Luminescent Sub-nanometer Clusters for Metal Ion Sensing: A New Direction in Nanosensors

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Supplementary data 1. Methods

1.1 Synthesis of Ag₂₅ Clusters

We have started our initial efforts of using the gel cavities for synthesis within the PAGE set-up itself. The thiolates were prepared along with the gels and NaBH₄ was taken in place of buffer. Potential was applied as usual. The reduction resulted in the formation of a colored gel from which clusters could be extracted in aqueous medium. Later on this procedure was modified and it can be synthesized in beaker only without the help of PAGE set up. For that 47 mg of AgNO₃, 150 mg of GSH and 40 mg NaOH are mixed in 1 ml of water. In a beaker 3 ml of gel (acrylamide : bisacrylamide = 47:3) solution was taken, to that 0.7 ml of above prepared thiolate solution was added and well mixed. Now to poly 40 μ l of APS and 40 μ l of TEMED was added to polymerize it .Then 10 ml of NaBH₄ solution (10mg/ ml) was added to reduce it. After that it was crashed and washed with methanol to remove unreacted NaBH₄ otherwise it will leads to nanoparticle. Finally it was extracted in water; clusters are coming out in solution while gel remain as such. The schematic photographs are given here (figure S1).

Supplementary data 2. Instrumentation

2.4 Instrumentation

UV-Vis spectra were collected from Perkin Elmer Lamda 25 instrument in the range of 200-1100 nm. Luminescence measurements were carried out on a Jobin Vyon Nanolog instrument. For excitation and emission the band pass was set as 2 nm. The FT-IR spectra were measured using Perkin Elmer Spectrum One instrument, KBr crystals were used as a matrix for preparing the samples. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analyses (EDAX) were done in FEI QUANTA – 200 SEM. For measurements, sample were drop casted on an indium tin oxide coated

conducting glass and dried in vacuum. As a result of the substrate, the EDAX spectrum shows features due to In, Sn and Si. High resolution Transmission Electron Microscopy (HRTEM) and EDAX were carried out with a JEOL 3010 instrument. Samples were taken on carbon coated copper grids and allowed to dry in ambient conditions. Powder XRD patterns of the samples were recorded using PANalytical X'pert Pro diffractometer . The powder samples of clusters were taken on a glass plate and the X-ray diffractogram was collected for 5 to 100 degree in 2 theta using Cu K α radiation.



Figure S1. Photographs at different stages of reaction during synthesis of Ag₂₅ cluster. i) Thiolate solution, ii) after addition of NaBH₄, iii) after 20 minutes and iv) after removing unreacted NaBH₄.



Figure S2. UV-Vis absorption spectra upon addition of various metal ions (50 ppm concentration) to aqueous Ag_{25} cluster solution. Inset is a photograph of the corresponding solutions under visible light.



Figure S3. UV-Vis features of Ag_{25} cluster with different system and conditions. Upon addition of Hg^{2+} the change in UV-Vis spectra with time is shown in "A". An exceptionally different feature was observed with Cd^{2+} solution (B). Characteristic feature is also observed in C, where 10 ppm solution of Hg^{2+} added to cluster (red one), and also after centrifuging the solution, and redisolving the ppt in aqueous medium (black one). Effect of anion is given by "D", which shows anion is not responsible for this interaction



Figure S4. UV-Vis absorption spectra of various concentrations of Hg^{2+} treated aqueous Ag₂₅ cluster solutions. Inset is a photograph of corresponding solutions under visible light. The bottles a, b,..., h correspond to pure Ag₂₅(SG)₁₈, Ag₂₅(SG₁₈) + 1 ppb Hg²⁺,.... Ag₂₅(SG)₁₈ + 10 ppm Hg²⁺.



Figure S5. Effect of various metal ions on the luminescence spectra of Ag_{25} cluster solution. Trace a is showing the cluster feature whereas b and c are the cluster with 10 and 50 ppm solutions of metal ion, respectively.



Figure S6. HRTEM image of cluster with low concentration (10 ppb) of Hg^{2+} showing the presence of cluster (A). Some of the distinct spots due to the cluster are marked with white circles. B and C are images taken after electron beam irradiation. D is showing the EDAX spectrum of corresponding sample.



Figure S7. SEM image and EDAX spectrum of Ag_{25} cluster after exposure to 10 ppb Hg^{2+} solution. The elemental maps of Hg, Ag and S are given by B, C and D, respectively.



Figure S8. The EDAX spectra of Ag_{25} cluster treated with 10 ppm of Hg^{2+} . A is the corresponding EDAX spectrum of an isolated hexagonal species (Ag₃Hg₂) and B is the corresponding aggregated mass (whole area EDAX) formed during the treatment of Hg^{2+} with Ag₂₅ cluster.



Figure S9. HRTEM images of the aggregated mass formed during the interaction of Ag_{25} cluster with Hg^{2+} solution. Various types of geometries are formed during the course of the reaction (A-G). Lattice has been found with a regular spacing of 0.227 nm (H).



Figure S10. HRTEM images of aggregated mass after centrifugation: Hexagonal (A), square (B), triangular (C) and octagonal (D) type of geometries were observed.



Figure S11. TEM and EDAX images of aggregated mass formed by the addition of 10 ppm Hg^{2+} solution (A) showing an isolated hexagonalobject. The elemental maps of Hg, Ag and S of the particle are given in B, C and D.



Figure S12. XPS survey spectra of cluster treated with low (100 ppb) (black) and high (100 ppm) (red) concentrations of Hg^{2+} . Individual peaks are assigned.



Figure S13. The S 2p, C 1s, O 1s and N 1s peaks in the XPS spectra for the residue formed after reacting with low (10 ppb) and high (100 ppm) concentrations of Hg^{2+} .