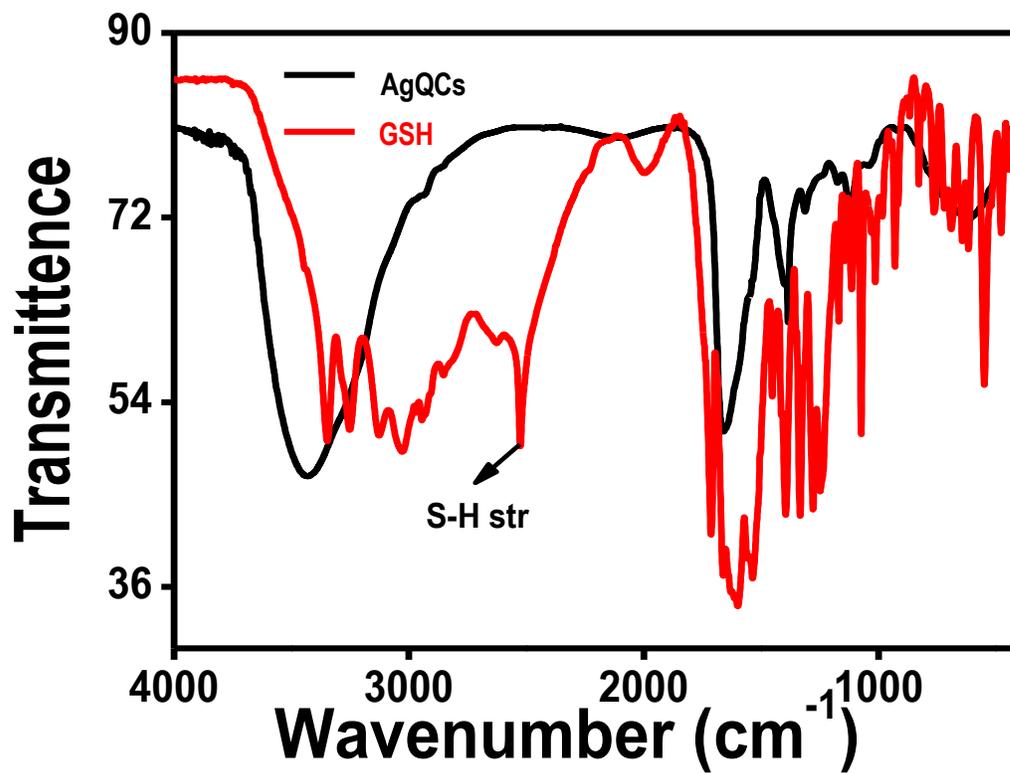


Fig. S8. Comparative IR spectra of AgQCs and GSH. The absence of band at 2552 cm⁻¹ confirms the attachment of glutathione to the cluster core.

Supporting information 9

ESI MS data of Ag@QC

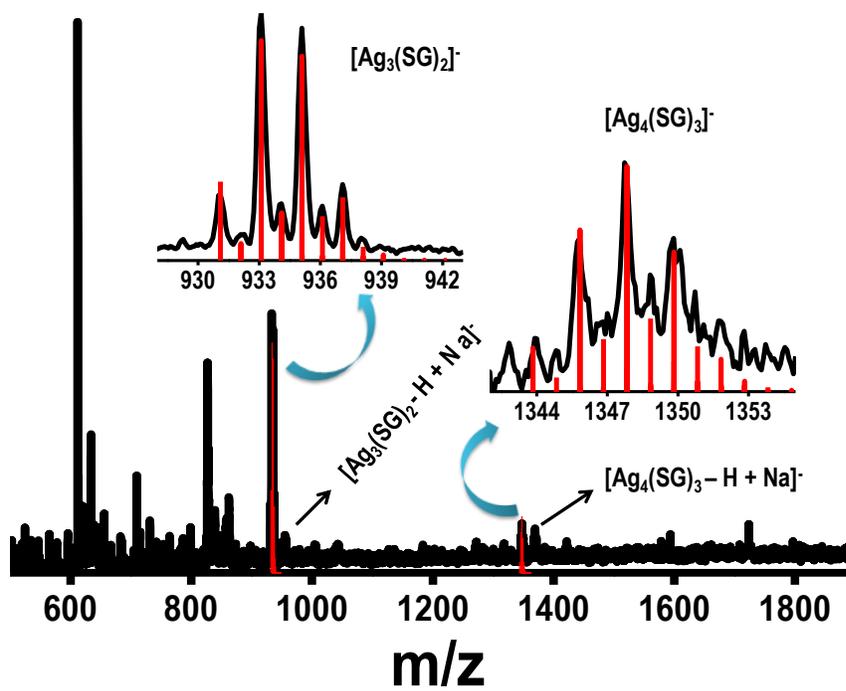


Fig. S9. ESI mass spectrum of as-synthesized cluster in negative mode. Inset shows some fragments with good isotope distribution.

