

## Supplementary data

**A practical silver nanoparticle-based adsorbent for the removal of Hg<sup>2+</sup> from water**

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## Supplementary data 1. Materials and methods

### 1.1. Chemicals

All chemicals were of analytical grade and were used as received without further purification.  $\text{AgNO}_3$  (99.9%) was purchased from CDH, India.  $\text{Hg}(\text{OOCCH}_3)_2$  (98.5%) was from RANKEM, India. Activated neutral alumina (column chromatography grade, surface area is  $900 \pm 50 \text{ cm}^2/\text{g}$ ) and methanol (99%) were from SRL, India.  $\text{NaBH}_4$  (98%) and mercaptosuccinic acid (98%) were from Wako. Rhodamine 6G (standard) was from Fluka, KI (99.8%) was from Merck, potassium hydrogen phthalate (99.5%) and NaOH (97%) pellets were from RANKEM. Triply distilled water ( $\text{pH} = 6.7$ ) was used throughout the experiments.

### 1.2. Synthesis of Ag@MSA nanoparticles

Silver nanoparticles protected with MSA were synthesized by the reduction of  $\text{AgNO}_3$  using  $\text{NaBH}_4$ . The 1:6 Ag@MSA sample was prepared as follows. A mixture of about 0.5 mM  $\text{AgNO}_3$  and 3 mM MSA were taken in 100 mL methanol. About 25 mL of ice-cold 0.2 M  $\text{NaBH}_4$  was added drop-wise to the initial solution using a syringe with thorough stirring. A dark brown precipitate was obtained and stirring was continued for 30 minutes. The supernatant was gently decanted and the precipitate was washed several times with methanol by repeated centrifugation. The precipitate was dried with rotavapor to obtain the powder. The 1:3 sample of Ag@MSA was similarly obtained except that the concentration of MSA was changed to 1.5 mM instead of 3 mM. The ratios, 1:6 and 1:3 denote the ratio of molarity of  $\text{AgNO}_3$  to MSA taken in the solution.

### 1.3. Batch experiments for $\text{Hg}^{2+}$ interaction

A suspension of silver nanoparticles was prepared by dispersing 5 mg of 1:6 Ag@MSA in 50 mL water. The 1:3 Ag@MSA colloid ( $\text{pH} = 8.1$ ) was similarly prepared by dispersing 2.7 mg of the powder in 50 mL water. These amounts corresponded to the same mass of Ag in them. These were kept as blank. The pure water used for dispersing Ag@MSA was replaced by 25, 100 and 250 ppm  $\text{Hg}^{2+}$  solutions ( $\text{pH} = 5.8$ ) to study the interaction of mercuric ions with silver. These concentrations were considered as low, medium and high

concentrations, respectively throughout the study. The Ag@MSA particles were kept in solutions of  $\text{Hg}^{2+}$  ions for 24 hours before analysis.

#### **1.4. Loading of Ag@MSA nanoparticles on $\text{Al}_2\text{O}_3$**

The full loading capacity of 1:6 Ag@MSA on alumina was obtained by adding 2 mL stock solution of Ag@MSA in aliquots to alumina. The beaker containing alumina was shaken gently with a shaker till each aliquot became colorless. Addition of Ag@MSA solution was stopped when alumina became fully saturated. The capacity of loading of 1:6 Ag@MSA on alumina was 0.5% by weight. The 1:6 Ag@MSA loaded alumina was thus prepared by loading it with its full capacity. The 1:3 Ag@MSA loaded alumina was similarly prepared and loading on alumina was 0.3% by weight. The loaded samples were washed with distilled water and dried under ambient conditions.

#### **1.5. Column experiments and mercury detection**

To illustrate a practical application of this material, a column experiment was done.  $\text{Hg}^{2+}$  stock solution of 2 ppm concentration was passed through three different columns with 3 g each of pure alumina, 1:3 and 1:6 Ag@MSA loaded alumina. Columns were made intact by using glass wool on the top and bottom. All the three columns were run simultaneously. The flow rates of the three columns were made equal with the help of flow controllers. The residual mercury concentration in the output water was monitored after each 100 mL initially till 2000 mL and after each 500 mL thereafter. The initial flow rate was 2 mL/min. The flow rate got reduced gradually and it was 1 mL/min at the end of 6 L. The output water from the column was tested for mercury using inductively coupled plasma-optical emission spectrometry (ICP-OES). The detection limit was 30 ppb.

