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SUPPORTING INFORMATION

Title: Synergistic Effect in Green Extraction of Noble Metals and Its Consequences

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Table S1: Concentration of possible metals from different vessels analyzed by ICP MS. All the experiments were carried out with 70 mg glucose in 70 mL DI water at 65 °C for 7 days and the final concentrations of different metals are listed in the table.

Metals	Steel Vessel (ppb)	Copper Vessel (ppb)	Brass Vessel (ppb)	Silver Vessel (ppb)
Ni	3	102	85	299
Cu	121	248000	10500	3420
Ag	2	10	2	756
Al	0	0	38	0
Mn	166	2	6	1
Fe	576	105	65	0
Zn	73	6400	127100	125
Cr	4	0	1	1
Co	0	229	2	13
V	0	0	0	0
Ti	0	0	3	1
Mo	2	0	0	1

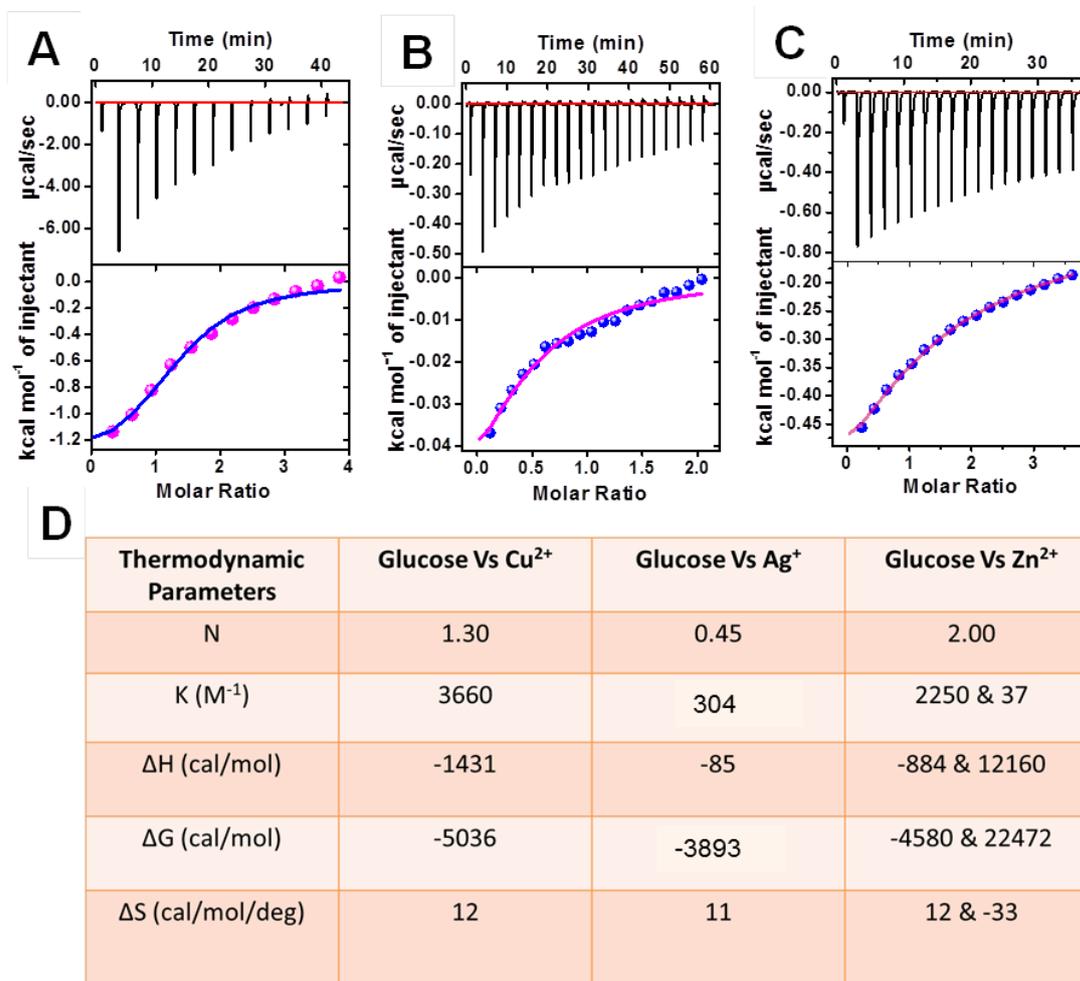


Figure S1 Isothermal calorimetric data for A) Glucose Vs CuSO₄, B) Glucose Vs AgNO₃, and C) Glucose Vs ZnSO₄ solutions. D) Thermodynamic parameters obtained from both the reactions are given as a table.

