Supporting Information for the paper:

Luminescent Silver Clusters with Covalent Functionalisation of Graphene

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Experimental

Materials

Natural graphite was purchased from Active Carbon India Pvt. Ltd., India. Sulfuric acid (H_2SO_4, 95-98%) and hydrochloric acid (HCl, 36%) were purchased from Ranbaxy Chemicals, India. Phosphorus pentoxide (P_2O_5), hydrazine monohydrate ($N_2H_4.H_2O$, 99-100%), hydrogen peroxide (H_2O_2), were purchased from SD Fine Chemicals, India. Potassium persulphate ($K_2S_2O_8$) was purchased from Sisco Research Laboratories Pvt. Ltd., India. Potassium permanganate ($KMnO_4$) was purchased from Merck.

Silver nitrate ($AgNO_3$, 99%), glutathione (GSH, 97%) and methanol (G.R grade), ammonium per sulphate (APS), $N,N^/$ methylene bisacrylamide (A.R grade), acryl amide (A.R grade), and $N,N,N^/,N^/$ -tetramethylethelenediamine (TEMED), were purchased from SRL Chemicals Co. Ltd. Sodium borohydride (99.99%), methanol (HPLC grade) and tetra-octyl-ammonium bromide (TOAB) were purchased from Sigma Aldrich. 1-(3-(dimethylamino) propyl)-3-ethyl-carbodiimide hydrochloride (EDC) was purchased from Sigma Aldrich.

Synthesis of solution phase graphene

The synthesis of graphite oxide from graphite powder was achieved by a two-step oxidation. Graphite powder (2 g) was treated with phosphorous pentoxide (1 g), and potassium persulphate (1 g) in conc. sulphuric acid (8 mL). This partial oxidation gave pre-oxidised graphite. These were mixed together with stirring at 80 ^{0}C. The reaction was allowed to cool, distilled water was added carefully, and the product was filtered over vacuum. The light grey powder was allowed to dry overnight. Pre-oxidised graphite (2 g) was further subjected to strong oxidation by potassium permanganate (6 g) in ice cold concentrated sulphuric acid (46 mL). This was done over an ice bath. $KMnO_4$ crystals were added to the reaction very slowly and the temperature of the reaction mixture was maintained below 20^{0}C throughout the addition. After the complete dissolution of $KMnO_4$, the reaction was stirred for 2 hours at 35 ^{0}C. The resulting brown powder was washed with 500 mL of 1:10 HCl to remove metal ions. The resultant solid

was dried and 1 % (w/w) dispersion was prepared in distilled water. This dispersion was dialyzed for 3 weeks through a semi-permeable cellulose membrane to remove all unwanted contaminants like salts and acid. De-ionized water was used for dialysis and was changed every 3-4 hours. The dispersion was later diluted to 0.05 % (w/w).

Reduction of the dialysed graphite oxide was done by a hydrothermal method. 15 mL of 0.05% w/v graphite oxide dispersion was poured into a hydrothermal bomb. The reaction was maintained at 180 ^{0}C for 6 hours. A black dispersion of the graphene was obtained, which is stable to centrifugation at moderate speeds.

Synthesis of silver quantum clusters

Silver quantum cluster (Ag_{QC}) was prepared by the following procedure. $AgNO_3$ (47 mg) and GSH (150 mg) were dissolved in a solution of NaOH (45 mg in 1 mL) at room temperature and the mixture was vigorously stirred and sonicated to make a uniform yellow solution of Ag(I)thiolate complexes. This precursor was added at the time of gel preparation (see below). For the preparation of the gel, acrylamide (T)/ bisacrylamide(C) (51% T, 7.8% C) 50 μL of 0.1% ammonium persulfate were first mixed and 1 mL of the above prepared silver thiolate solution was added and stirred. With the addition of 50 μL N,N,N',N'-tetramethyl-ethane-1,2-diamine (TEMED), polymerization leading to the gel formation occurred. The above gel was allowed to set for 20 minutes at room temp. It was then transferred to a cold temperature for 10 min. 10 mL of ice cold $NaBH_4$ solution (10 mg/mL) was added on top of the gel and the mixture was stored undisturbed for 30 min. The colour of the gel changed from light yellow to dark brown from top to bottom indicating the formation of clusters within the gel. The $NaBH_4$ solution on top of the gel was removed. The gel was crushed and washed with methanol 5 to 6 times to remove excess $NaBH_4$ and other soluble impurities. Free clusters were extracted into water from the crushed gel (the gel was insoluble in water). The cluster solution obtained was used in further reactions. Previous studies indicated that the clusters have a composition of $Ag_{25}SG_{18}$[1].

