Silver Extraction

Extraction of Silver by Glucose

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Abstract: *Unprecedented silver ion leaching, in the range of 0.7 ppm was seen when metallic silver was heated in water at 70°C in presence of simple carbohydrates, such as glucose, making it a green method of silver extraction. Extraction was facilitated by the presence of anions, such as carbonate and phosphate. Studies confirm a two-step mechanism of silver release, first forming silver ions at the metal surface and later complexation of ionic silver with glucose; such complexes have been detected by mass spectrometry. Extraction leads to microscopic roughening of the surface making it Raman active with an enhancement factor of 5×10^8.*

Noble metals are resistant to chemical corrosion. Extraction of noble metals from minerals and subsequent processing requires highly reactive conditions and toxic chemicals.[1] Silver, one of the important and precious coinage metals is sourced from the ores, and mostly extracted by chemical and electrolytic methods.[2] Major use of silver lies in photography and 60% of the total silver produced every year is recycled from photographic plates.[3] This situation demands extraction and recycling of silver via green methods at mild conditions. Silver ions react strongly with biomolecules including carbohydrates, peptides and DNA.[4] Similar interactions with biomolecules are observed in biomineralization pathways in microorganisms.[5] Silver nanoparticles are made using glucose and starch as reducing as well as capping agents.[4–6]

Herein, we show the extreme chemical affinity of silver to carbohydrates leading to their extraction in solution, directly from the metallic state, which is enhanced in presence of common ions suggesting a new method of extractive metallurgy. The process is thermodynamically favorable as seen from a calorimetric study. Continuous extraction of silver leads to corrosion of the surface and subsequent microscopic roughness was observed. This roughened surface acts as an effective substrate for surface enhanced Raman spectroscopy (SERS).

In a typical experiment, a silver foil of 6 cm × 6 cm area and 3 g in mass leaches out 656 ppb silver in 27.8 mM glucose (G) solution in 7 days, when the extraction was performed at 70°C in a Teflon beaker. Surface area and mass of the silver

foil were kept constant for all the experiments. This foil decreases its mass by 0.5% in this time. Exposure for 90 days can lead to 10% mass loss of the silver foil, in the above condition. Time dependent variation of the mass during an experiment is shown in Figure 1. Silver mirrors coated on glass slides also show similar leaching. However, as we keep our reaction in stirring conditions, the silver mirror gets damaged and therefore we continued our experiments with silver foils.
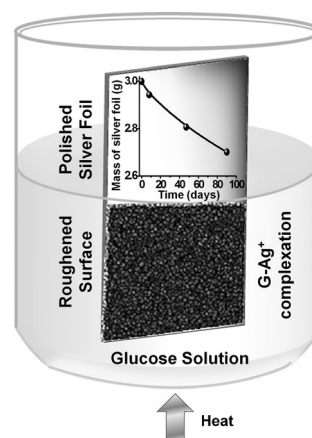

Figure 1. Schematic representation (not to scale) of silver extraction by glucose (G). A silver foil was kept partly immersed in a solution of glucose, maintained at 70°C. The immersed portion turns black with time, owing to roughening. Weight loss of the foil with respect to time is shown.

The weight loss is due to the leaching of Ag as Ag^+ and the existence of glucose–Ag^+ (G-Ag^+) complexes in the solution was studied. G-Ag^+ and 2G-Ag^+ complexes were detected by electrospray ionization mass spectrometry (ESI MS) (Figure 2). In tandem mass spectrometry (ESI MS/MS), the G-Ag^+ complex ions (*m/z* 287 and 289, arising from ^{107}Ag and ^{109}Ag isotopes, respectively) fragment to their components at nominal collision energy of 20 V (Figure 2C). The 2G-Ag^+ complex shows a similar pattern, fragmentation leads to G-Ag^+ and Ag^+ ions (see Figure S1 in the Supporting Information). Similar adducts were seen when glucose was treated with $AgNO_3$ which established the formation of G-Ag^+ complexes in solution by silver ions derived from silver foils (Figure S2). Similar complex was predicted by Boutreau et al. with a series of monosaccharides, such as glucose, sucrose, fructose, through computational studies.[7] Owing to presence of multiple stereoisomeric forms of glucose, it can bind to metal ion at different positions. They have computed the structures of such G-Ag^+ complexes and found that α-anomer of glucose binds effectively with Ag^+ through hydroxyl groups