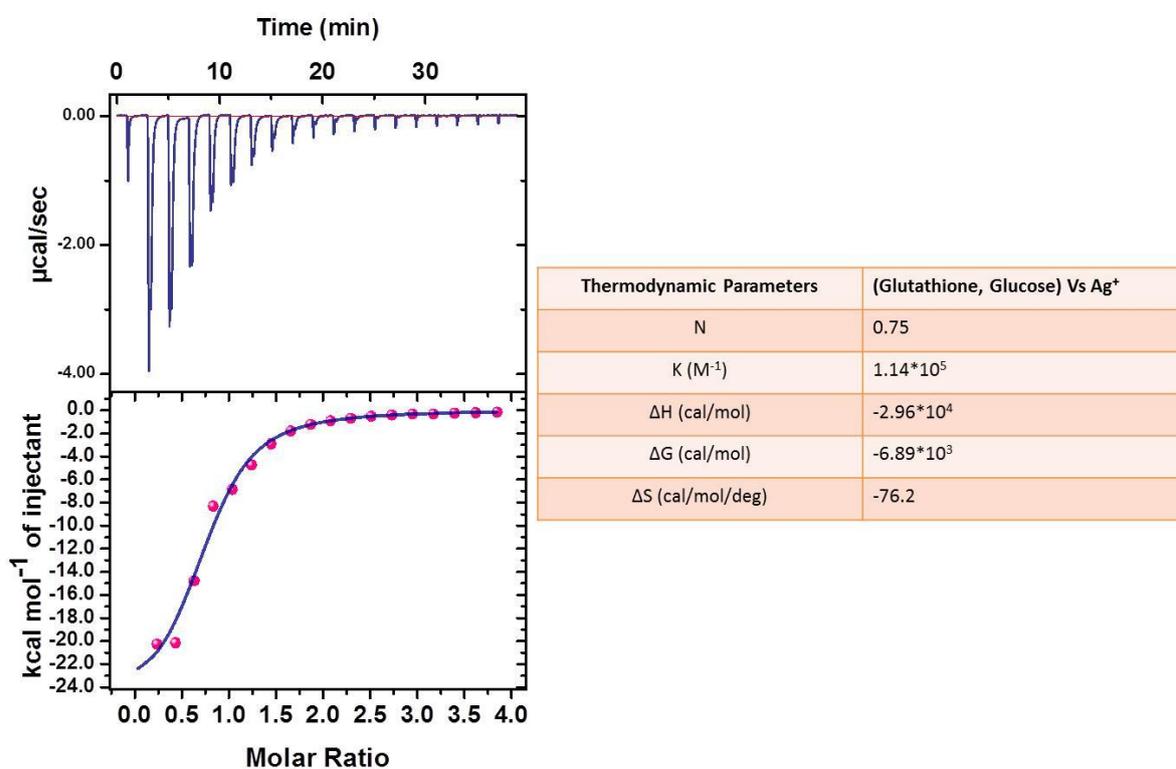


Figure S2 Isothermal calorimetric data for glutathione-glucose mixture Vs AgNO₃ solution. Thermodynamic parameters obtained from the reactions are given as a table.