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Excitation and emission spectra of the cluster, synthesized using different filters

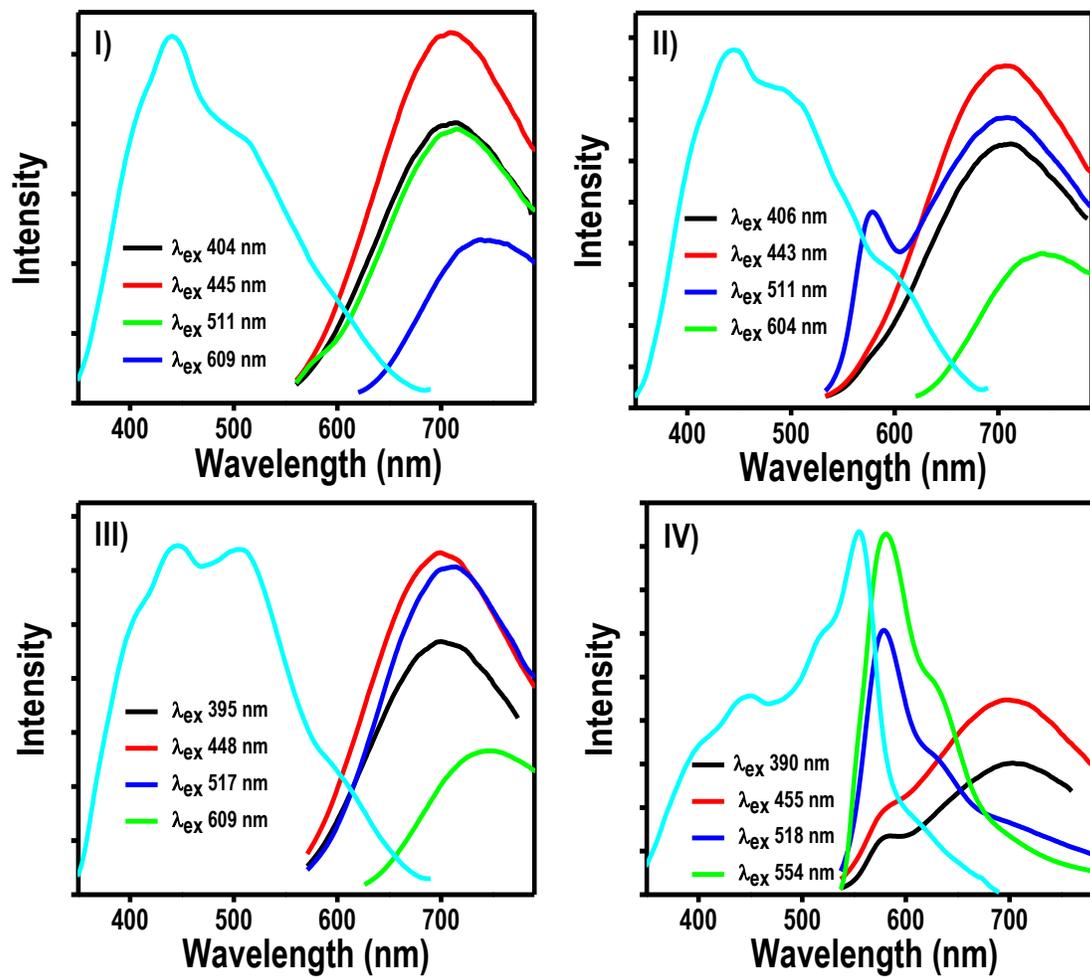


Fig. S10. Excitation and emission spectra of C_R (I), C_Y (II), C_G (III) and C_B (IV).

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Reaction in dark

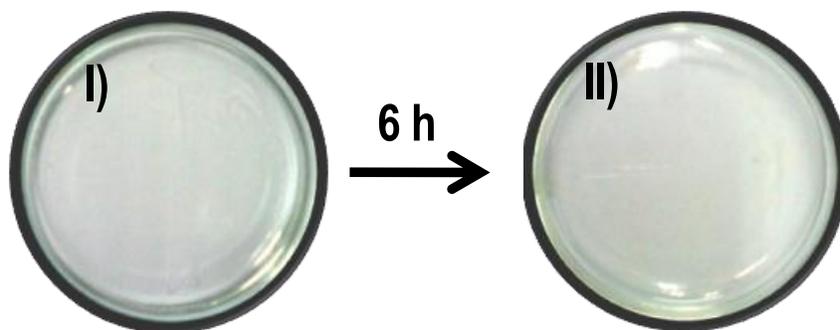


Fig. S11. I) Photograph of the polymeric gel + Ag(I)SG taken in a petri dish kept in dark. Note that gel is transparent. II) After six hours, the same petri dish shows no change in color indicating the absence of reaction under dark conditions.

Supporting information 12

Effect of heat, in the absence of sunlight



Fig. S12. I) Polymerized acrylamide gel along with Ag(I)SG. II) Sample covered with aluminium foil and exposed to sunlight in outdoor air. III) No visible color change after 6 h of exposure to sunlight. The ambience was at 35°C.

