Supporting Information

Amino Acid Based Smart Hydrogel: Formation, Characterization and Fluorescence Properties of Silver Nanoclusters within the Hydrogel Matrix

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Experimental Section.

General Methods and Materials.

9-fluorenylmethyl Choloroformate (Fmoc-Cl) and L-Phenylalanine were purchased from local chemical SRL. $AgNO_3$, 1, 4-dioxane, sodium carbonate etc were purchased from Merck. Atto 520 dye was purchased from Fluka.

Synthesis of Fmoc-Phe-OH.

Fmoc-protection of L- phenylalanine:

Fmoc-protected amino acid was synthesized by standard methods (10.0 mM of L- phenyl alanine, 30 mL of 1 (M) Na_2CO_3, 1:1 dioxane–H_2O, 0°C, 10 min; then 10 mM of Fmoc-Cl at 25°C, 6 hrs). Upon acidification to pH 5~6, the product was precipitated out and the suspension was filtered. The residue was washed with H_2O and hexanes, and dried in *vacuum* desiccators to give Fmoc-Protected L- Phenylalanine as a white solid with 90 % yield. The Fmoc-L-Phenylalanine has been characterized by mass spectrometry, 300 MHz ^{1}H NMR spectroscopy, FT-IR spectroscopy and ^{13}C.

m.p. = 182°C.

300 MHz ^{1}H NMR (DMSO-d_6, δ ppm, 26°C): 12.74 (CO_2H, 1H, br); 7.87 (NH, 1H, d, J= 7.47); 7.73-7.19 (aromatic proton, 13H, m), 4.20-4.13 (CH_2 and CH of N-(9-Fluorenylmethoxycarbonyl) and α-proton of L-phenyl alanine, 4H, m); 3.11-2.82 (CH_2, 2H, m).

^{13}C NMR 75 MHz (DMSO-d_6, δ ppm, 26°C): 173.32 (CO_2H of Phe), 155.93 (amide bond Carbonyl group), 143.74, 140.67, 137.99, 129.09, 128.15, 127.60, 127.04, 126.34, 125.24, 120.05, 65.62 (CH_2 of N-(9-Fluorenylmethoxycarbonyl)), 55.51, 46.60 and 36.51 (CH_2 of Phe).

Anal. Calcd. For $C_{24}H_{21}NO_4$ (387.15) C, 74.4 and H, 5.46; N, 3.62: found C, 74.38; H, 5.41 and N, 3.58. ESI-MS: m/z $(M+Na)^+$ = 410.1242 and $(M+K)^+$ = 426.0924.

FT-IR: Amide A, 3431.13; Amide I, 1687.60 and Amide II, 1537.16.

UV-Vis spectroscopic analysis.

We have used a Cary Varian 50 scan UV-Vis optical spectrometer equipped with 'Cary Win' UV software to elucidate the optical properties of the Ag-nanoclusters-hydrogel matrix. Actually, the silver nanocluster has been synthesized in an optical quartz cell within the hydrogel matrix. The *in situ* formation of Ag-nanoclusters has been monitored time to time over a range of wavelengths 300-700 nm.

NMR Experiments.

All 300 MHz NMR studies have been carried out on a Brüker DPX 300 MHz spectrometer at 300 K.

Mass Spectrometry.

Mass spectra have been recorded on a Q-tof Micro YA263 high-resolution mass spectrometer.

Fluorescence spectroscopy.

Fluorescence studies of the hydrogel in a sealed cuvette have been carried out in a Horiba Jobin Yvon Fluoromax 3 instrument. The gel sample in a quartz cell of 1 cm path length has been excited at 265 nm wavelength and emission scans have been recorded from 285 to 550 nm using a slit width of 2 nm. The Ag-nanoclusters-hydrogel hybrid sample has been excited at 500 nm and the corresponding emission at 629 nm using same slit width.

