Gum Acacia based silver nanoparticles as a highly selective and sensitive dual nanosensor for Hg(II) and fluorescent turn-off sensor for S^{2-} and malachite green detection

Ambreen Abbasi[a], Summaiya Hanif[a], and Mohammad Shakir[a*]

A Division of Inorganic Chemistry, Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India.

[*]Tel: 00919837430035

[*]Email: shakir078@yahoo.com

S1 EXPERIMENTAL

S1.1 Reagents

Silver nitrate, chlorides of different metals, gum acacia, and malachite green were obtained from Sigma Aldrich and used without further purification. Double distilled water used throughout the experiment.

S1.2 Instrumentations

UV-vis measurements were done on Shimadzu UV- 2450 spectrometer. Fluorescence spectra recorded on Hitachi F-2700 spectrometer. Fourier-transform infrared (FT-IR) spectrum obtained from Perkin Elmer Spectrum Two FT-IR Spectrometer. GA-AgNPs morphology was analyzed using a scanning electron microscope (SEM) (JSM-6510LV, JEOL, Japan) coupled with energy dispersive X-ray (EDX) instrument at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) was carried out in a JEM-2100, JEOL, Japan operating at the maximum accelerating voltage of 200 kV. For this, 5 µL of the sample was drop coated on a carbon-coated copper TEM grid followed by air drying. Acquired micrographs were analyzed using ImageJ (http://imagej.nih.gov/ij/download.html) by randomly selecting individual nanostructures of silver nanoparticles in the TEM images to compute size distribution histograms. X-ray diffraction (XRD) experiments were carried out using SMARTLAB Rigaku with Cu-Kα1radiation.

Samples were dropped cast on glass cover slides and were dried in an oven at 80^0C. Confocal images were obtained using a confocal laser scanning microscope (LSM780, Carl Zeiss, Germany) and the processing of the images was done by ZEN Image processing software.

S1.3 Synthesis of Gum acacia stabilized silver nanoparticles (GA-AgNPs)

The AgNPs were prepared by the method reported [1], but with some changes. For the synthesis of silver nanoparticles, 0.1 g of gum acacia was added to 70 ml double distilled water in a beaker. The solution was stirred on a magnetic stirrer at 120^{o}C for about 20 minutes to obtain a homogeneous solution. At this stage, 0.05 g of silver nitrate solution in 30 ml distilled water was added to a clear gum acacia solution. The whole solution was maintained at 120^{0}C for half an hour thereupon color changes from colorless to yellow, indicating the formation of AgNPs.

S1.4 Detection of Hg(II) ions using GA-AgNPs

The same procedure for UV-vis and fluorescence measurements was adopted. The adopted method was as follows: 10 mmol L^{-1} stock solution of Hg (II) ions was obtained by dissolving the required amount of $HgCl_2$ in double distilled water; this stock solution was used to prepare 2 nmol L^{-1} -13 µmol L^{-1} solution of Hg(II) ions. The yellow colloidal solution of GA-AgNPs was diluted five times for Hg (II) determination. In a typical experiment, 20 µL of Hg(II) solution of different concentrations was mixed with 3 ml of diluted GA-AgNPs solution after shaking the mixture once UV-vis and fluorescence spectra were recorded at room temperature with 300 nm excitation wavelength. The slit width of excitation and emission was 5nm and 10 nm, respectively.

S1.5 Detection of S^{2-} by GA-AgNPs and Hg(II) ions ensemble

For typical detection of S^{2-} ions 20µL of S^{2-} solution of different concentrations were added to 2ml of GA-AgNPs and Hg(II) ions ensemble. The mixture was shaken once at room temperature, and finally, fluorescence intensity was recorded with an excitation wavelength of 300 nm at room temperature. The slit width of excitation and emission was 5nm and 10 nm, respectively.

S1.6. Detection of MG using GA-AgNPs nanosensor

The same procedure for UV-vis and fluorescence measurements was adopted. The adopted method was as follows: 1 mmol L^{-1} stock solution of MG was obtained by dissolving the required amount of MG in distilled water; this stock solution was used to prepare 7µ mol L^{-1} -130 µmol L^{-1} solution of MG. The yellow colloidal solution of GA-AgNPs was diluted five times for MG determination. In a typical experiment, 20 µL of the MG solution of different concentrations was mixed with 3 ml of diluted GA-AgNPs solution after shaking the mixture once UV-vis and fluorescence spectra were recorded at room temperature with 300 nm excitation wavelength. The slit width of excitation and emission were 5nm and 10 nm, respectively.