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Oligomeric Ag (I) SG in water and in sunlight

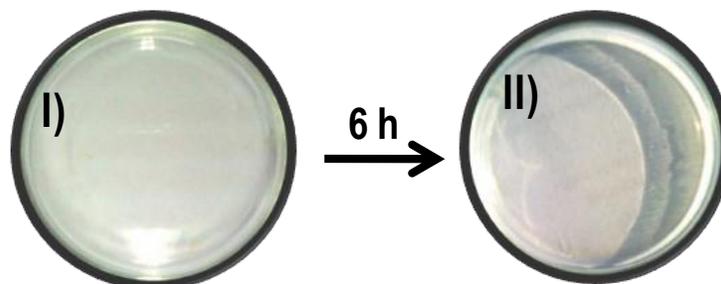


Fig. S13. I) Photograph of the Ag(I)SG in water taken in a petri dish kept under sunlight. II) After six hours the petri dish does not show any change in color indicating that the reaction did not occur.

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Effect of acetonitrile in the absence of gel

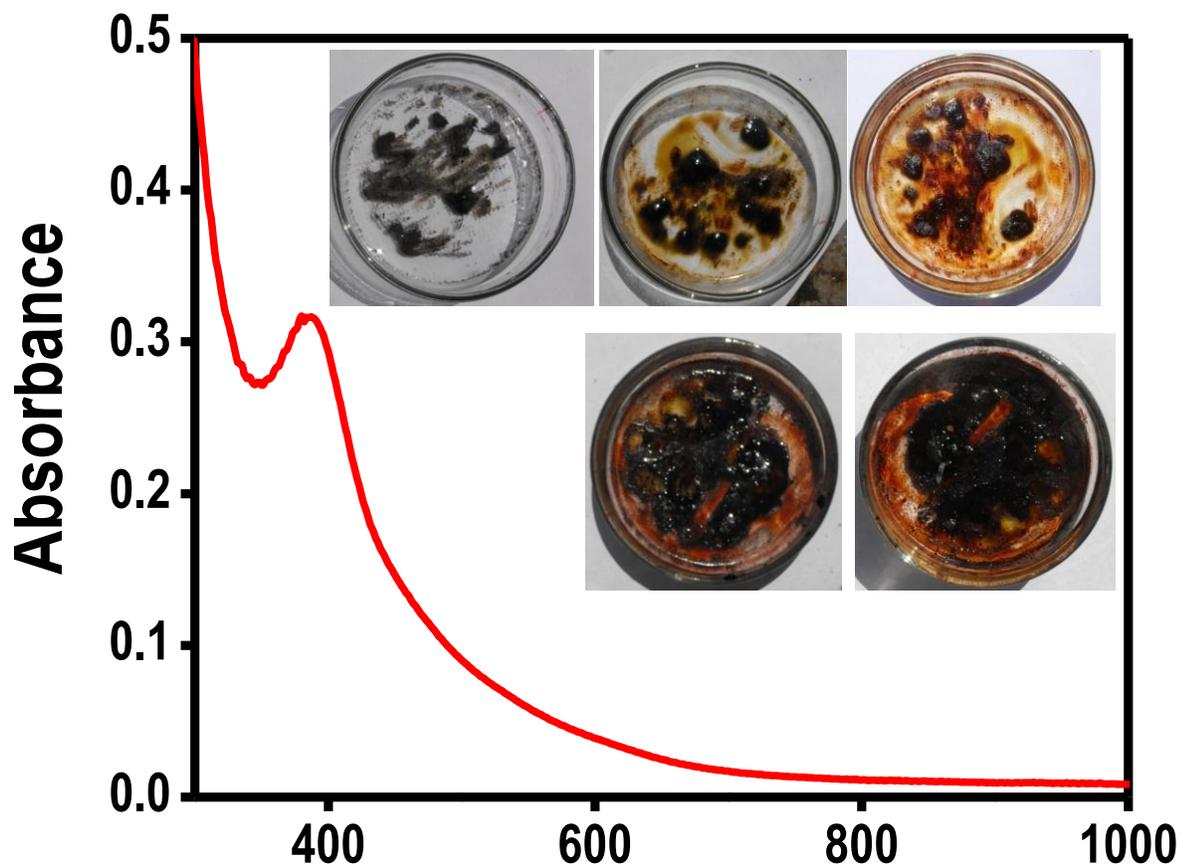
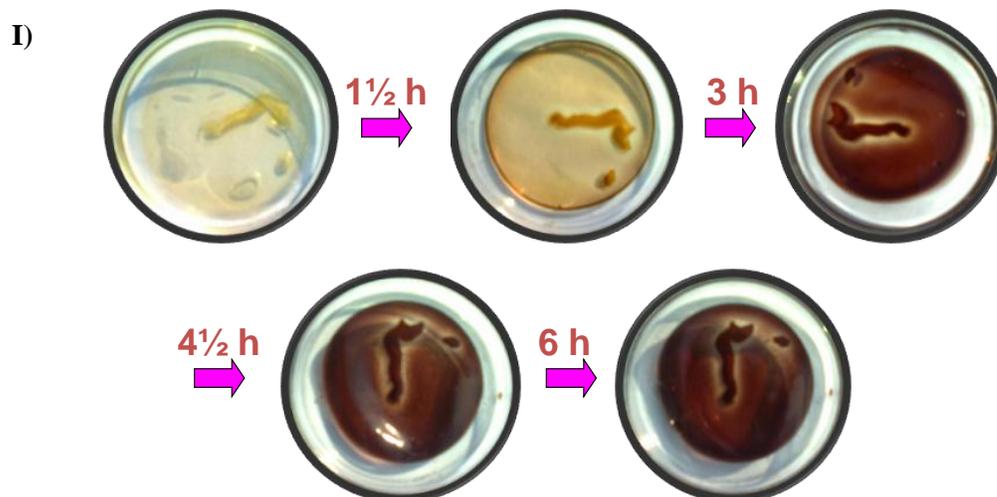