#### **Supplementary data 2. Instrumentation**

The UV-vis spectra of the samples were collected using Perkin Elmer Lambda 25 spectrophotometer. FT-IR spectra were obtained using Perkin Elmer Spectrum One spectrometer and the samples were made in the form of pellets in KBr matrix. X-ray diffraction (XRD) data were collected using a Bruker AXS, D8 Discover diffractometer using  $\text{Cu-K}\alpha$  radiation. High resolution transmission electron microscopy (HRTEM) imaging

was done using a JEM 3011 (JEOL Ltd.) 300 kV instrument with a UHR polepiece. Scanning electron microscopy images and energy dispersive analysis of X-rays (EDAX) were done using a FEI-QUANTA 200 SEM. Dynamic light scattering (DLS) measurements were performed with Zetasizer 3000HSA (Malvern Instruments, UK). X-ray photoelectron spectroscopic studies (XPS) were done using an ESCA probe TPD of Omicron Nanotechnology. Unmonochromatized Mg K $\alpha$  was used as the X-ray source. The binding energy was calibrated with respect to C 1s at 285.0 eV. ICP-OES measurements were done using Perkin Elmer Optima 5300 DV.

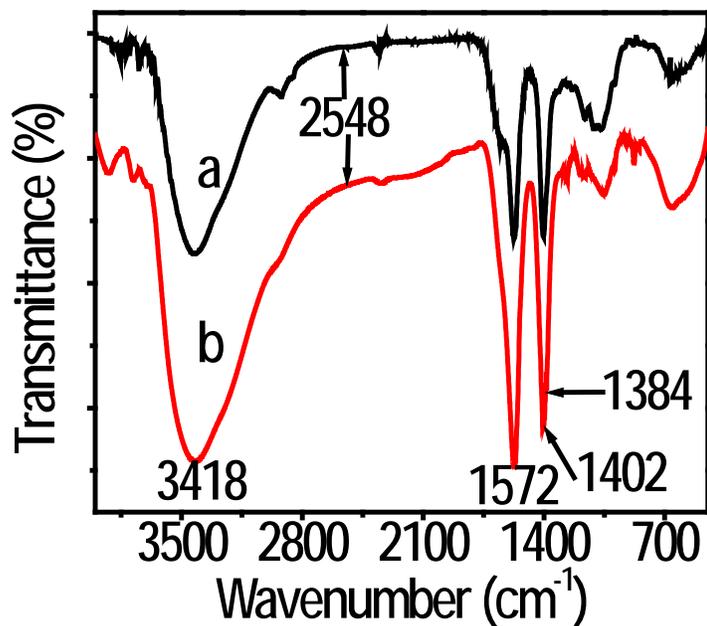


Fig. S3. FT-IR spectra of (a) 1:6 and (b) 1:3 Ag@MSA nanoparticles. The S-H stretching ( $2548\text{ cm}^{-1}$ ) is absent indicating the thiolate capping of MSA to the Ag nanoparticles.

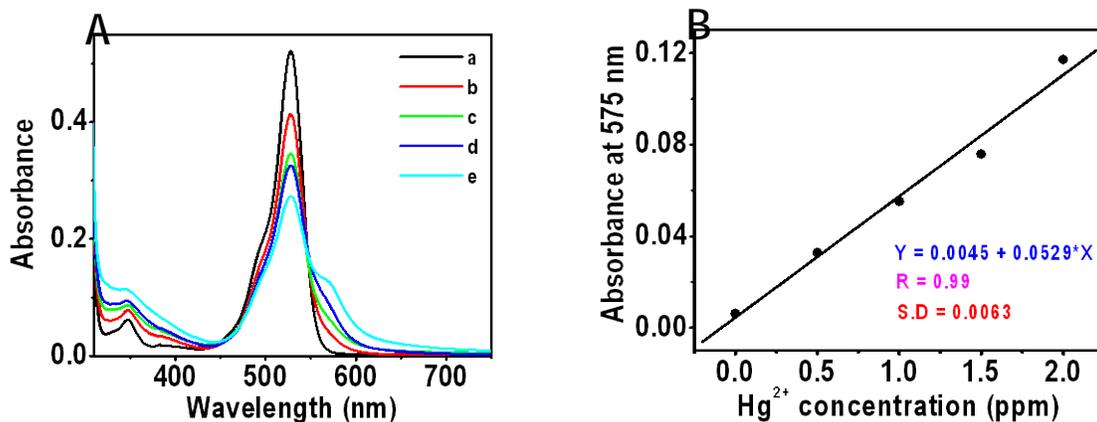


Fig. S4. A) UV-vis absorption spectra of standard  $\text{Hg}^{2+}$  solutions-Rhodamine 6G complex. Trace a corresponds to pure water, b, c, d, and e correspond to 0.5, 1.0, 1.5 and 2.0 ppm  $\text{Hg}^{2+}$ -Rhodamine 6G complex, respectively. B) Calibration graph which is a plot between the concentrations of standard  $\text{Hg}^{2+}$  and the absorbance of  $\text{Hg}^{2+}$ -Rhodamine 6G complex at 575 nm.

