

Supporting Information

Extraction of Silver by Glucose

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Supporting Information

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Materials: D(+)-G, Sucrose, α , β and γ -CD were purchased from Sigma Aldrich. D(+)-Mannose was purchased from SRL chemicals with 99% purity. D(-)-Fructose was purchased from Merck and γ -CD was purchased from TCI, Japan. Silver foils were purchased from local market. All the chemicals were used without further purification. Deionized water was used throughout the experiments (if not specified). Sodium nitrate, sodium sulphate, sodium carbonate, sodium phosphate and water soluble starch were purchased from Sigma Aldrich.

Instrumentation:

ICP MS analysis: ICP MS was performed using a Perkin Elmer NexION 300X instrument equipped with Ar plasma. Before doing any sample, the instrument was first calibrated with Ag standard (AgNO₃) of five different concentrations (0, 10, 100, 1000 and 10000 ppb) to get a calibration curve with R^2 =0.9999. Blank experiment (0 ppb) was performed with milliQ water (18.3 M Ω resistance) with 5% nitric acid. Standards were also prepared in 5% nitric acid. Same amount (5%) of nitric acid was added to the collected samples also before analyses.

ESI MS: ESI MS analysis was carried out using an Applied Biosystems 3200 QTRAP LC/MS/MS system in the mass range of m/z 80 to 1700. Optimized conditions were as follows: Ion spray Voltage 3 kV; Declustering Potential (DP) 30 V, Entrance Potential (EP) 10 V. For MS/MS analyses, collision energy was varied from 5 to 100 (instrument unit). Optimum fragmentation was observed in the range of 30-50.

ITC: Isothermal calorimetric experiments were performed using a GE Microcal iTC200. The instrument is having two cells made of hastelloy with 200 μ L cell volume of which one is used for sample and another is used as reference. Maximum volume that can be injected is 40 μ L through a syringe with sub-micro liter precision. Each time 2 μ L of AgNO₃ was injected for a total of 20 injections for a glucose-AgNO₃ experiment. In the other cases, optimized injection volume was found to be 3 μ L and a total of 13 injections were performed. The heat change due to interaction of water-water, water-AgNO₃ and AgNO₃-Na₂CO₃/Na₃PO₄ were subtracted from the original data before fitting. The data were fitted using one site model. The experimental error was less than 5% for each parameter.

Raman Spectroscopy: Raman measurements were done using a WITec GmbH, Alpha-SNOM alpha300 S confocal Raman microscope having a 532 nm laser as the excitation source. Background correction was done with the help of the software supplied with the Raman instrument (WiTec). Initially, the spectrum is fitted with a polynomial which was subtracted from the original spectrum. The analyte (CV) was drop cast on the roughened surface at various concentrations and Raman spectra were measured under these conditions (Figure S6A). For SERS study, 5µL of the analyte was drop cast on the respective silver foil and air dried before analysis. In each case, nine spots were checked for each concentration of CV to see the reproducibility of the data. These data are complied in Table S2. Raman spectra in the concentration range of 5×10^{-5} to 5×10^{-9} M were measured and the detection limit was 5×10^{-7} M (see Figure S7). Reproducibility of the data was ensured by collecting spectra from nine different spots.

Enhancement Factor Calculation: The enhancement factor (EF) was calculated using the standard formula,

$EF = I_{SERS} * C_{NR} / I_{NR} * C_{SERS},$

where, I_{SERS} and I_{NR} are the integral intensity obtained by SERS and normal Raman scattering measurements, respectively. C_{SERS} and C_{NR} are the concentration of molecules used for SERS and normal Raman scattering measurements, respectively. Intensity of the maximum intense peak of the analyte (CV) at 1620 cm⁻¹ was considered for EF calculations.

UV-vis Spectroscopy: UV-vis spectra were collected using a PerkinElmer Lambda 25 instrument in the 200-1100 nm range. The band pass filter was set at 1 nm.