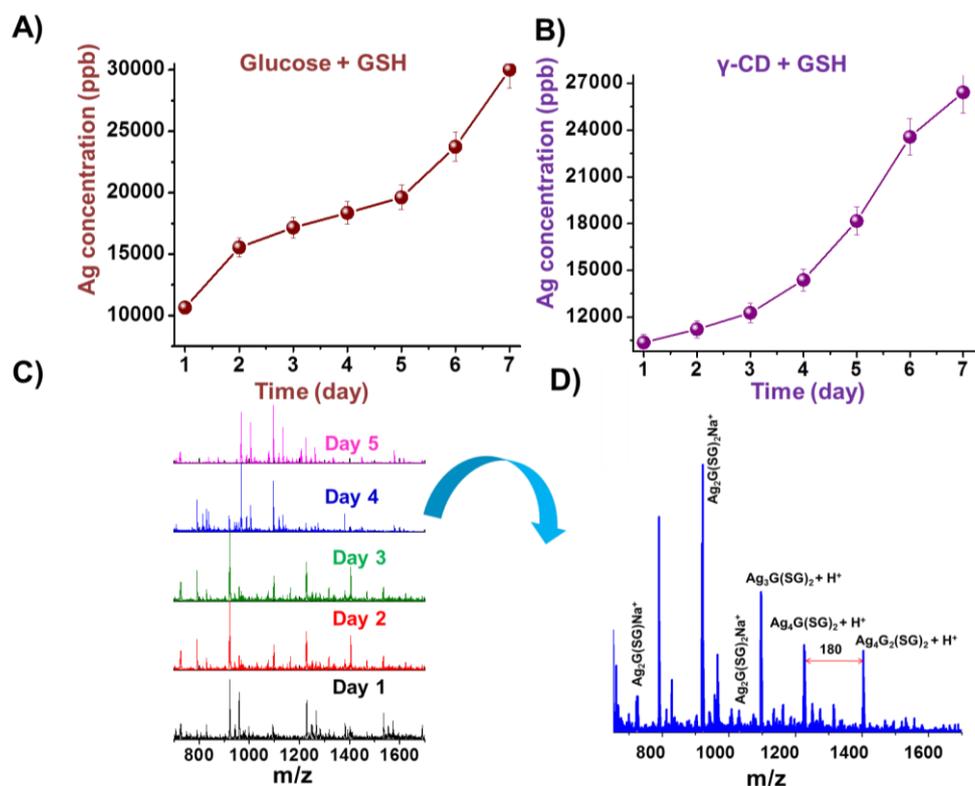


Figure S3 Silver concentration was measured as a function of time (day) in A) glucose + glutathione and B) γ -cyclodextrin + glutathione. In C), time dependent ESI MS spectra of the glucose + glutathione solution are shown. D) ESI MS data of day 4 is expanded view. In positive mode, $\text{Ag}_2\text{G}(\text{SG})\text{Na}^+$ (m/z 723), $\text{Ag}_2\text{G}(\text{SG})_2\text{Na}^+$ (m/z 922), $\text{Ag}_2\text{G}(\text{SG})_2\text{Na}^+$ (m/z 1029), $\text{Ag}_2\text{G}_2(\text{SG})_2\text{Na}^+$ (m/z 1102), $\text{Ag}_4\text{G}(\text{SG})_2^+$ (m/z 1220), $\text{Ag}_4\text{G}_2(\text{SG})_2^+$ (m/z 1404) species were seen.

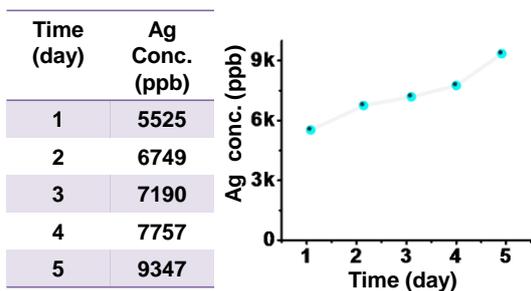
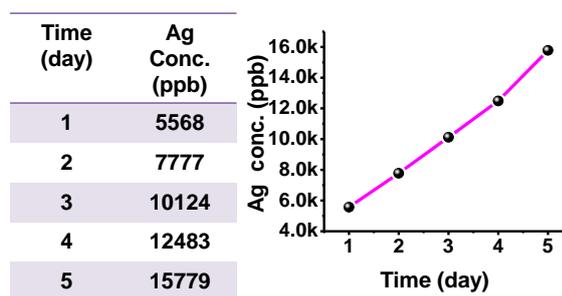
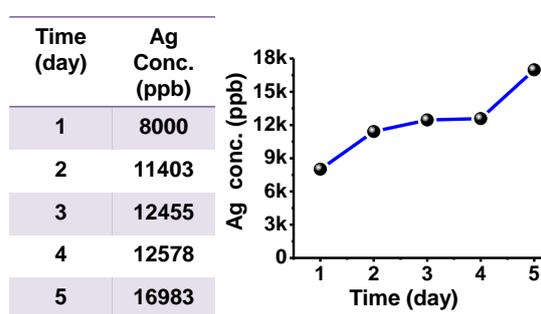
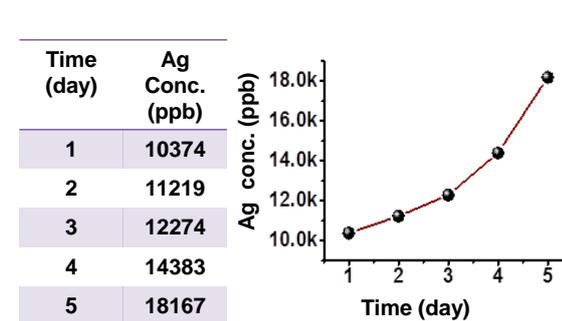
A) 60 mg Y-CD + 50 mg GSH**B) 60 mg Y-CD + 100 mg GSH****C) 60 mg Y-CD + 150 mg GSH****D) 60 mg Y-CD + 200 mg GSH**

Figure S4 Dependence of GSH amount on silver extraction showing enhanced extraction with respect to the time of the reaction. Quantitative data were obtained from ICP MS analyses. Various amounts such as: A) 50 mg, B) 100 mg, C) 150 mg, D) 200 mg of GSH were added in 200 mL solution keeping the γ -CD concentration intact (60 mg in 200 mL solution). Exact values are listed in the respective tables.