Actual quantum yields have been generally measured relative to an optically dilute standard fluorophore solution that exhibits a well-known quantum yield (ϕ_s). The quantum yield of an unknown fluorophore (ϕ_u) has been determined using the parker-rees method.[29]

$$\phi_u = (A_s F_u n_u^2 / A_u F_s n_s^2) \times \phi_s$$

Where, A_u denotes the absorbance of the unknown sample at the excitation wavelength, F_u represents the total, integrated fluorescence intensity for the unknown sample when it is excited at the same excitation wavelength of the unknown sample, F_s is the integrated fluorescence intensity of the reference sample when it is excited at the same excitation wavelength of the known sample. The refractive indices of the solvents in which the unknown and the standard samples have been prepared, are given by N_u and N_s respectively. Here, in our study we have selected atto-520 in water as a standard and its quantum yield (ϕ_s) is known to be 90 % in water. The quantum yield of the silver nanoclusters has been determined to be 3.76 %.

Field Emission Scanning Electron Microscopy (FE-SEM).

Morphologies of the hydrogel materials have been investigated by FE-SEM. For the SEM study, the gel material has been dried and coated with platinum. Then the micrographs have been taken in a SEM apparatus (JEOL microscope JSM-6700F).

Atomic Force Microscopic Study.

Morphologies of the reported hydrogel have been investigated using atomic force microscope (AFM). AFM studies have been done by placing a small amount of gel (at its minimum gelation concentration) of the corresponding compounds on a microscopic cover glass and then it has been dried by slow evaporation. The material has been then allowed to dry in vacuum at 30 °C for 2 days. Images have been taken by an AUTOPROBE CP base unit, di CP-II instrument, model no. AP-0100.

Transmission Electron Microscopy.

Transmission electron microscopic (TEM) experiments have been carried out to investigate the morphology of the hydrogel and the particle sizes of the Ag-nanoclusters

within the gel. TEM images have been recorded on a JEM 2010 electron microscope at an accelerating voltage of 200 KV.

X-ray diffraction study.

X-ray diffraction study of the xerogel has been done by placing it on a glass plate. The Ag-nanocluster containing hydrogel has been dried to get solid materials and then it has been placed on a glass plate. Experiments have been carried out by using an X-ray diffractometer (Bruker D8 Advance) with a parallel beam optics attachment. The instrument has been operated at a 35 kV voltage and 30 mA current using Ni-filtered CuKa radiation and the instrument has been calibrated with a standard silicon sample before use. Samples have been scanned from 1º to 80º (2θ) at the step scan mode (step size 0.03°, preset time 2 s) and diffraction patterns were recorded using a scintillation scan detector.

Rheology.

Rheological experiments have been performed with an AR 2000 advanced rheometer (TA Instruments) using cone plate geometry in a Peltier plate. The plate diameter has 40 mm, with a cone angle of 4 degrees.

System	N_1	N_2	N_3	N_4	τ_1	τ_2	τ_3	τ_4	$<\tau>$	χ^2
Hydrogel	0.02	0.03	0.001	0.08	1.6	6.17	0.16	15.6	11	1.0
Hydrogel + Ag^I ions	0.03	0.002	0.03	-	5.6	15.8	0.71	-	3.53	1.1
Ag-nanoclusters Within the gel	0.01	0.001	-	-	0.1	1.08	-	-	0.175	1.1

Table S1. Showing the important parameters of the time resolved fluorescence study.