Fig. S14. UV/Vis spectrum of the material formed when acetonitrile was taken in place of gel. Inset shows photographs at different time intervals. This shows the formation of plasmonic nanoparticles.

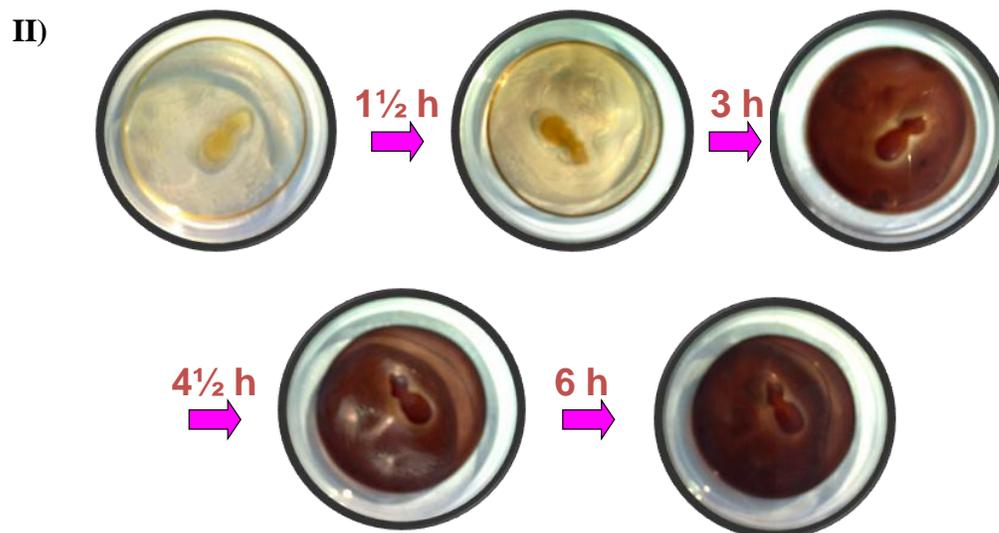
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Effect of various solvent during cluster growth

Toluene:

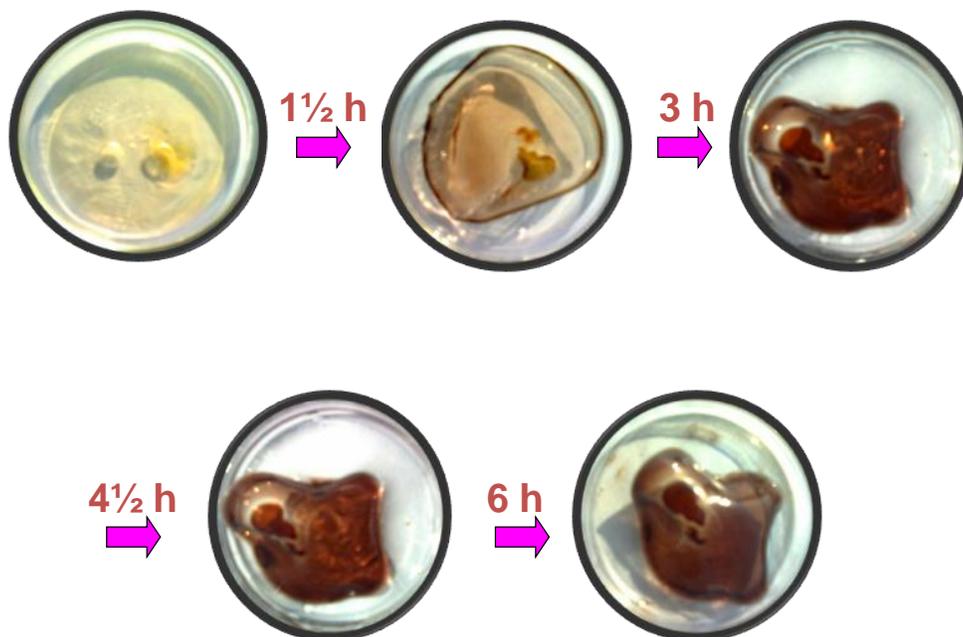


Methanol



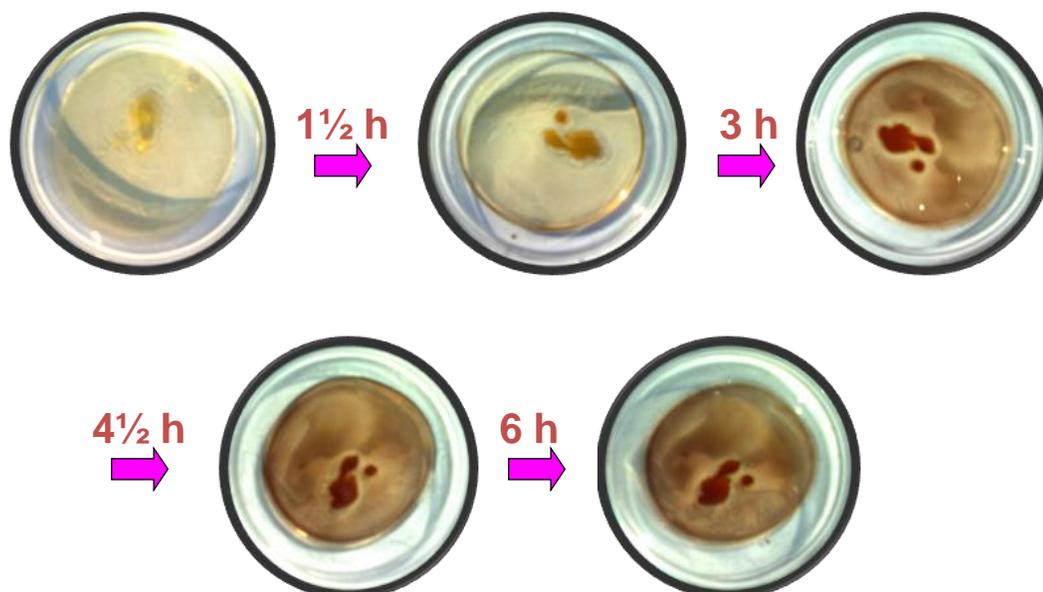
Acetonitrile

III)

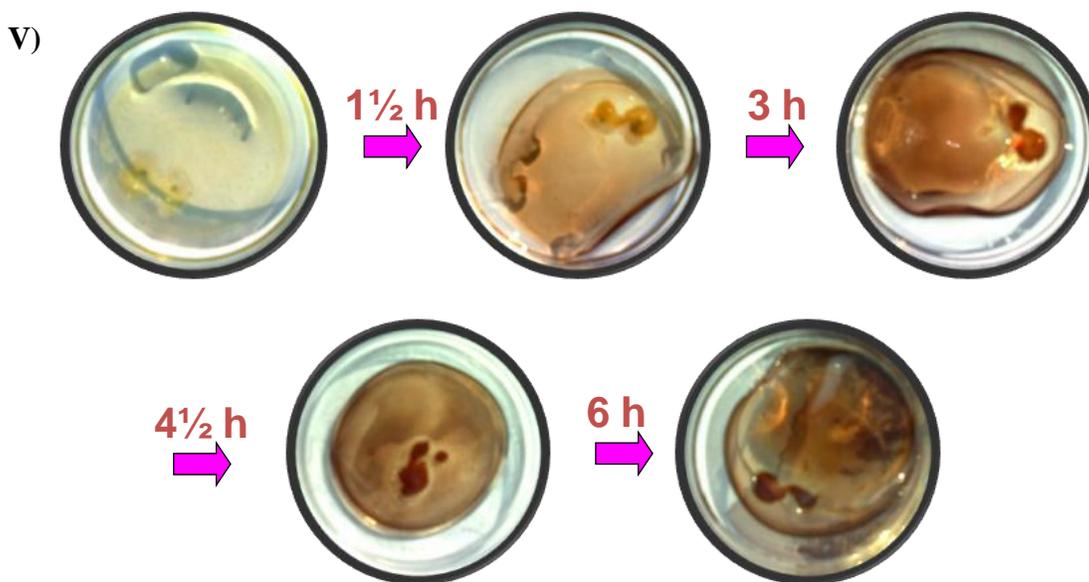


Tetrahydrofuran

IV)