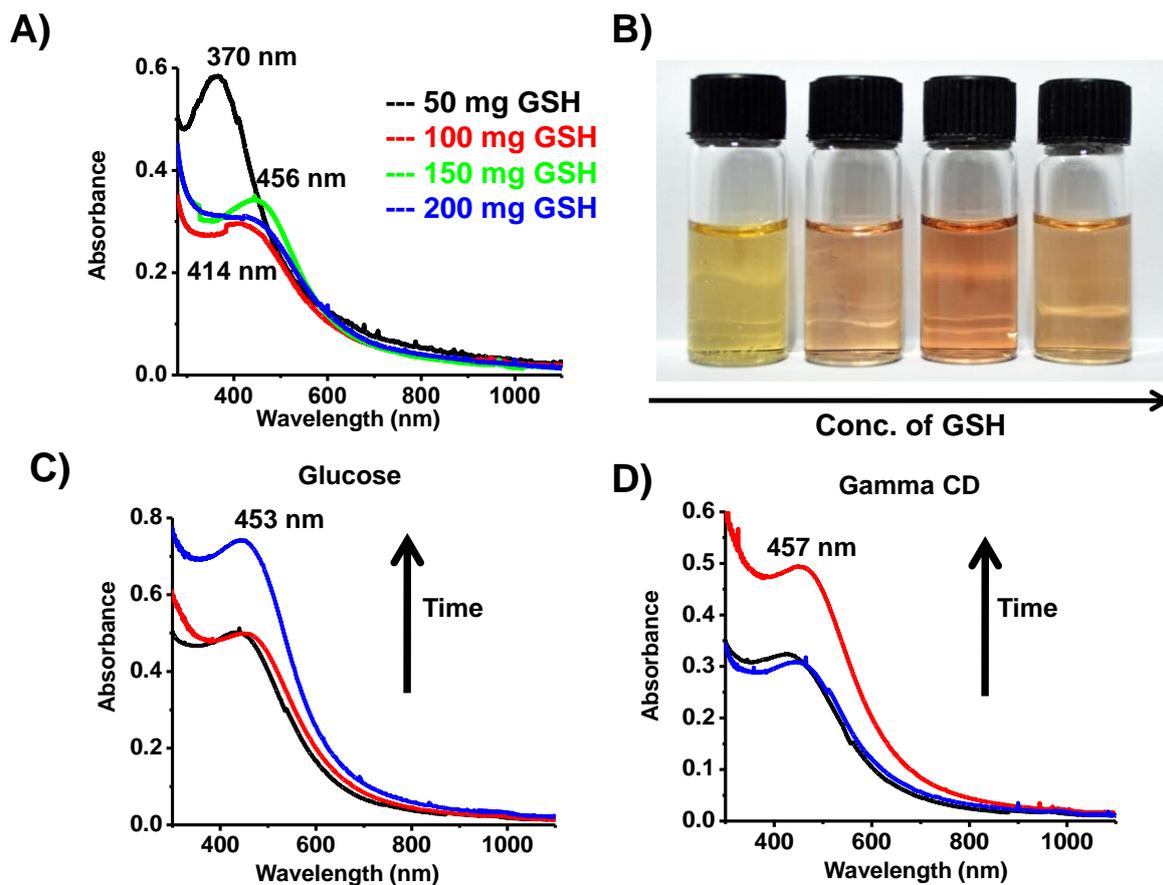


Figure S5 A) Amount (GSH) dependent UV-vis absorption spectra of the as-synthesized material after addition of ice cold NaBH_4 solution showing thiolate formation at lower GSH concentration and cluster formation as higher GSH concentration. B) Corresponding photographs are shown in the ascending order of GSH concentration. C) Time-dependent evolution of the cluster in a mixture of G and GSH and D) in a mixture of γ -CD and GSH showing increased absorption at 453 nm and 457 nm, respectively with time.