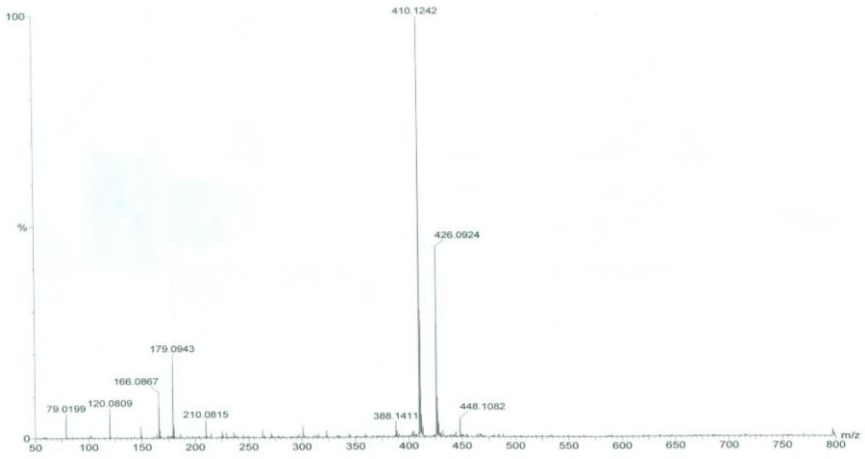

Fig. S1 ESI-MS spectrum of Fmoc-Phe-OH.

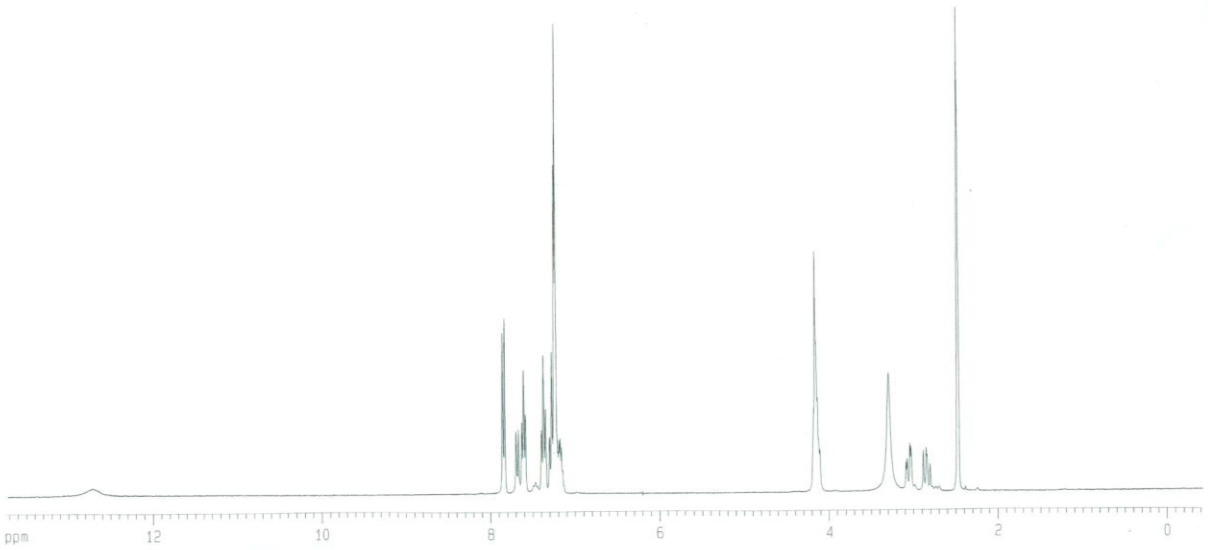

Fig. S2 ^{1}H NMR spectrum of Fmoc-Phe-OH.