Dimethyl formamide



Water

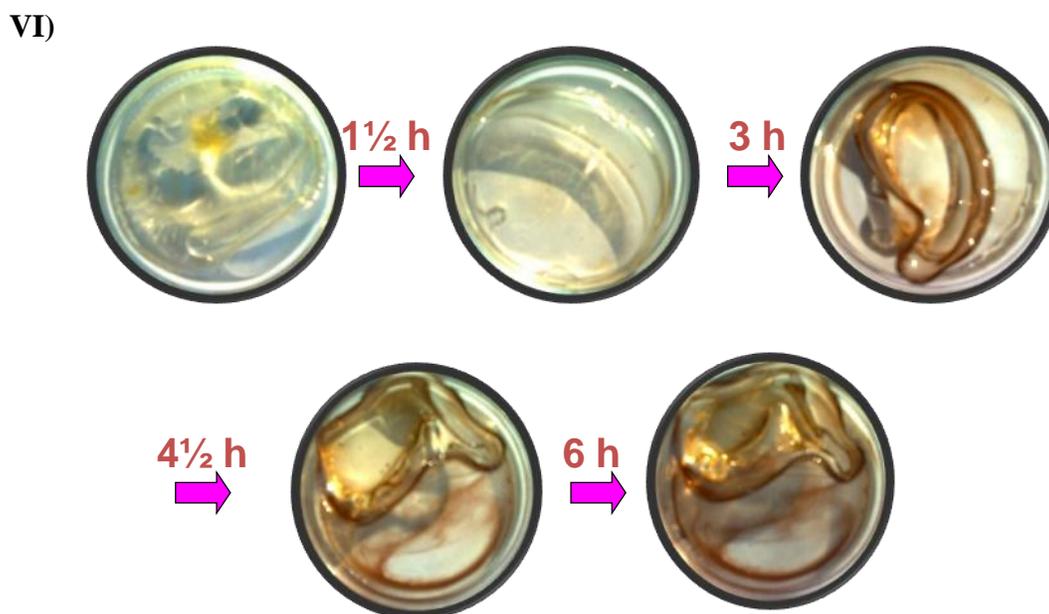


Fig. S15. Effect of various solvents: (I) toluene, II) methanol, III) acetonitrile, IV) tetrahydrofuran, V) dimethyl formamide and VI) water during cluster growth. Solvent volume was kept constant. In water, the clusters were extracted.

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Evaluation of Ag@MSA cluster growth

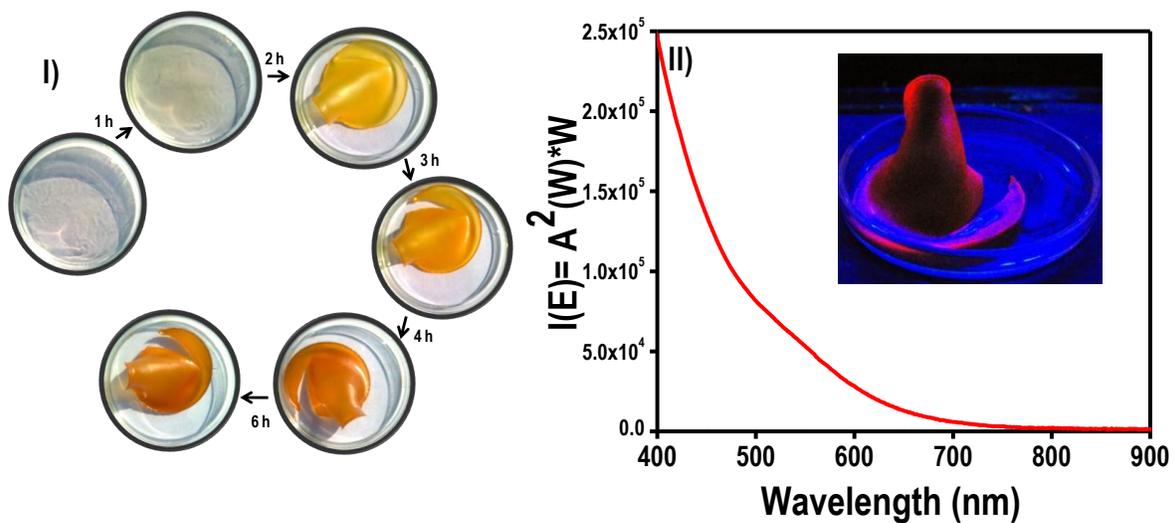


Fig. S16. I) Polymerized acrylamide gel along with Ag (I) MSA. Photographs are of different periods of exposure of sample to sunlight. II) UV/Vis spectrum of Ag@MSA clusters extracted after 6h of exposure. Inset of II) shows a photograph of the sample collected under UV lamp showing red luminescence.

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Evaluation of Ag@cysteine cluster growth