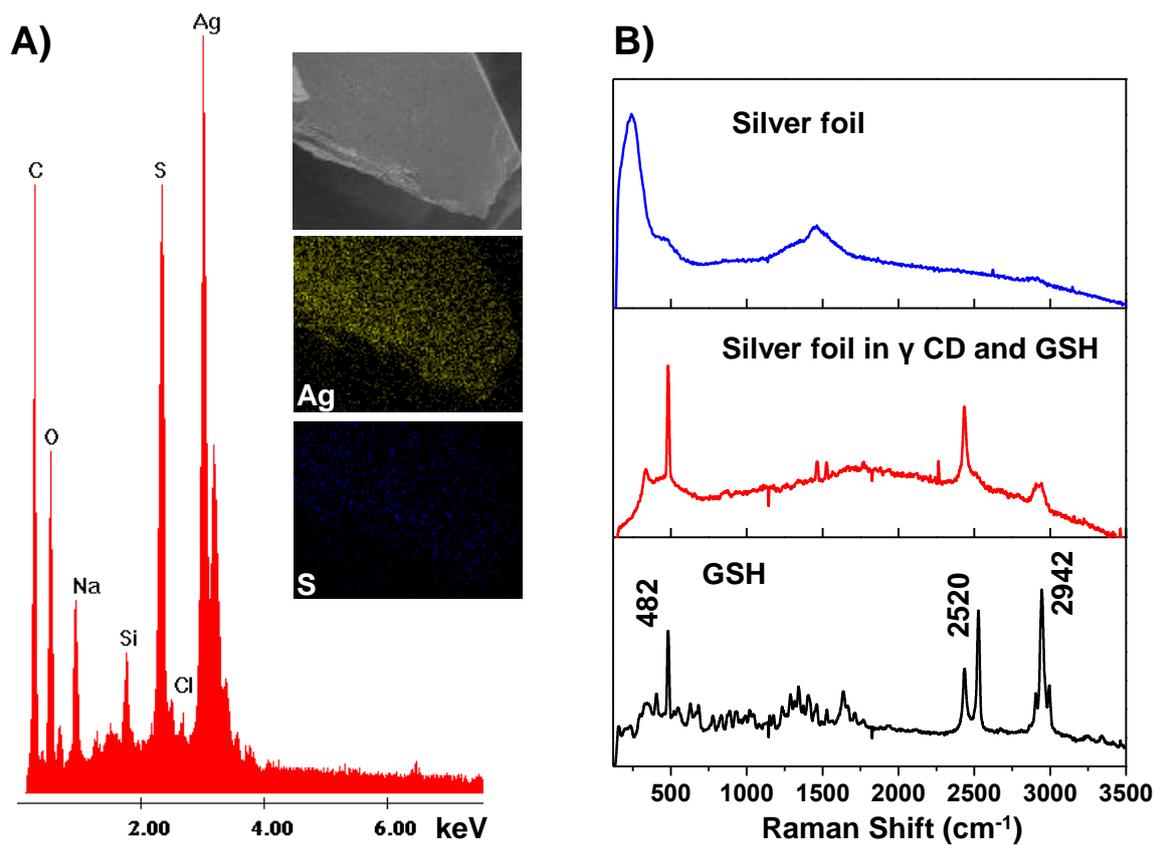


Figure S6 A) SEM EDS and elemental mapping of the immersed silver foil after the reaction. Uniform distribution of S over the silver foil was confirmed by EDS mapping of the same. (B) Raman spectra of the (i) silver foil, (ii) silver foil in γ -CD and glutathione, and (iii) glutathione alone are presented. Characteristic peaks of GSH are present on silver foil after reaction, confirming strong absorption of GSH on the silver surface.