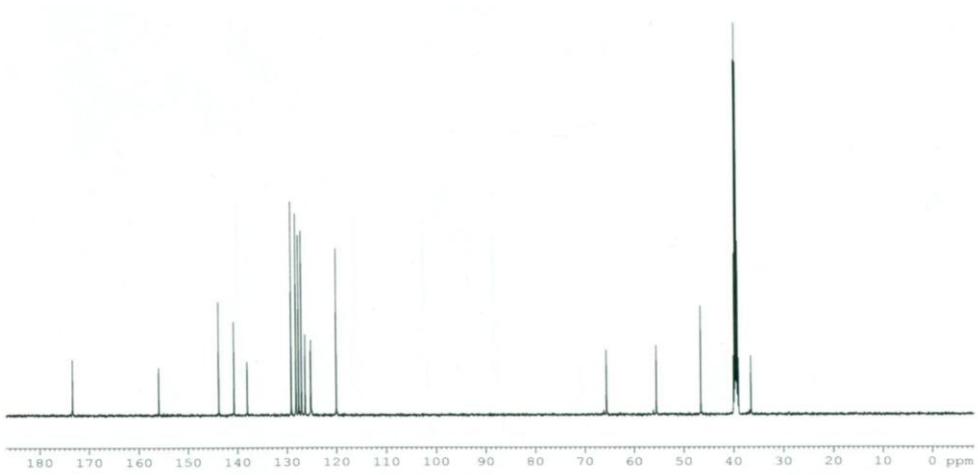

Fig. S3 ^{13}C spectrum of Fmoc-Phe-OH.

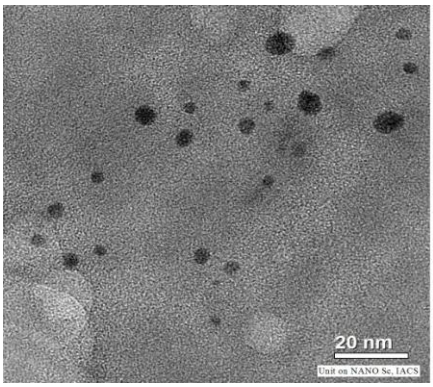

Fig. S4 Transmission electron microscopic analysis of the solution of hydrogelator containing Ag-nanoparticles which is synthesized at physiological pH and at room temperature in presence of diffused sunlight.

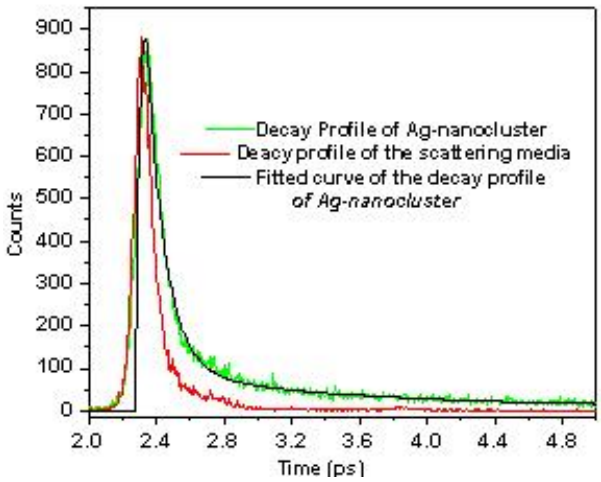

Fig. S5 Fluorescence decay profile of Ag-nanoclusters. The fast and slow component of the Ag-nanoclusters are 108 ps (93%) and 1.06 ns (7%). The decay profile has been fitted with biexponential curve. The average fluorescence life time of the Ag-nanoclusters was 175 ps.

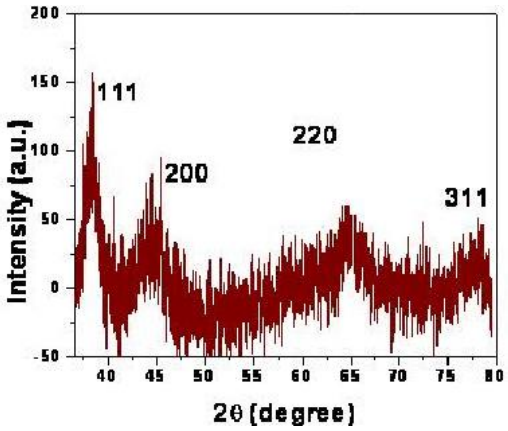

Fig. S6 XRPD analysis of the hydrogel containing Ag –nanoclusters.