S1.7. Detection of Hg (II) and S^{2-} ions and MG in real water samples

Tap water, packaged drinking water, and bore-well water were selected for actual water samples.

Tap water and bore-well water were collected from our university campus. Bisleri was purchased from the store. Before the analysis, water samples were filtered through 0.22 µm membranes. Water samples were spiked with mercury ions, sulfide ions and MG of different concentrations and then were used for detection adopting the procedure described in sections S1.4, S1.5 and S1.6.

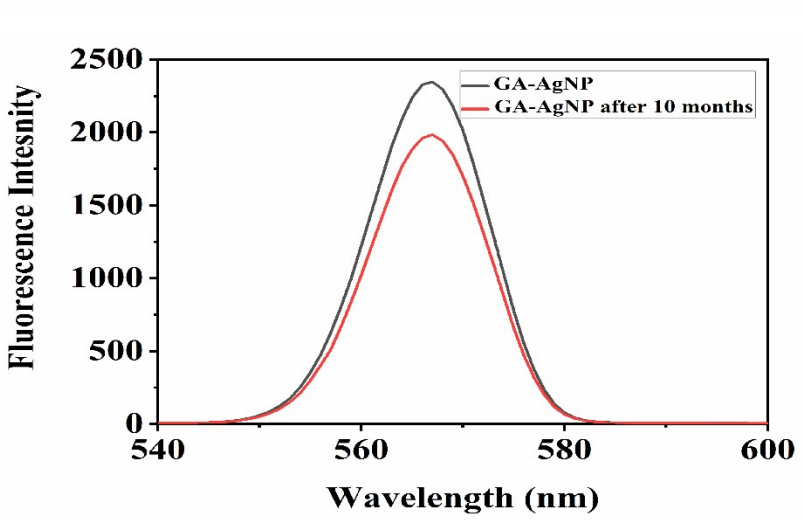

Fig. 1S. Fluorescence spectrum of GA-AgNP after one day and after ten months.

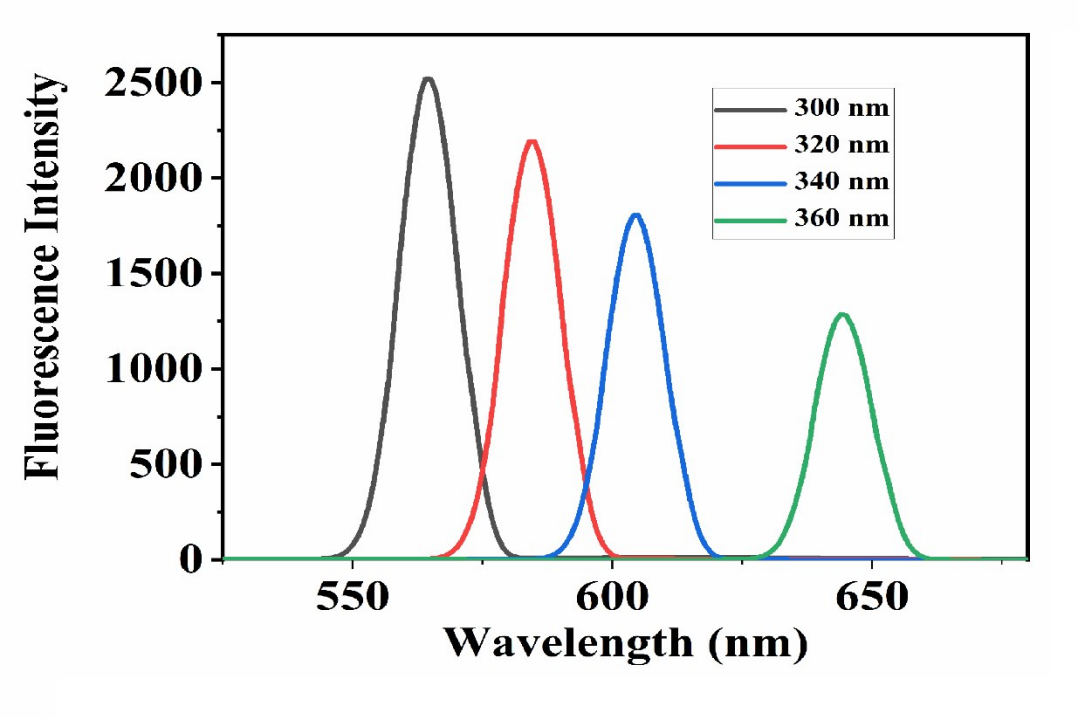

Fig. 2S. Change in emission wavelength with the change in excitation wavelength.