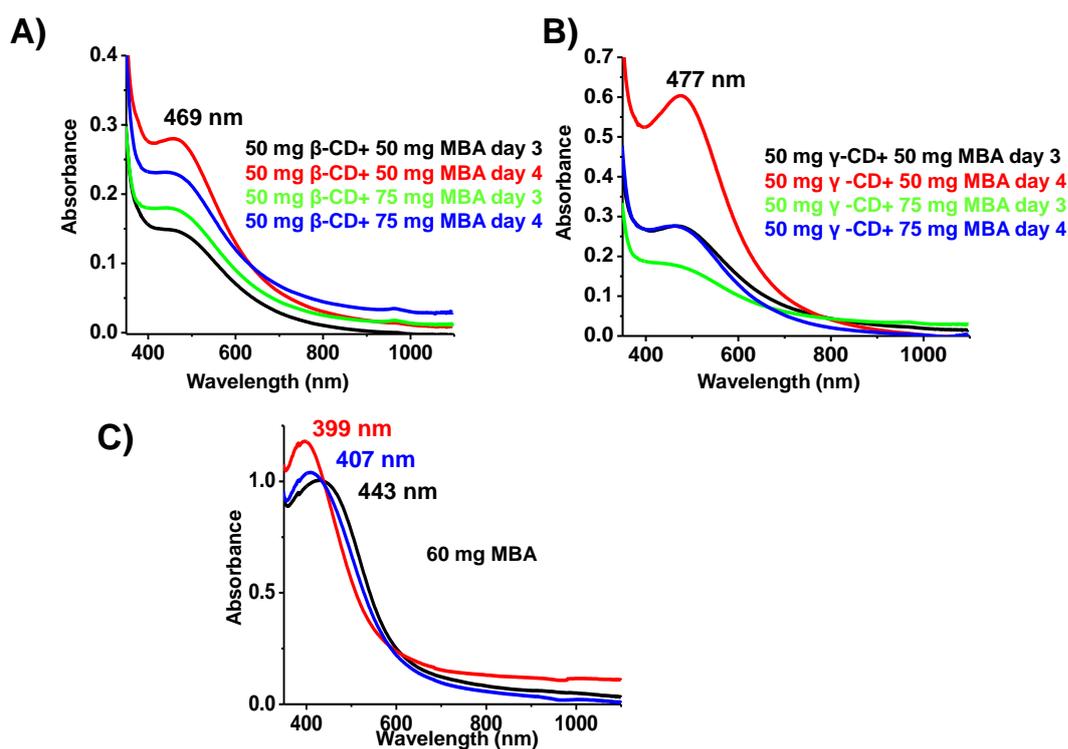


Figure S7 Amount (MBA) dependent and time dependent UV-vis absorption spectra of the as-synthesized material after addition of ice cold NaBH_4 solution, showing characteristic cluster features at 469 and 477 nm, for respectively, for A) 50 mg β -CD and B) 50 mg γ -CD containing solutions. (C) In the case of 60 mg MBA solution, plasmonic Ag nanoparticles were forming and the peak was shifting towards blue. A narrow peak at 399 nm (C) is characteristic of plasmonic silver nanoparticles.

Table S2 Silver concentration was measured as a function of time (day) using ICP MS.

Dependence on the quantity of β -CD and MBA

Time (Day)	Ag concentration (ppb) 50 mg β-CD + 50 mg MBA	Ag concentration (ppb) 50 mg β-CD + 75 mg MBA
2	7191	8320
3	5168	8661
4	5763	9276
9	6878	5470

Dependence on the quantity of γ -CD and MBA

Time (Day)	Ag concentration (ppb) 50 mg γ-CD + 50 mg MBA	Ag concentration (ppb) 50 mg γ-CD + 75 mg MBA
2	8490	14776
3	5001	17037
4	5763	19573
9	6878	5470