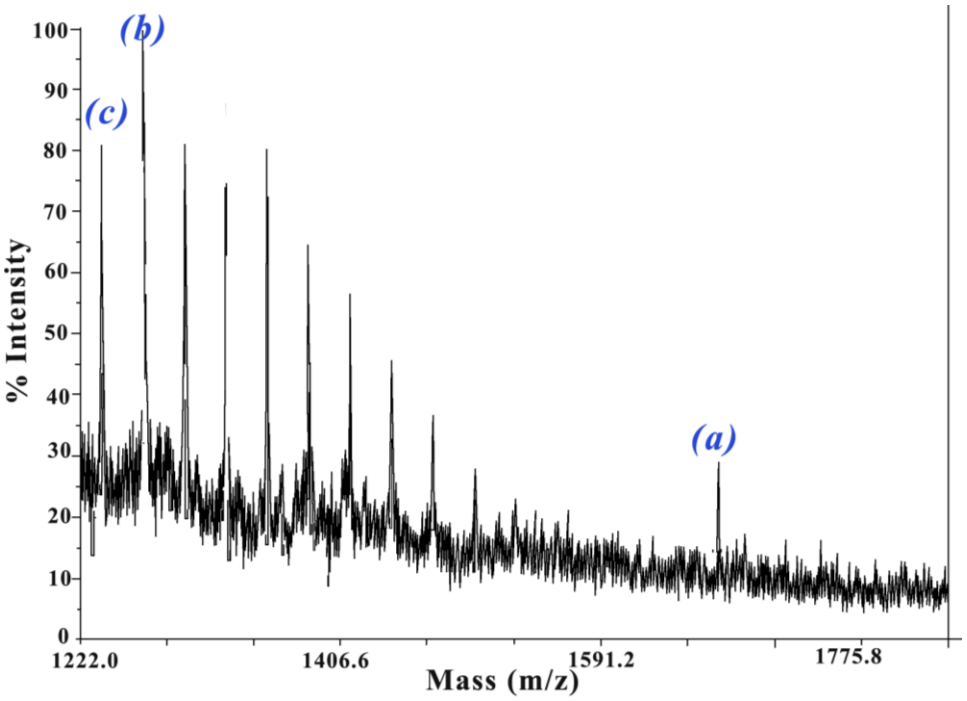

Fig. S7 MALDI-TOF analysis of the silver nanoclusters.

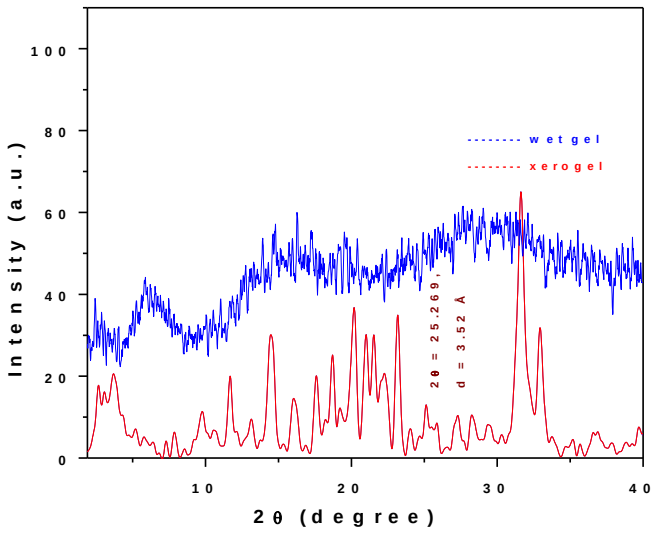

Fig. S8 XRPD analysis of the dried hydrogel. The peak at 2θ = 25.269 corresponding to the d spacing 3.52 Å indicates the presence of π-π interaction within the system.