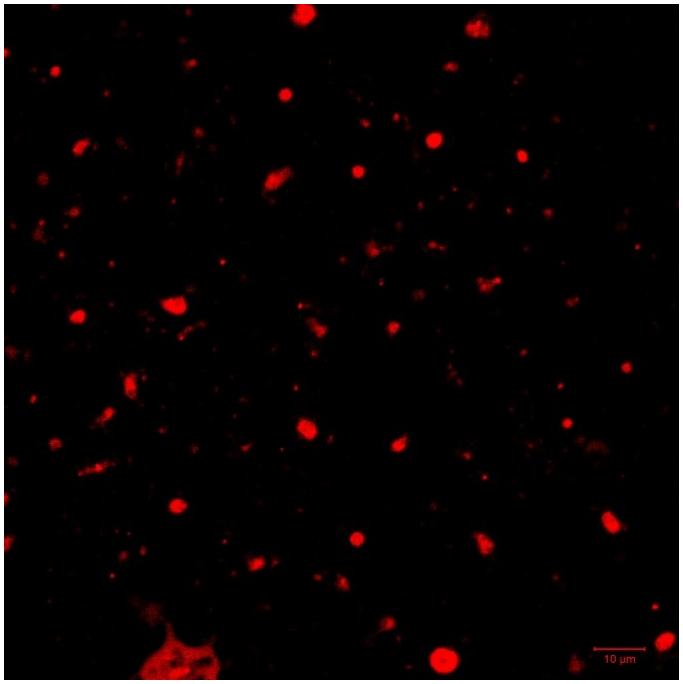

Fig. 3S Confocal image of GA-AgNPs

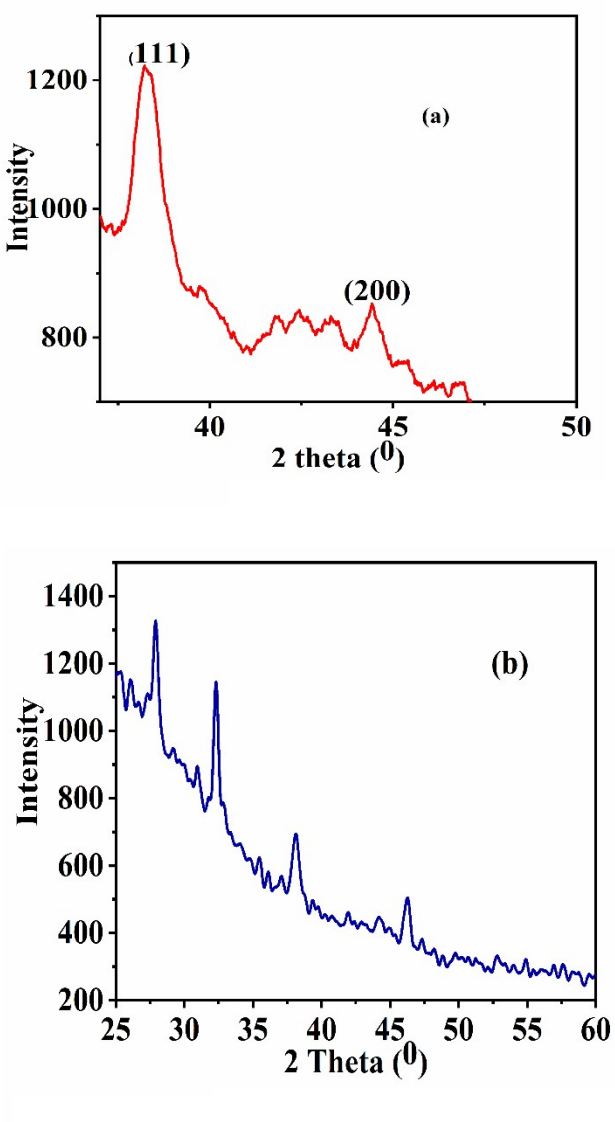

Fig. 4S. XRD patterns of GA-AgNPs in the absence of Hg(II) (a) and presence of Hg(II) ions (b)