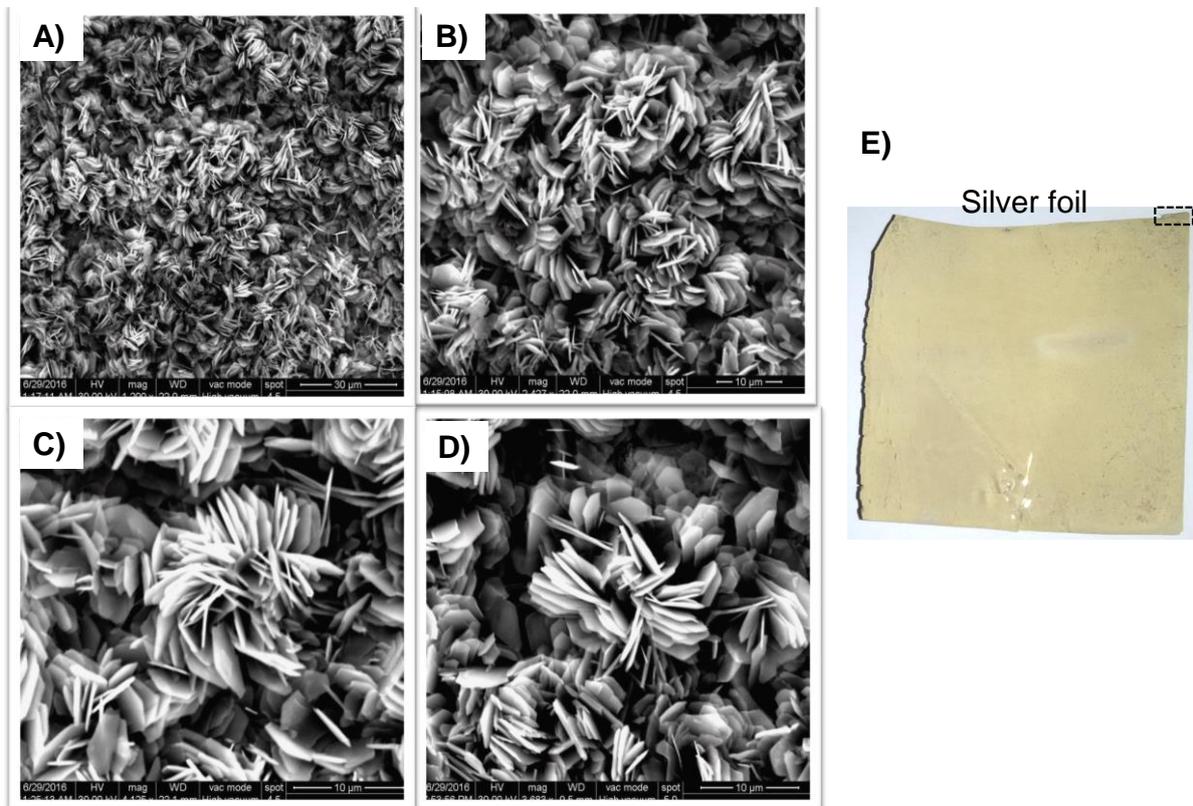


Figure S8 A), B), C), and D) SEM images of the silver foil at different magnifications after exposure to MBA. Blade like sharp structures were observed. E) The colour of the silver foil was changed after 3 days of immersion in MBA solution. The area imaged in SEM is marked on the top corner.

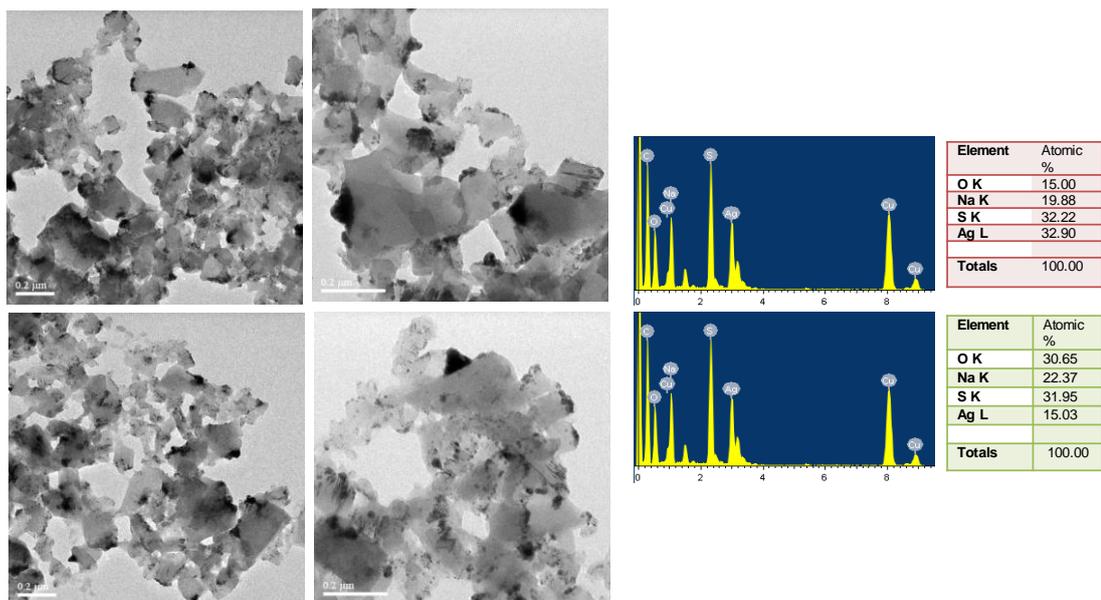


Figure S9 TEM images/EDS of the material at different magnifications after reaction with MBA. The material was extracted from the silver foil.