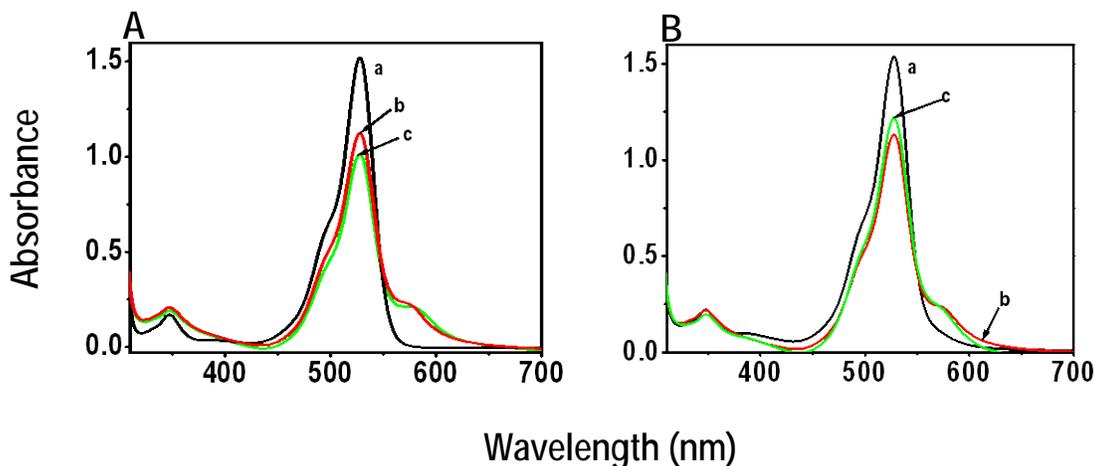


Fig. S5. Spectrophotometric detection of  $\text{Hg}^{2+}$  after passing 2 ppm  $\text{Hg}^{2+}$  solution through the columns of bare alumina (A) and silver particles on alumina (B). (a) Pure water (blank), (b) 2 ppm mercuric solution (input solution) and (c) water collected from the column. These  $\text{Hg}^{2+}$  detections (traces c) were done after passing 200 and 400 mL  $\text{Hg}^{2+}$  solutions in A and B, respectively.

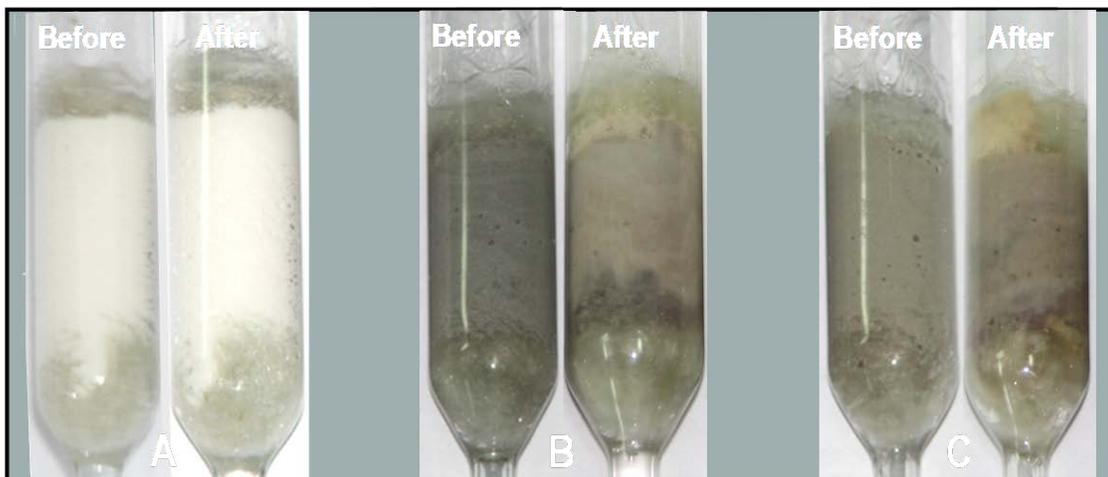


Fig. S6. Photographs of the column before and after the experiment. A) Activated alumina, B) 1:6 Ag@MSA loaded on alumina and C) 1:3 Ag@MSA loaded on alumina.