Analytical procedures

UV-vis spectroscopy

Perkin Elmer Lambda 25 UV-vis spectrometer was used for the measurements. Spectra were typically measured in the range of 200-1100 nm.

Luminescence spectroscopy

Luminescence measurements were carried out using HORIBA JOBIN VYON Nano Log instrument. The band pass for excitation and emission was set as 5 nm.

X-ray photoelectron spectroscopy

The photoelectron spectra of the samples were obtained using an ESCA probe/TPD of Omicron Nanotechnology. Sample in water was spotted on a Mo plate and allowed to dry in vacuum. The size of the analyzed area was about 3 mm^2. In view of the sensitivity of the sample, surface cleaning was not attempted. Al K_α radiation was used for excitation; a 180° hemispherical analyzer and a seven-channel detector were employed. The spectrometer was operated in the constant analyzer energy mode. Survey and individual regions were collected using pass energies of 50 and 20 eV, respectively. The pressure in the analyzer chamber was in the low 10^{-10} mbar range during spectrum collection. Binding energies of the core levels were calibrated with C 1s BE, set at 284.7 eV.

Raman spectroscopy

A Witec GmbH confocal Raman spectrometer, equipped with a helium- neon laser at 633 nm was used as the excitation source to collect the luminescence images. The laser was focused onto the sample using a 100X objective with the signal collected in a back scattering geometry. The signal, after passing through a super notch filter, was dispersed using a 150 grooves/mm grating onto a Peltier-cooled charge coupled device (CCD), which served as the detector. Some data were collected with 532 nm excitation also.

Mass spectrometry

All the ESI mass spectra have been acquired using a triple quadrupole mass spectrometer (3200 QTrap) from AB Sciex between the mass range of m/z 50 – 1700 in negative ion mode.

The glutathione funtionalised graphene was dispersed in 1:1 water- methanol solution. This was centrifuged at around 8000 rpm for 10 minutes to allow the undissolved particle, if any, to settle and to avoid clogging of the electrospray capillary of the apparatus. The samples were electrosprayed at a flow rate of 10uL/min.The spectra were averaged for 60 scans.

Energy dispersive X-ray analysis

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 completely dried before the mesurement.

Transmission electron microscopy

TEM images were collected using a JEOL 3010 microscope. A diluted solution was spotted on carbon coated copper grid and was dried in the laboratory ambience. Images were collected at 200 keV, to reduce beam induced damage of the clusters.

S2: Supporting information 2
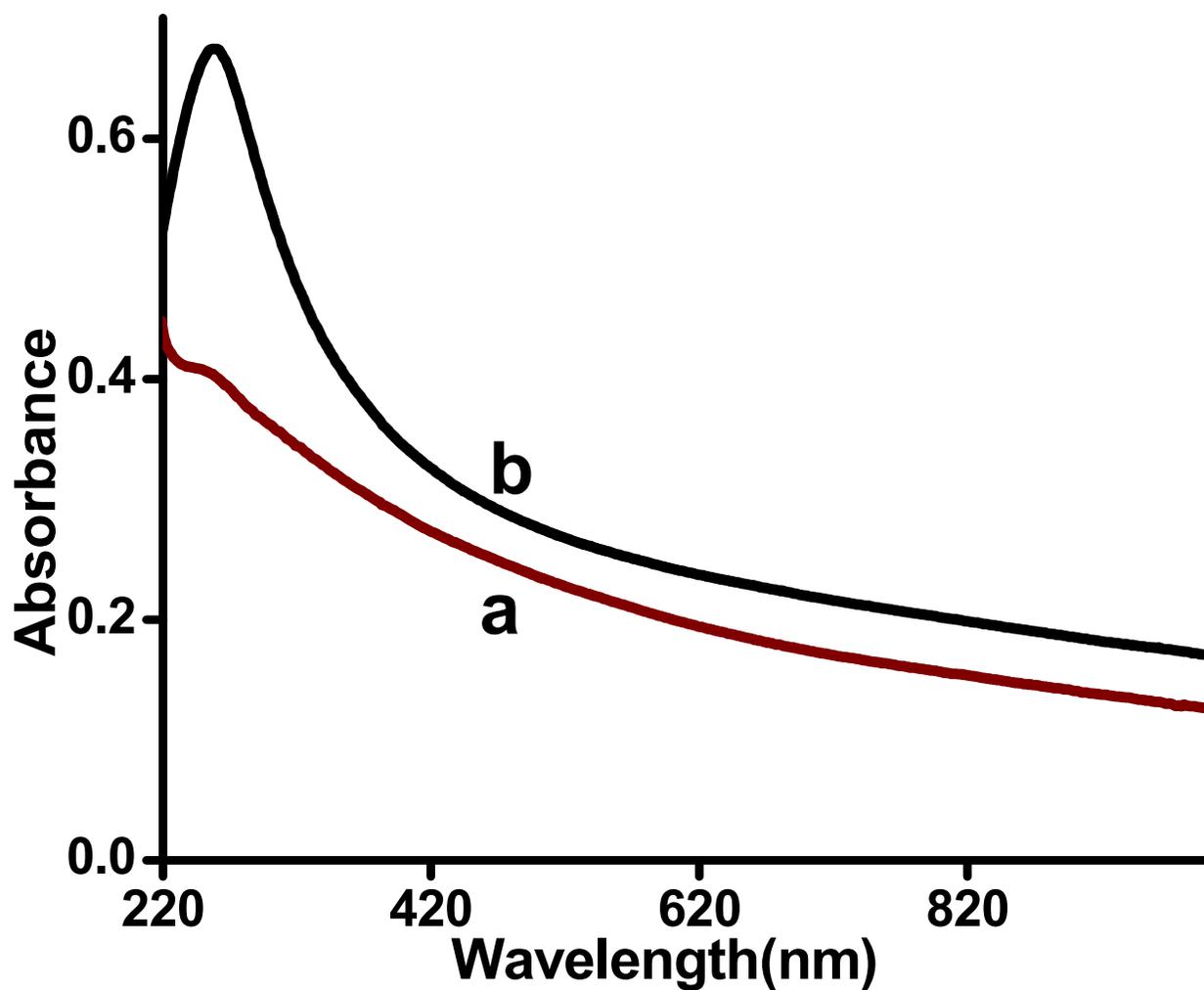
Characterisation by absorption spectroscopy