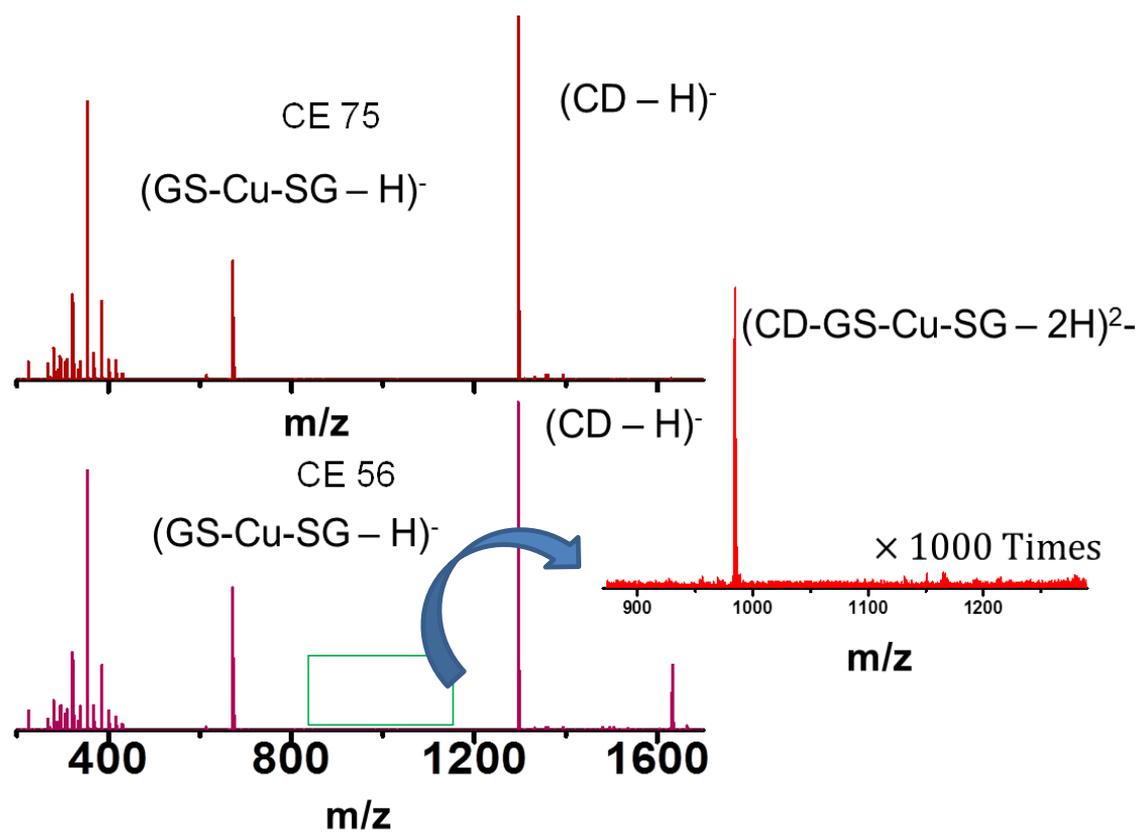


Figure S10 MSMS data of $(\text{CD-GS-Cu-SG-CD-2H})^{2-}$ ($m/z = 1633$) at various collision energies. CE refers to laboratory collision energy in eV.

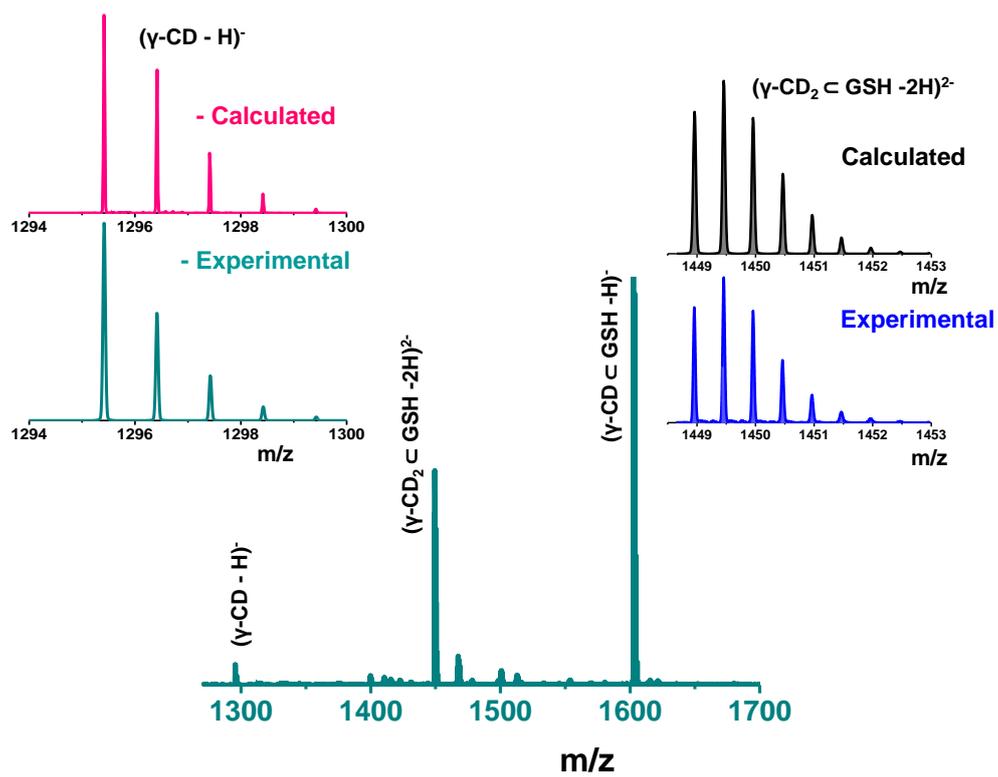


Figure S11 ESI MS of a mixture of γ -CD and GSH solution. 1:1 and 1:2 types (GSH: γ -CD) inclusion complexes were seen. Experimental data are compared with calculated data.