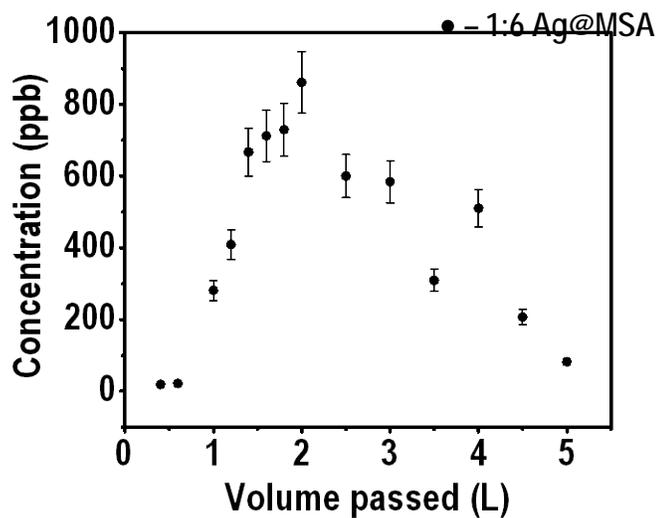


Fig. S7. A plot of the concentration of silver detected in ppb (obtained by ICP-OES) as a function of the volume of  $Hg^{2+}$  solution passed.

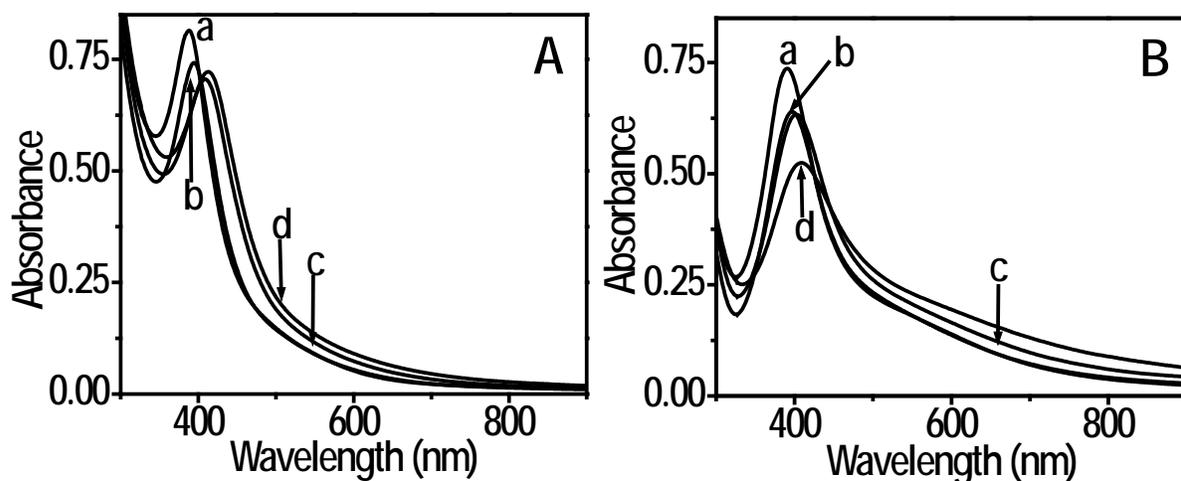


Fig. S8. The UV-vis spectra of both the silver nanoparticle systems on the introduction of 25 ppm  $\text{Hg}^{2+}$  solution with respect to time. A and B represent the time dependent spectrum of the interaction of 1:6 and 1:3 Ag@MSA nanoparticles, respectively upon the introduction of 25 ppm mercuric solution. a) Pure silver nanoparticles, b) silver nanoparticles in mercuric solution initially, c) after 6 h and d) after 24 h.