Figure S2 (A): Absorption spectra of (a) GSH functionalised graphite oxide and (b) graphene. The peak at 253 nm is a standard feature of chemically synthesised graphene due to a secondary $\pi \rightarrow \pi^*$ transition in the graphene ring system.
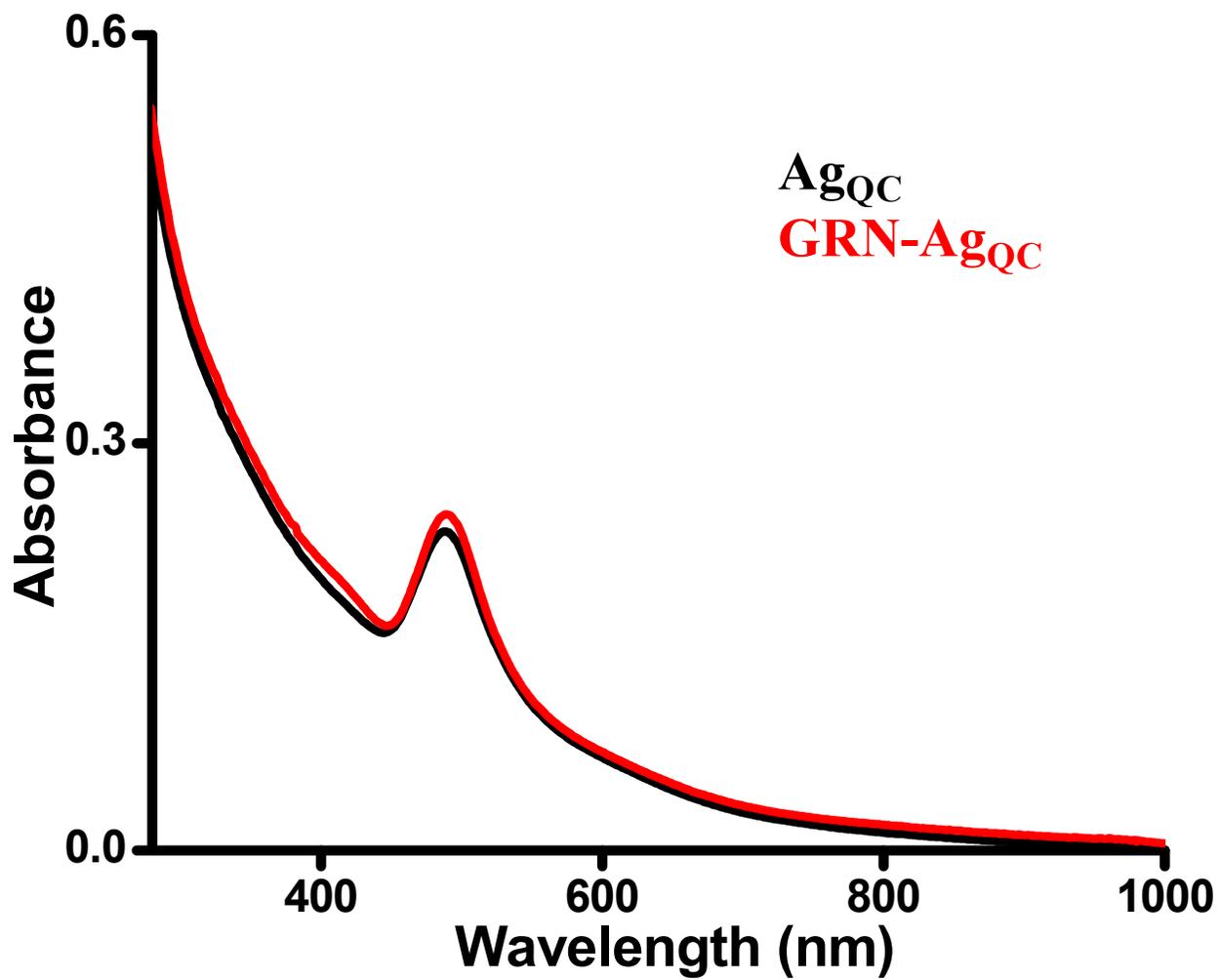
Figure S2 (B): Absorbance spectrum of AgQC and GRN-AgQC after phase transfer to toluene.