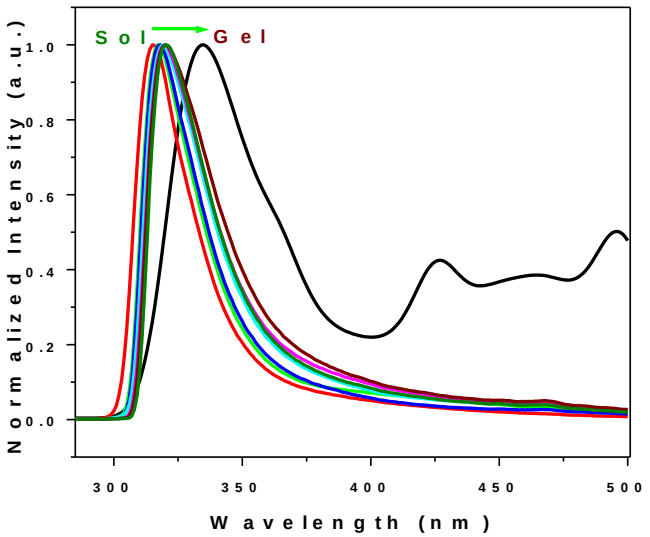

Fig. S9 Fluorescence spectroscopic analysis of sol to gel transitions.supramolecular hydrogels.

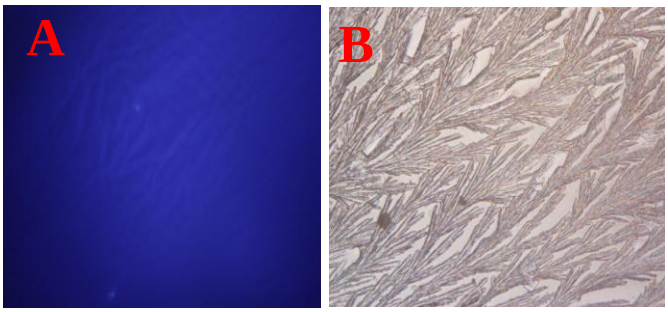

Fig. S10 (A) Fluorescence microscopic view of the hydrogel at slit 1 (330-385 nm) and (B) Microscopic analysis of the hydrogel at bright field.

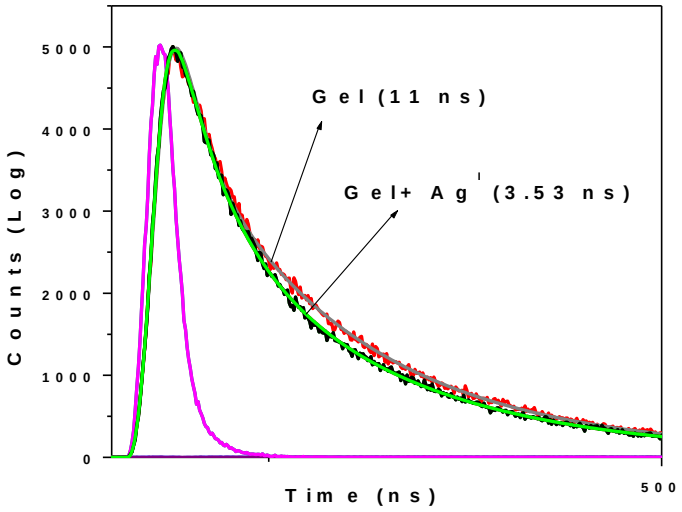

Fig. S11 Fluorescence decay profile of the Fmoc-Phe-OH hydrogel and Fmoc-Phe-OH hydrogel-silver ion at the fluorescence excitation of hydrogel itself (295 nm laser). The fast and slow components of the hydrogel itself are 1.69 ns (17.6 %), 6.17 ns (21.9 %), 0.16 ns (0.9 %) and 15.6 ns (59.4 %) and for the hydrogel-Silver ion hybrid materials are 5.6 ns (50 %), 15.8 ns (2.5 %) and 0.71 ns (47.4 %). The decay profiles have been fitted with an exponential curve. The average fluorescence life time of the hydrogel it was 11ns and the hydrogel-silver ion hybrid materials at the excitation of hydrogel itself was 3.53 ns.