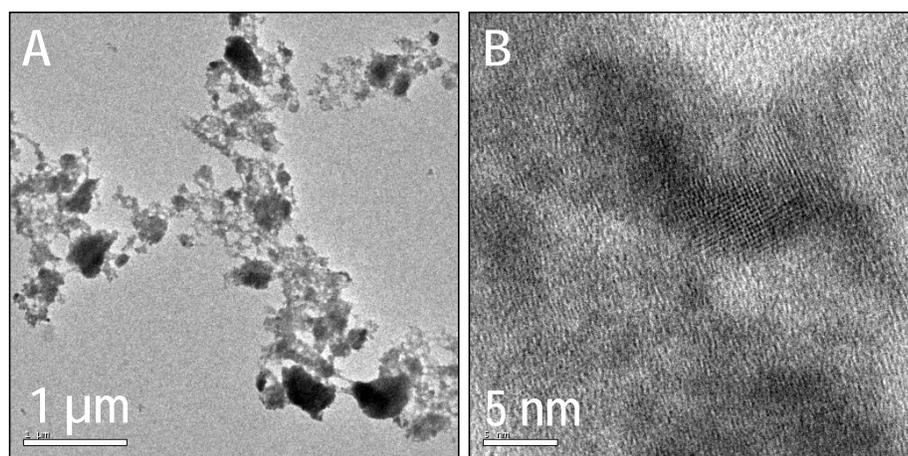


Fig. S9. TEM image of the residue obtained when 1:6 Ag@MSA nanoparticles treated with 250 ppm  $\text{Hg}^{2+}$  solution. A and B are large area and HRTEM images, respectively.

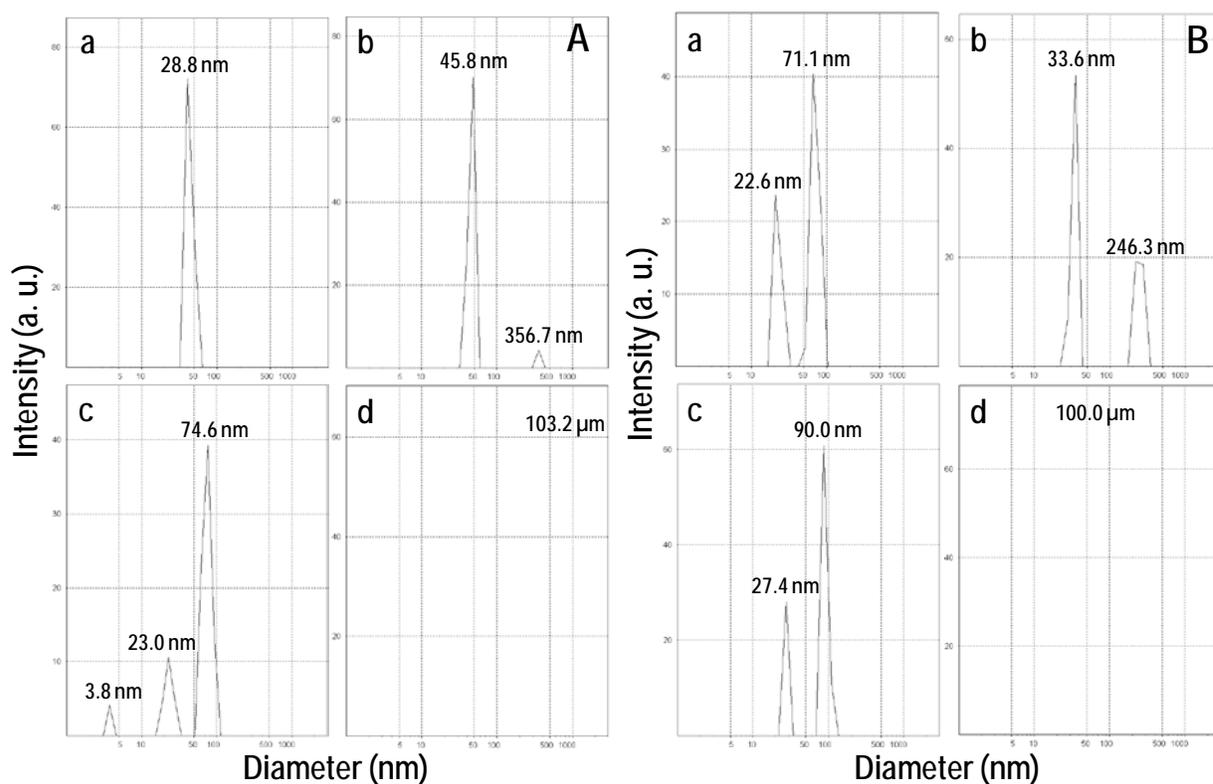


Fig. S10. DLS of 1:6 and 1:3 Ag@MSA (A and B) nanoparticles treated with 0.1, 10 and 100 ppm (b, c and d, respectively) Hg<sup>2+</sup> solutions. The trace a corresponds to parent Ag@MSA nanoparticles. In each graph the particle size distribution is shown. The parent 1:6 Ag@MSA is monodispersed whereas 1:3 Ag@MSA is polydispersed. After treating with Hg<sup>2+</sup> ions, particle size increased. In traces marked d, there are no peaks because the particle size is above the range.