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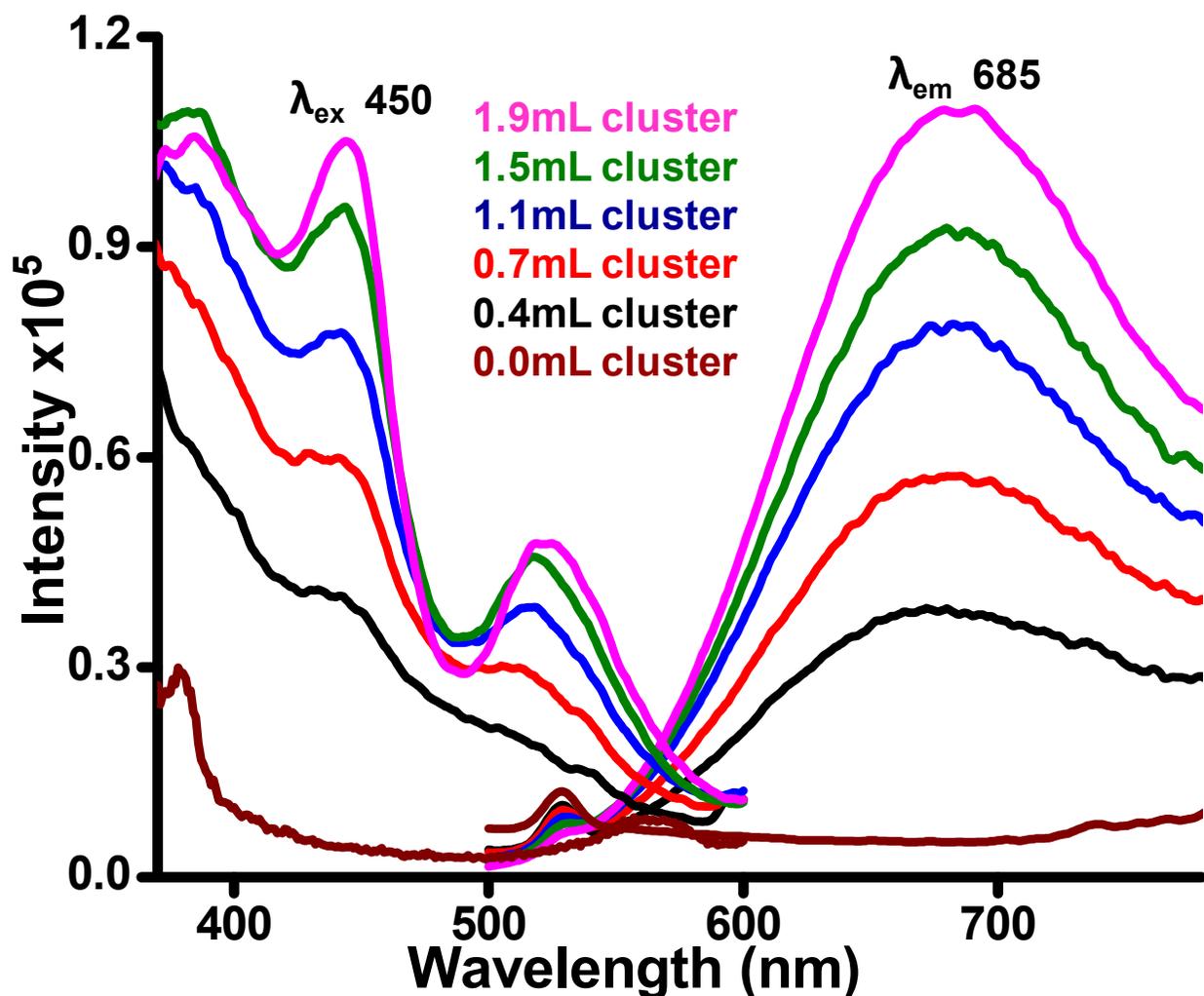**Characterisation by luminescence spectroscopy**