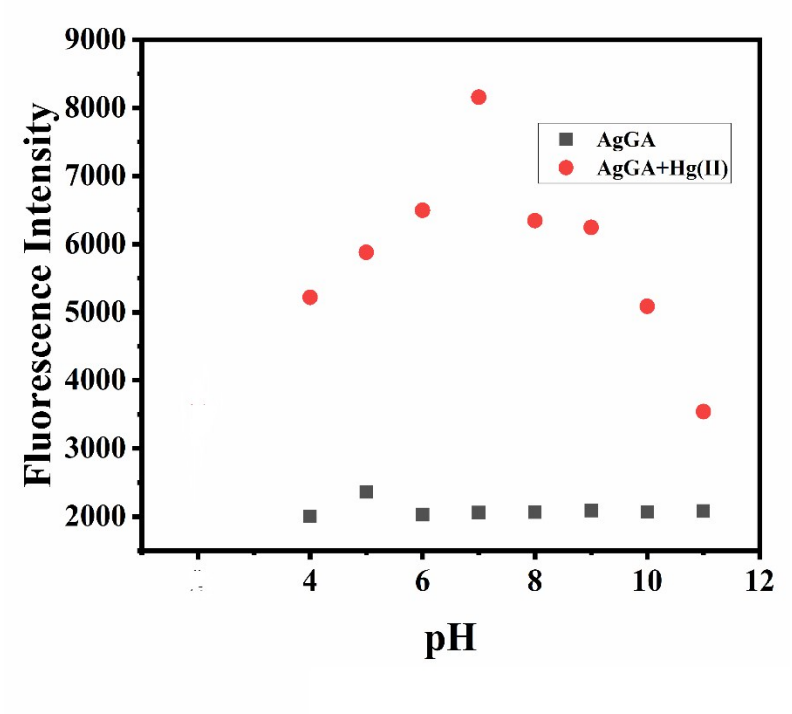

Fig. 5S. Effect of pH on fluorescence intensity of GA-AgNPs and GA-AgNPs in the presence of Hg(II) ions.

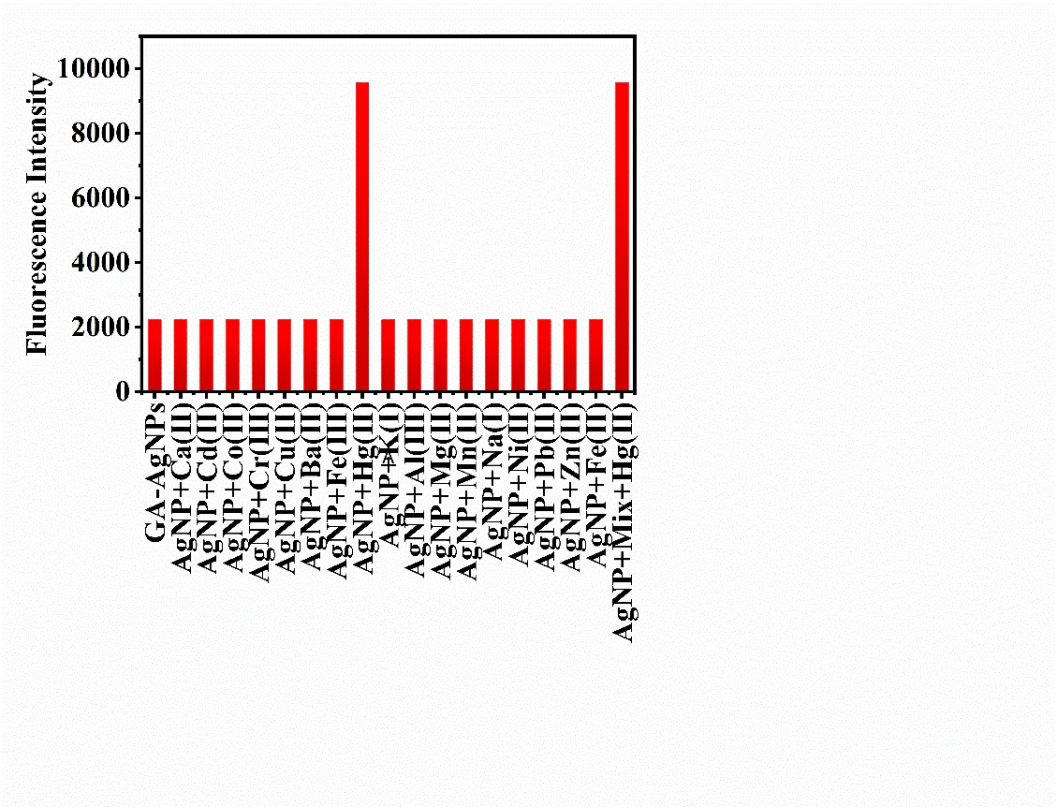

Fig. 6S. Effect of Hg(II) and other metal ions as well as Hg(II) in the presence of different metal ions on the fluorescence intensity of GA-AgNPs.