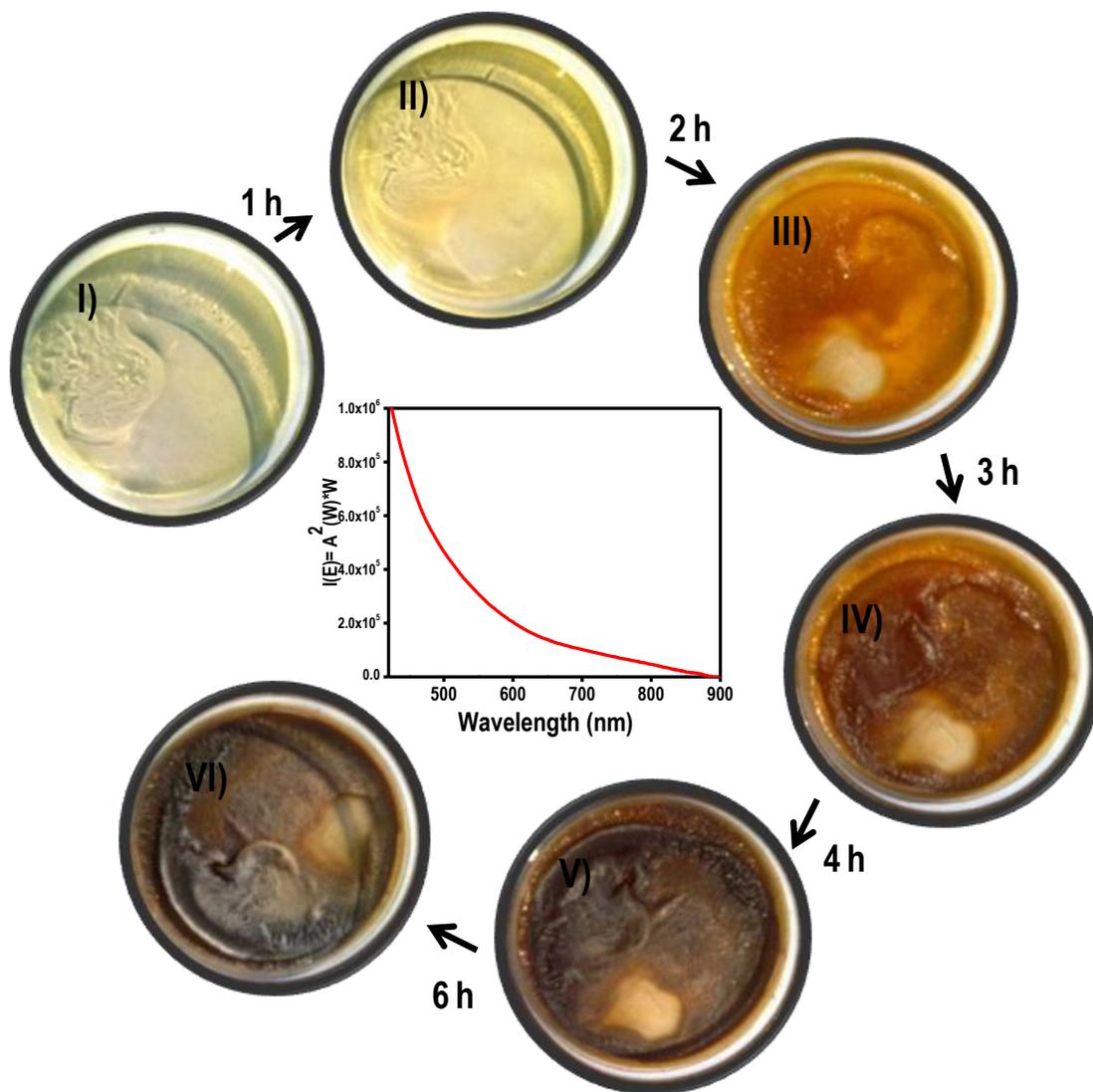


Fig. 17. Polymerized acrylamide gel along with Ag(I)cysteine. I) to VI) are different periods of exposure of sample I) to sunlight. Inset is the UV/Vis spectrum of Ag@cysteine clusters extracted from sample VI).

Supporting information 18.

Gold cluster evolution

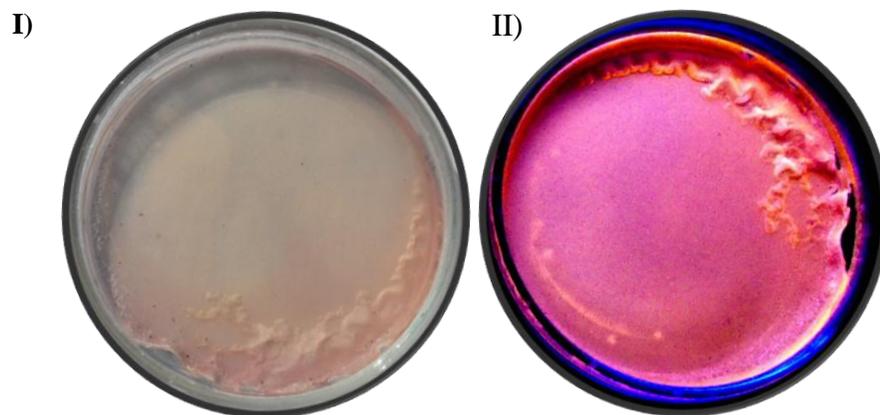


Fig. S18. The photographs of gold cluster made using the same synthetic method. I) Under visible light, and II) under UV light. Intense red fluorescence confirms the formation of clusters.

Supporting information 19.