Figure S3 (A): Overlayed luminescence spectra showing change in cluster luminescence with increase in cluster concentration. GRN-GSH concentration was kept constant. GRN-GSH showed no emission and the features seen are due to impurity lines from the excitation or second order lines from the excitation.
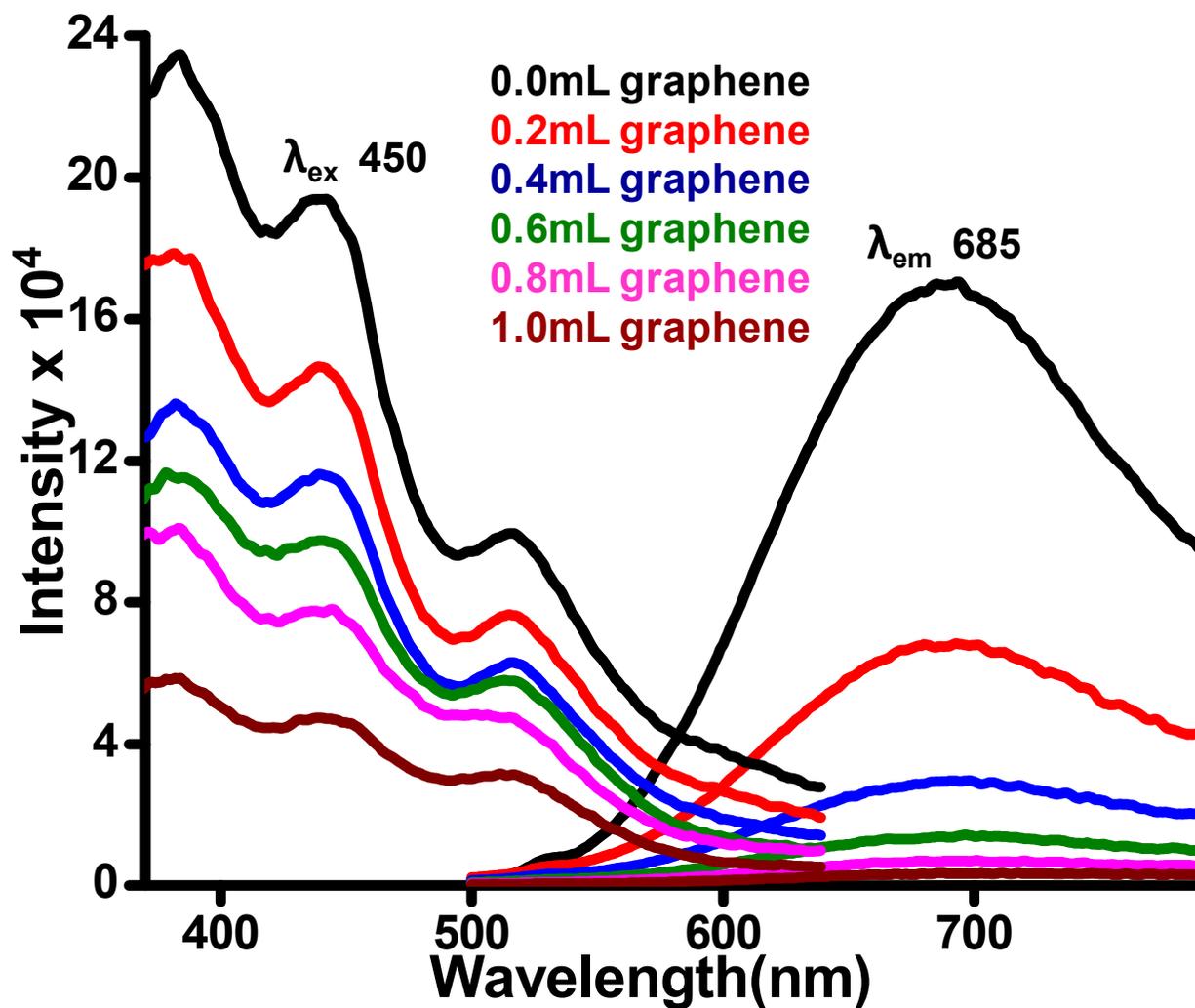
Figure S3 (B): Luminescence spectra of cluster and graphene mixtures showing change in cluster luminescence with increase in graphene concentration. Cluster