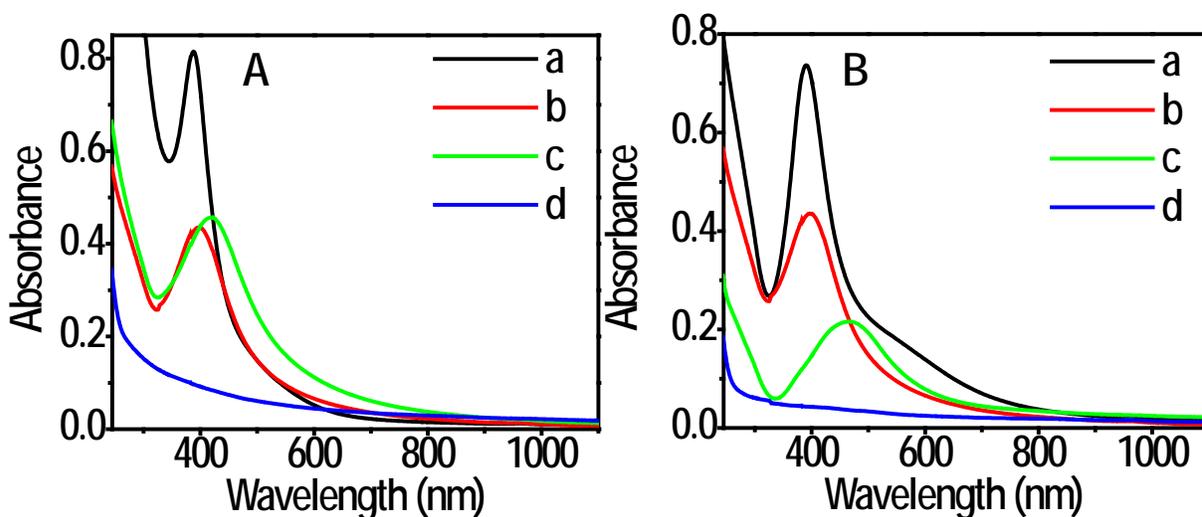


Fig. S11. UV-vis absorption spectra of 1:6 and 1:3 Ag@MSA (A and B) nanoparticles treated with 0.1, 10 and 100 ppm (b, c and d, respectively)  $\text{Hg}^{2+}$  solutions. The trace a corresponds to parent Ag@MSA nanoparticles.

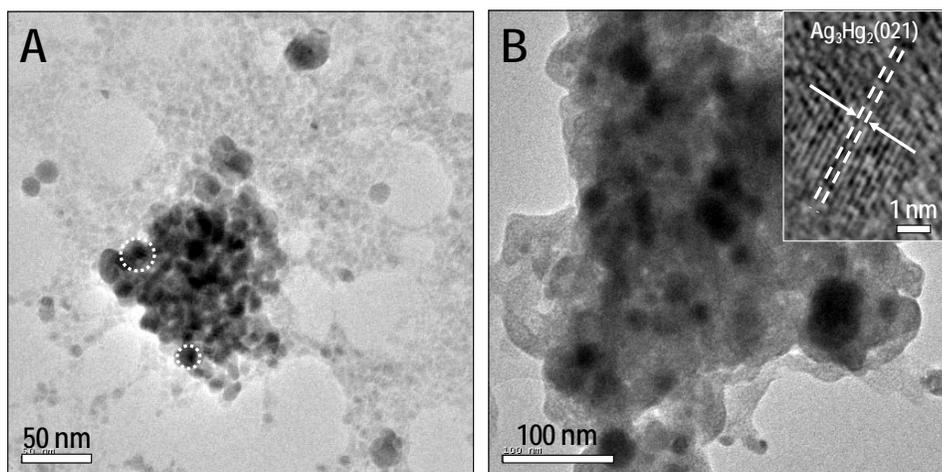


Fig. S12. TEM images of the aggregated masses. A) An aggregated mass formed after the addition of 25 ppm  $\text{Hg}^{2+}$  solution to 1:3 Ag@MSA colloid. Distinctly visible nanoparticles in the aggregated mass are shown in dotted circles. B) A sheet kind of a mass formed by the reaction of 1:3 Ag@MSA with 100 ppm  $\text{Hg}^{2+}$  solution showing aggregated areas and areas where etching has taken place. Inset shows a lattice plane corresponding to  $\text{Ag}_3\text{Hg}_2$  (paraschachnerite).