Figure S1. Isotope resolved (black trace for $2G^{-107}Ag^+$ and red trace for $2G^{-109}Ag^+$) ESI MS/MS of $2G^+$ Ag⁺ complex showing one G loss to give G^-Ag^+ complex and free Ag⁺. Respective peaks are expanded in A, B and D. Experimental mass spectrum of $2G^-Ag^+$ matches with the theoretically calculated pattern as shown in C.





Figure S2. ESI MS of 1:1 (molar) G and AgNO₃ mixture showing G-Ag, 2G-Ag and 3G-Ag complexes.





Figure S3. Time dependent silver leaching in DI water containing 50 ppm of A) CO_3^{2-} and B) PO_4^{3-} showing very less silver concentration compared to that with G. Na₂CO₃ and Na₃PO₄ were used as salts. Salts alone (without G) do not result in much extraction.



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Figure S4. Silver leaching of glucose at varying pH. Acidic pH was maintained by acetic acid and pH 8 was maintained by NaOH. At pH 8, it appears that the silver surface gets passivated by the formation of silver hydroxide.



Figure S5. Isothermal calorimetric data for A) G and AgNO₃, B) G with carbonate and AgNO₃, C) G with phosphate and AgNO₃ titration. Thermodynamic parameters obtained from both the reactions are tabulated in D). Na₃PO₄ and Na₂CO₃were used for phosphate and carbonate.



Figure S6. Observation of SERS activity of the reactedAg foils. Crystal violet (CV) was taken as an analyte at 5×10^{-6} M. A 532 nm laser was used for this study. Note the change in numbers in the y-axis under various conditions. Intensity of the band at1620 cm⁻¹ of CV was used for calculating the enhancement factor (EF). MQW refers to MilliQ water and others correspond to respective species in DIW. B) Optical microscopic images of the silver foil before and after reaction in presence of G andcarbonate.





Figure S7. Observation of SERS activity in the reacted Ag foils. Crystal violet (CV) was taken as the probe analyte. Analyte concentration was 5×10^{-7} M. The peak used for SERS calculation is marked.

Compound	Solubility (gm/L)	
AgNO ₃	1220 (0°C) 2160 (20°C) 4400 (60°C) 7330 (100°C)	
Ag_2SO_4	7.9 (20°C) 13.0 (80°C)	
Ag ₂ CO ₃	0.032 $K_{SP} = 8.46 \times 10^{-12}$	
Ag ₃ PO ₄	0.0065 K _{sp} = 8.89×10^{-17}	
AgF	1720	
AgCl	0.0019 (20°C) 0.0052 (50°C) $K_{sp}=1.77\times10^{-10}$	
AgBr	0.00014 (20°C) $K_{sp}=5.4 \times 10^{-13}$	

Table S1: Solubility and solubility product data of different silver salts of relevance.

		v		
Substrate	CV conc. (C _{SERS})	Intensity of 1620 cm ⁻¹ peak (I _{SERS})	C _{NR} /I _{NR}	EF
Ag foil as blank	5×10-6	76	6.6×10 ⁻²	9.77×10 ⁵
In MQW	5×10-6	614	6.6×10 ⁻²	8.10×10^{6}
In MQW	5×10-7	41	6.6×10 ⁻²	5.41×10 ⁶
In Glucose soln.	5×10-6	3906	6.6×10 ⁻²	5.16×10 ⁷
In Glucose soln.	5×10-7	101	6.6×10 ⁻²	1.33×10 ⁷
In Glucose+ PO_4^{3-} soln.	5×10-6	828	6.6×10 ⁻²	1.09×10^{7}
In Glucose+ PO_4^{3-} soln.	5×10-7	211	6.6×10 ⁻²	2.78×10^{7}
In Glucose+ CO_3^{2-} soln.	5×10-6	38486	6.6×10 ⁻²	5.08×10 ⁸
In Glucose+ CO_3^{2-} soln.	5×10-7	165	6.6×10-2	2.18×10 ⁷

Table S2. EF at different reaction conditions showing maximum enhancement when the Ag foil was heated in 27.8 mM G solution containing 50 ppm carbonate.