Antibacterial study with gram positive bacteria

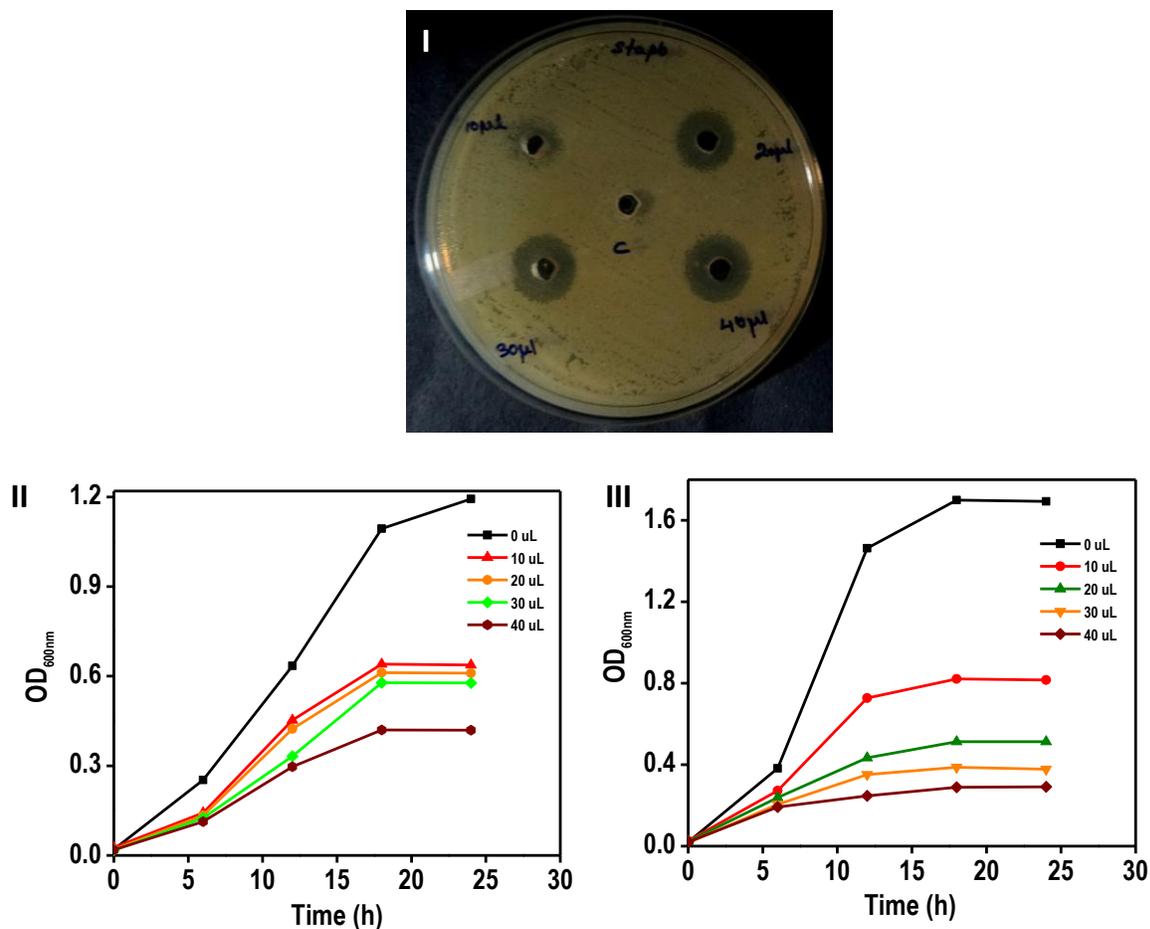
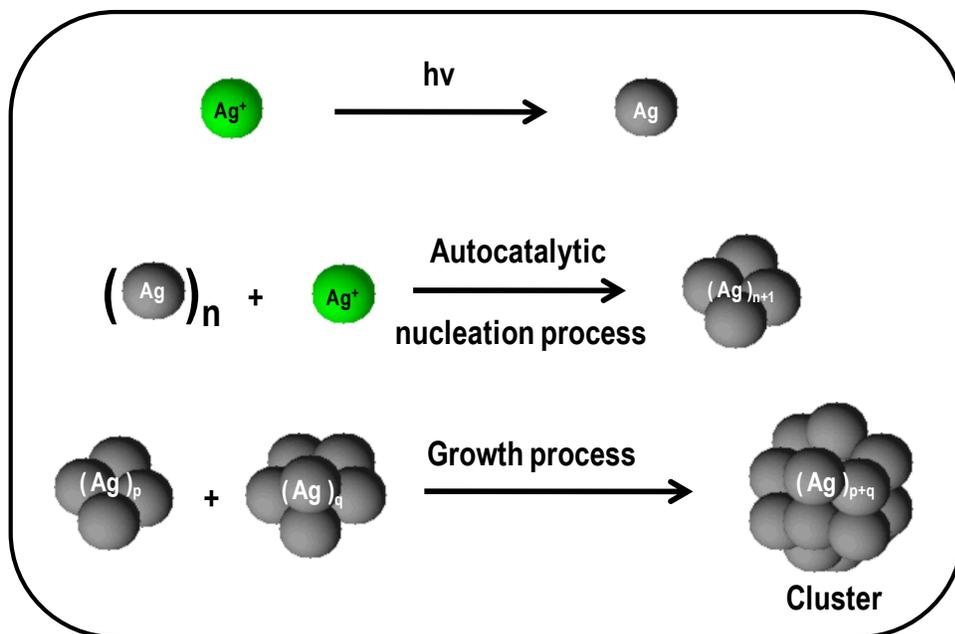


Fig. S19. The antibacterial activity of monolayer protected AgQCs against gram positive bacteria *Staphylococcus aureus* (I). Four different concentrations were used. II and III are the solution based antibacterial study for gram positive and gram negative bacteria, respectively. The spectra show the pronounced effect of AgQCs over gram negative compared to gram positive bacteria.

Scheme 1.



Schematic view of the formation of Ag@SG cluster by photoreduction.