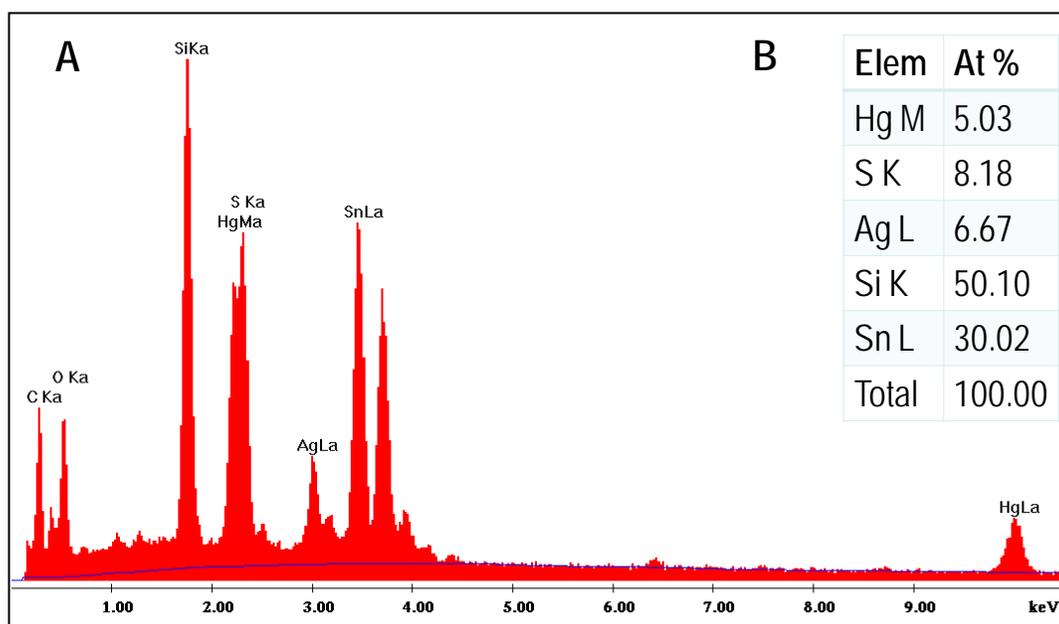


Fig. S13. A) SEM-EDAX spectrum and B) quantification table of 1:3 Ag@MSA sample after treating with 100 ppm  $\text{Hg}^{2+}$  solution. The quantification table gives the composition of Ag and Hg as  $\text{Ag}_{2.66}\text{Hg}_{2.0}$ . Si and Sn are due to the substrate used for SEM measurements.

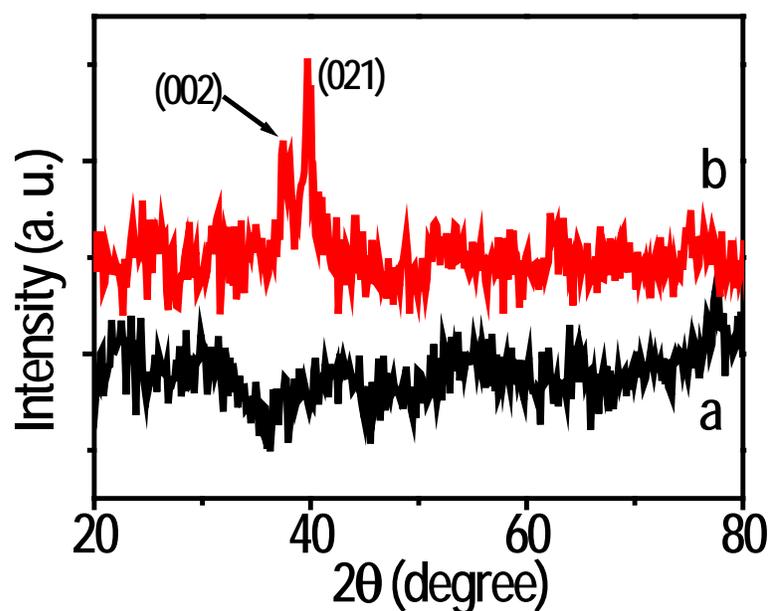


Fig. S14. XRD of the residues obtained when 1:6 and 1:3 Ag@MSA reacted (traces 'a' and 'b', respectively) with 100 ppm  $\text{Hg}^{2+}$  solution.