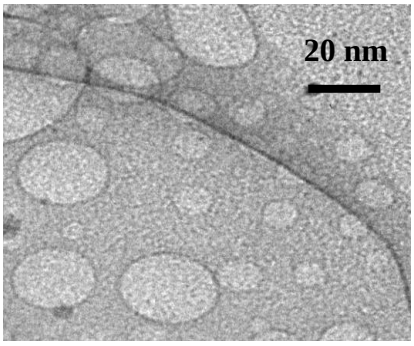

Fig. S12 Transmission electron microscopic image of the hydrogel containing Ag^{I} ions in absence of diffused sunlight showing vesicle type morphology.

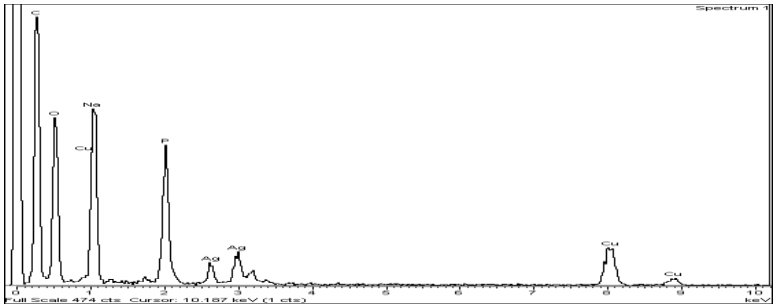

Fig. S13 EDX analysis of the Ag-nanoclusters.

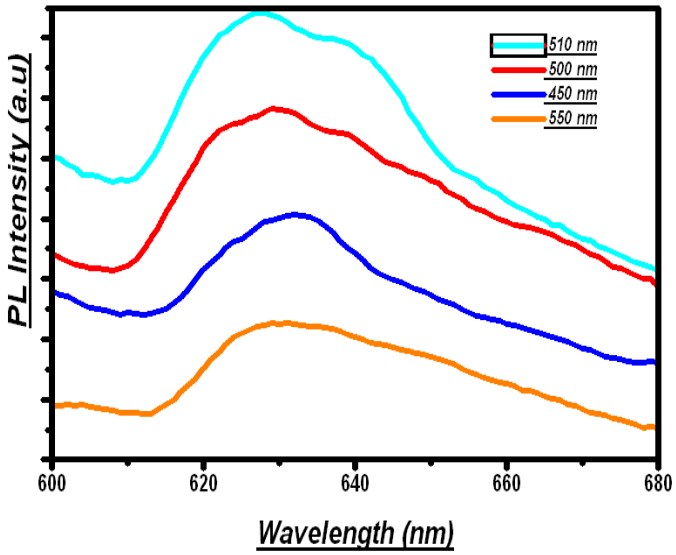

Fig. S14 Fluorescence emission spectra of the Ag-nanoclusters upon different excitation wavelength.

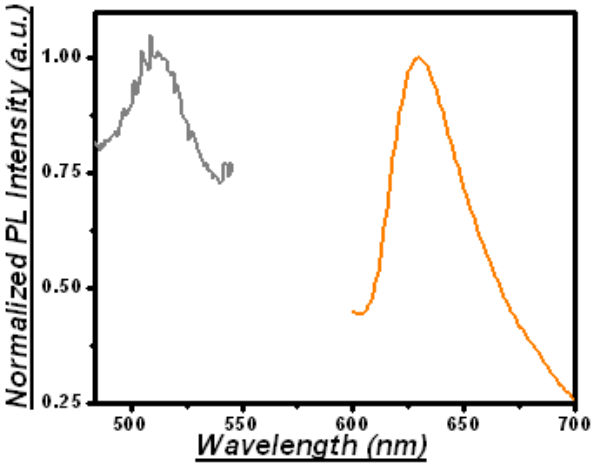

Fig. S15 PL and PLE spectra of the silver nanoclusters.