concentration was kept constant and graphene concentration was varied. No peak shift was observed.
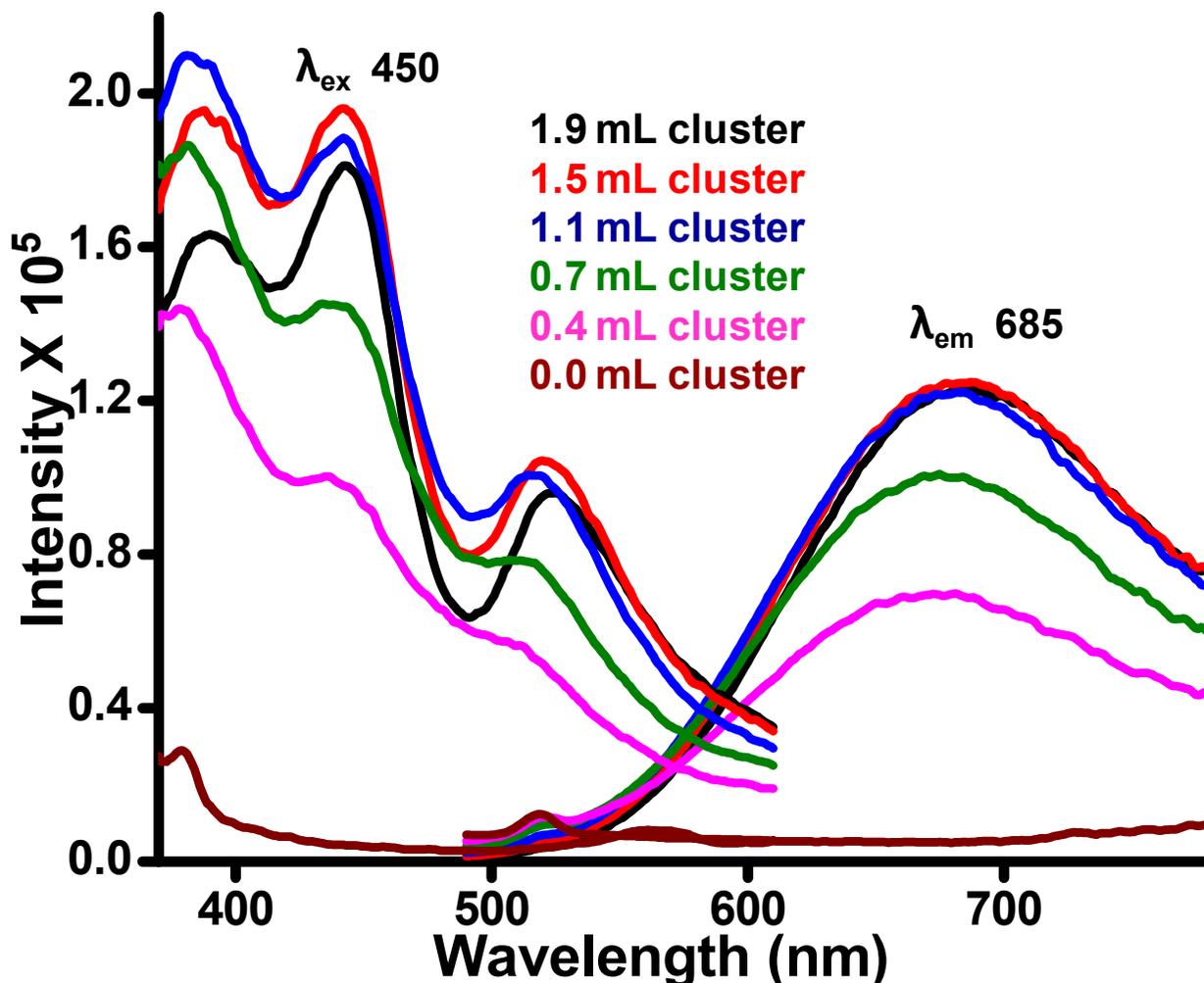
Figure S3 (C): Overlayed luminescence spectra showing change in cluster luminescence with increase in cluster concentration. Graphene concentration was kept constant. No spectral shifts were obtained. Graphene showed no emission and the features seen are due to impurity lines from the excitation or second order lines from the excitation.