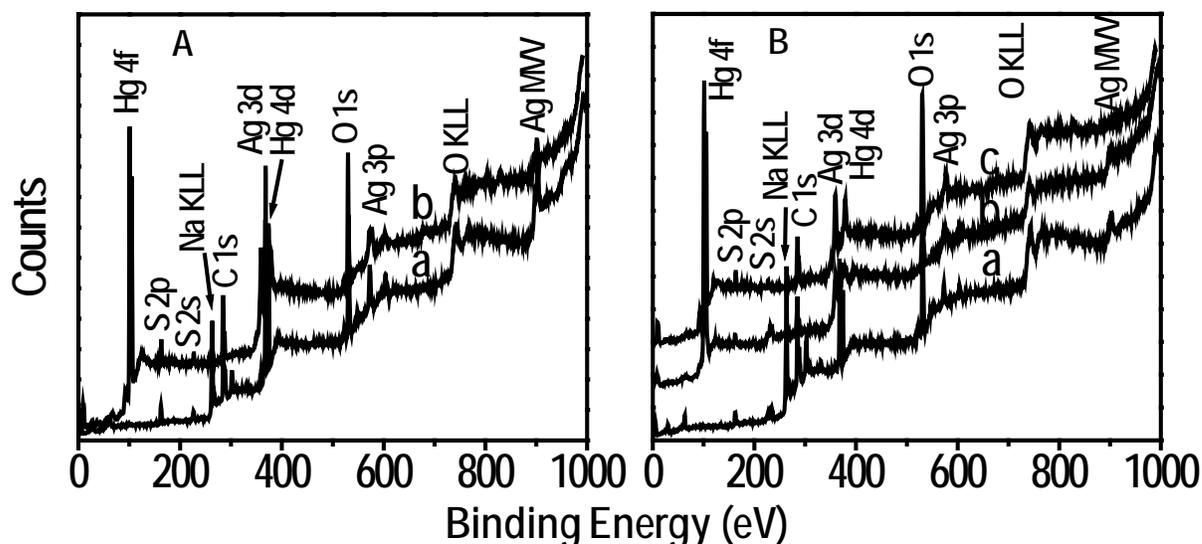


Fig. S15. XPS survey spectra of pure silver nanoparticles and the residue obtained after the introduction of  $\text{Hg}^{2+}$  ions. A) Survey spectra of 1:6 Ag@MSA systems and B) survey spectra of 1:3 Ag@MSA systems. a) Pure silver nanoparticles, b) after the introduction of 100 ppm  $\text{Hg}^{2+}$  ions and c) after introduction of 25 ppm  $\text{Hg}^{2+}$  ions.

Fig. S16. **Table S1.** The comparison of the capacities of different adsorbents for mercury removal [1].

Adsorbent used	Chelating ligand	Capacity(mg/g)
Poly vinyl alcohol	Procion Blue MX-3G	69
Styrene-divinyl benzene	Thiol	20
Polystyrene	Dithiocarbamate	32
Polystyrene	Sulfur-chlorinated jajoba wax	50
Poly(vinyl pyridine)	Dithizone	144
Poly(N-vinylimidazole)	Imidazole	200
Poly(GMA-DVB)	Thiol	400
PEGDMA	Acrylamide	54
N-hydroxymethyl thioamide	Thioamide	72
Amberlite IRC 718	Iminodiacetic acid	360
Silica	3-trimethoxysilyl-1-propanethiol	184
Silica gel	Polyethyleneimine	200
Cellulose	Polyethyleneamine	288
PMMA	Ethylenediamine	30
PHEMA	Polyethyleneimine	334
PHEMA	Thiazolidine	222

PHEMA	Dithizone	42
PHEMA	N-methacryloyl-(L)-cysteine	1018
PHEMA	N-methacryloyl-(L)-histidine	1234
PHEMA	N-methacryloyl-(l)-alanine	168
Cellulose	Polyethyleneamine	288

## References

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Fig. S17. **Table S2.** The comparison of the capacities of different commercial adsorbents for mercury removal.

S.No	Commercial adsorbent	Capacity (mg/g)
1	Thiol-SAMMS [1]	635
2	Duolite GT-73 [2]	363
3	Mg-MTMS [3]	603
4	SOL-AD-IV [4]	726
5	In this study	800

## References

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