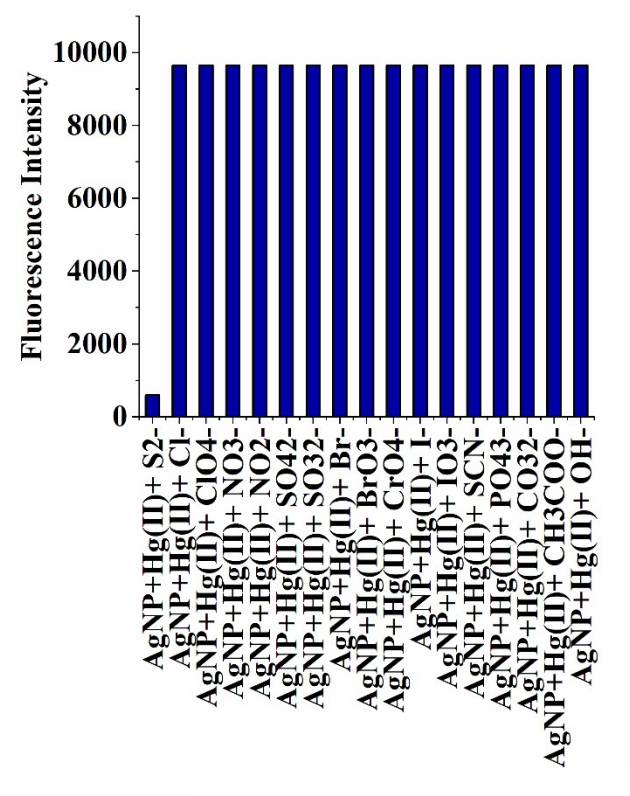

Fig. 7S. Effect of S^{2-} ions and other competing anions on the fluorescence intensity of the GA-AgNPs-Hg(II) ensemble.

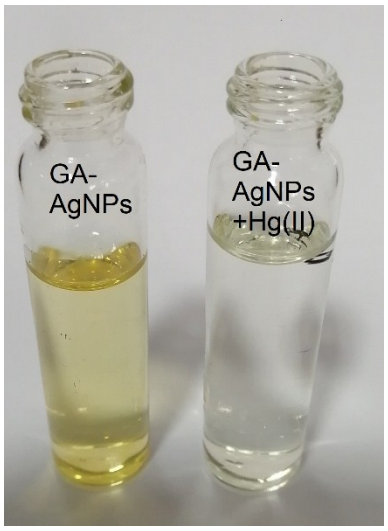

Fig. 8S. Photograph of GA-AgNPs alone and in the presence of Hg(II).

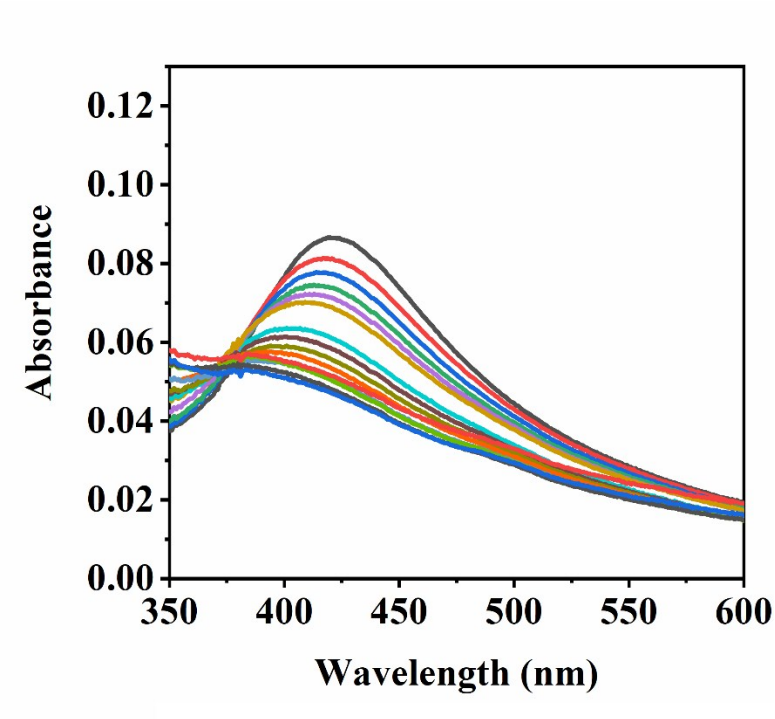

Fig. 9S. Absorption spectra of GA-AgNPs in the presence of increasing concentrations of Hg(II).