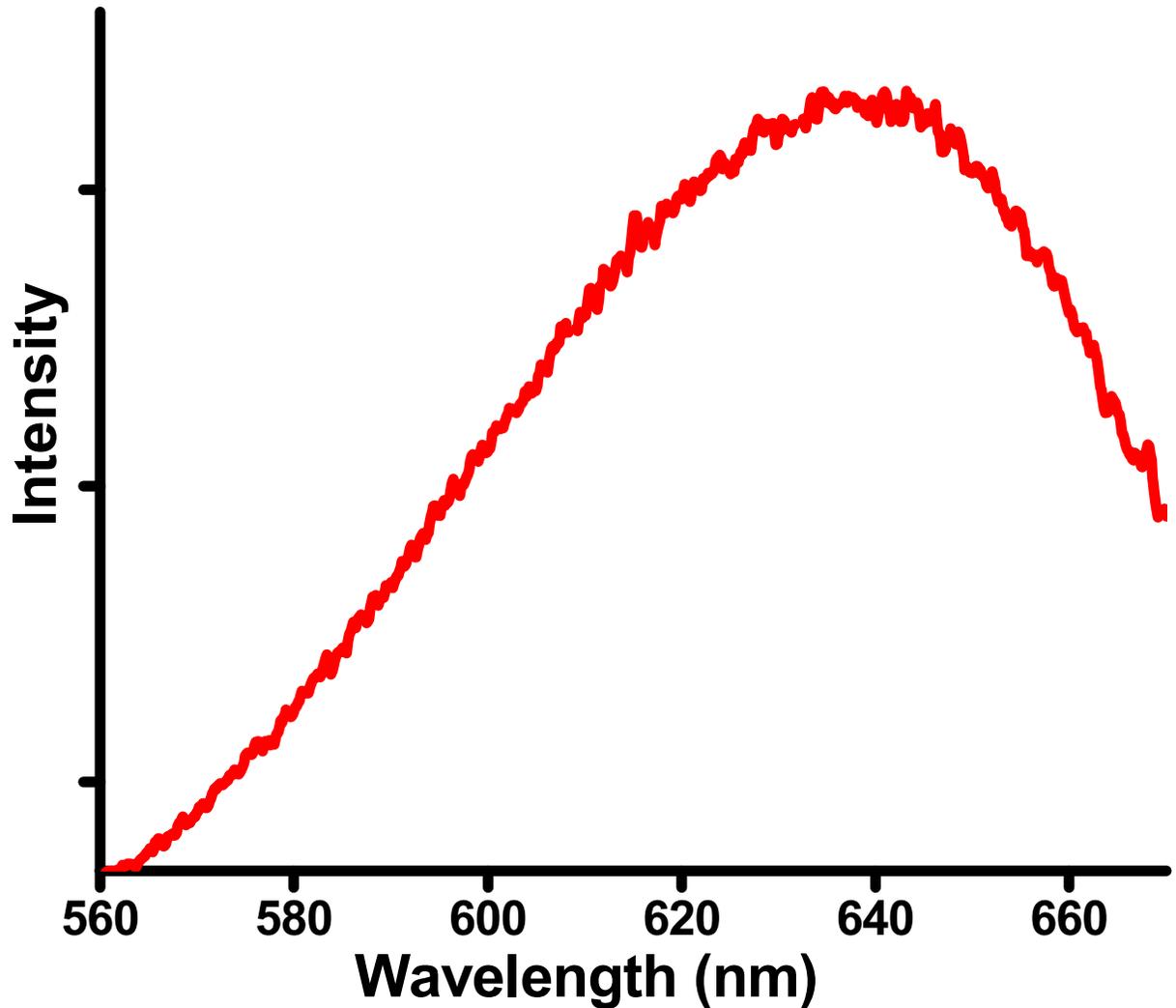# S4: Supporting information 4

Characterisation by Raman spectroscopy

Figure S4: Raman spectrum of the phase transferred GRN-Ag$_{QC}$ under 532 nm excitation. Raman shift (cm^{-1}) is converted to wavelength (nm) and plotted on the x-axis. The fall in intensity above 640 nm is due to the poor detector response. The data suggest the existence of the bound clusters which are luminescent.