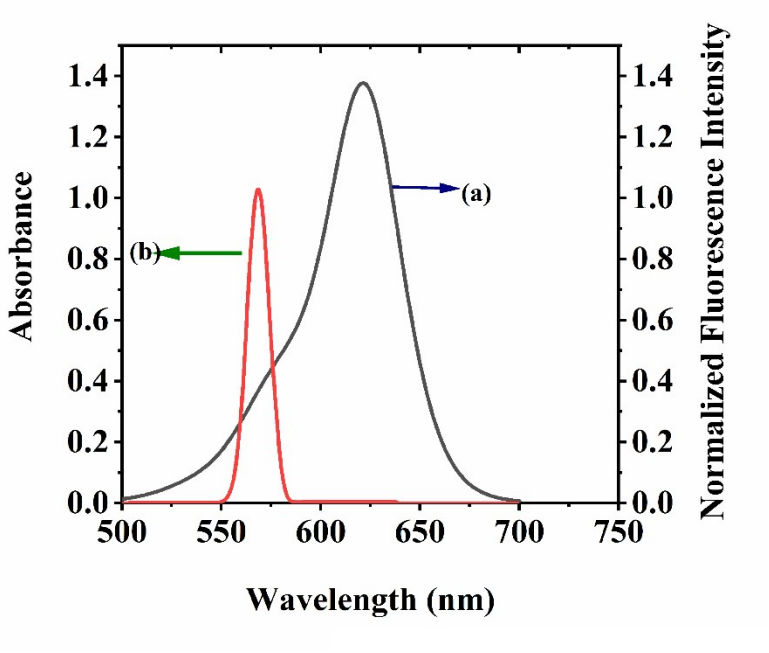

Fig. 10S. The absorption spectrum of MG (a) and emission spectrum of GA-AgNPs (b)

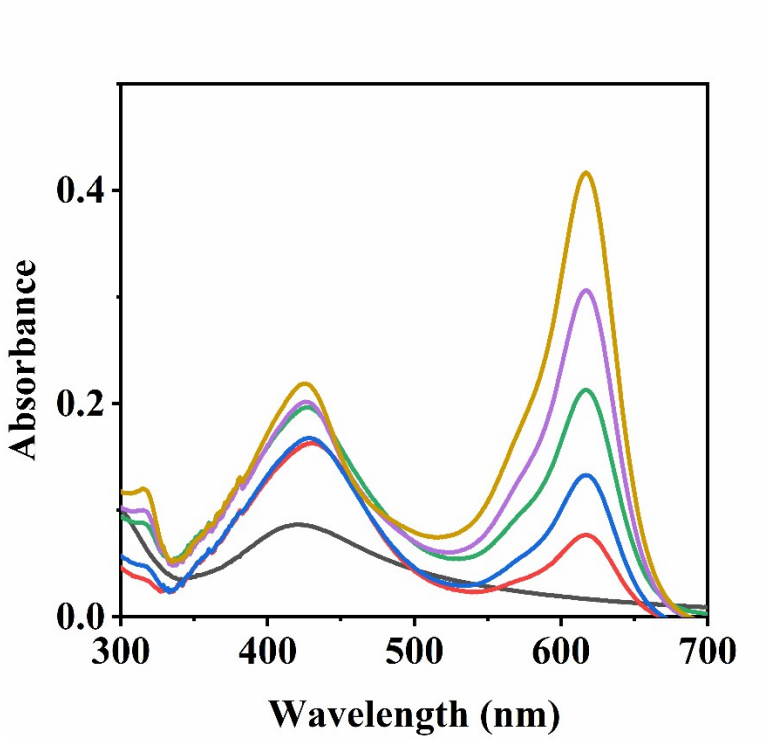

Fig. 11S. Absorption spectra of GA-AgNPs in the presence of an increasing concentration of MG.

References

1 C. Dong, X. Zhang, H. Cai and C. Cao, *J. Mol. Liq.*, 2014, **196**, 135–141.