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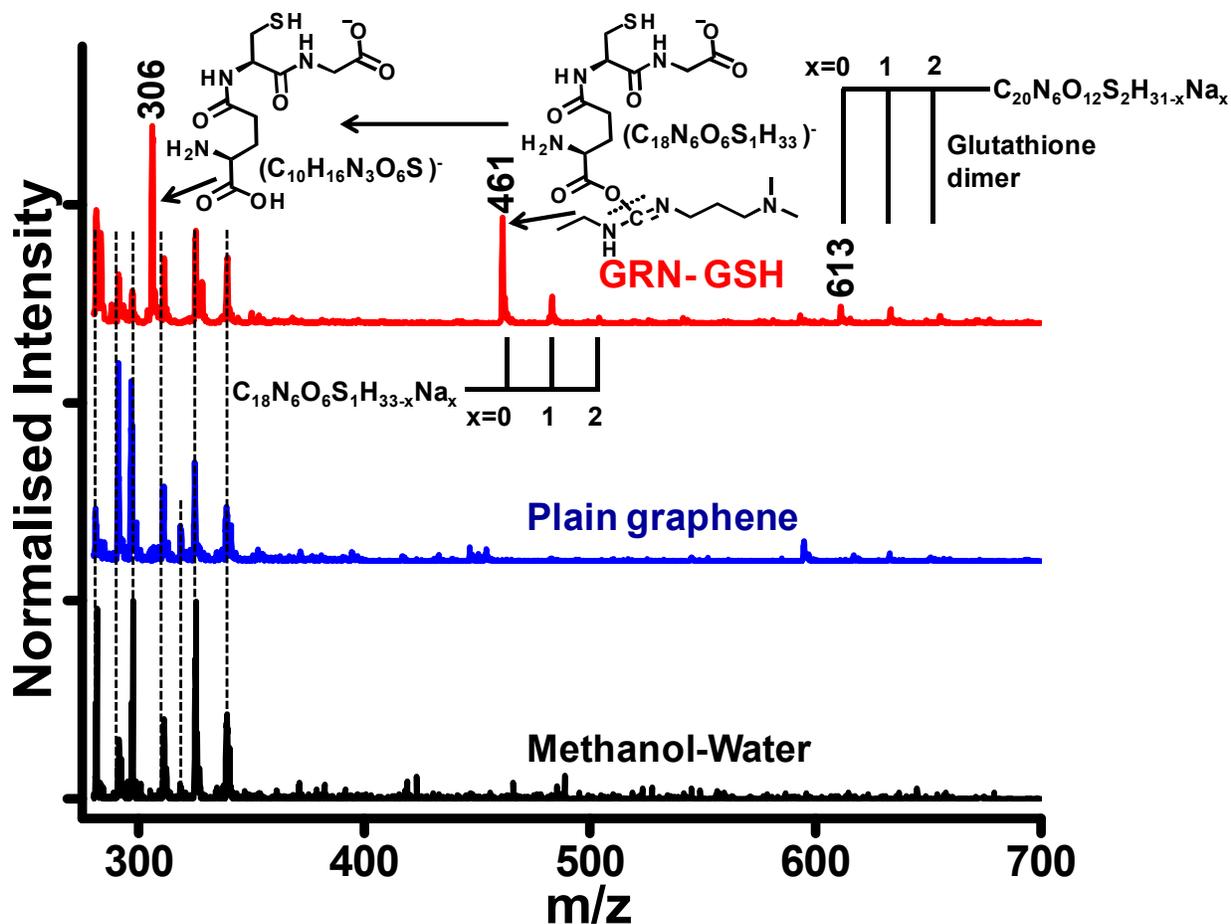
Characterisation by ESI mass spectrometry

Figure S5: Electrospray ionisation mass spectrum of GRN-GSH, graphene and plain methanol: water (solvent). The spectrum of GRN-GSH shows the GSH peak at m/z 306 and an EDC bound GSH peak at m/z 461. The peak at m/z 613 is the GSH dimer formed via the sulphur-sulphur linkage. The peaks with a spacing of m/z 22 a.m.u arise due to the exchange of protons with sodium.

Reference:

1. Chakraborty, I.; Rao T. U. B.; Pradeep, T. Luminescent Sub-Nanometer Clusters for Metal Ion Sensing: A New Direction in Nanosensors. *J. Haz. Mater.* **2012**, *211– 212*, 396– 403