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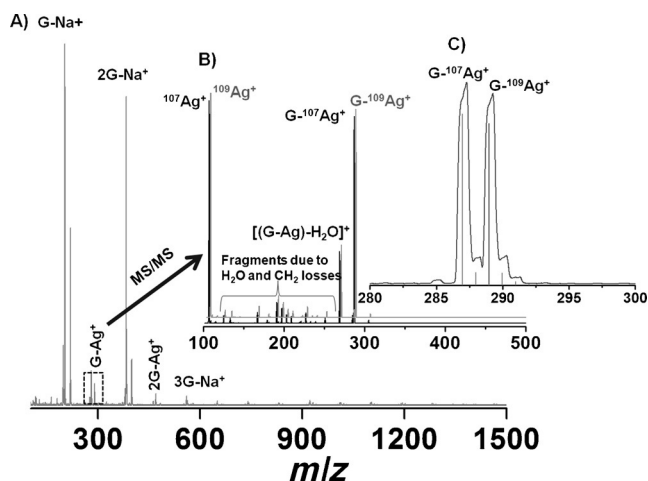   http://dx.doi.org/10.1002/anie.201510122.

Figure 2. A) ESI MS of glucose–silver complexes G-Ag obtained by the extraction of silver foil by glucose (in water) at 70°C, showing the formation of Ag containing ions. B) MS/MS of G-Ag$^+$ showing the loss of one G to give Ag$^+$. Data corresponding to ^{109}G-Ag$^+$ (gray) and ^{107}G-Ag$^+$ (black) are shown. C) Expanded view of G-Ag$^+$ complex region of (A) matching well with the calculated mass spectrum, with isotopes. See Supporting Information Figure S1 for isotope resolved MS/MS of 2G-Ag$^+$complex.
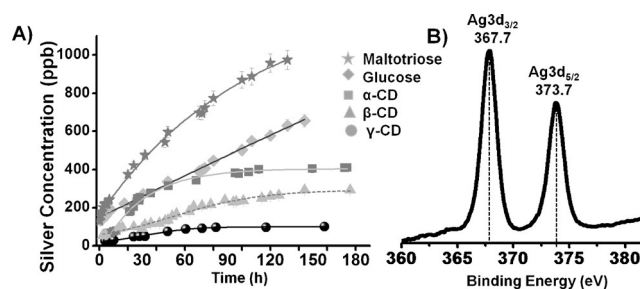

Figure 3. A) Silver-leaching capability of different carbohydrates in presence of a silver foil (6 cm × 6 cm, 3 g in mass). Maltotriose causes the maximum silver leaching among glucose, maltotriose, α-CD, β-CD, and γ-CD. Total silver-ion concentrations were obtained from ICP MS analyses. All the experiments were repeated three times and average data are plotted. The surface area of the Ag foil was kept constant throughout the investigation. B) XPS of Ag-G complex (formed during the silver leaching experiment) in the form of a dried film, showing the presence of Ag$^+$ in the solution.

at positions 3 and 4. The isotope pattern (Figure 2 C) and fragmentation from the isotopically pure ions confirm the identity of the ions.

Several experiments were performed to find the optimum condition of silver extraction, as outlined below:

1. Among three monosaccharides; glucose, fructose, and mannose, glucose was found to be most effective in extracting silver. In a typical experiment, 28.7 mM of glucose (1 g, 5×10^6 ppb) was used in 200 mL deionized water and the solution was heated at 70°C. For other carbohydrates equivalent quantity was taken.

2. Gradual increase in the number of glucose units may have some effect in the extraction process. We performed extraction using mono, di-, and trisaccharides and the data obtained were as follows: glucose (656 ppb), sucrose (120 ppb), and maltotriose (990 ppb). Although malto- triose had maximum effect (see Figure 3 A); owing to its high cost we continued our experiments with glucose.

3. In a concentration dependent study, we found that silver concentration is dependent on the glucose concentration and 27.8 mM of glucose (1 g, 5×10^6 ppb) was good enough to extract moderate amount of silver in solution. Higher concentration of glucose does not lead to increased silver leaching.

4. We have also performed the reaction using α, β, and γ- cyclodextrins (CDs) and found that silver concentration follows the order, α > β > γ. The observed trend of reactivity of different cyclodextrins towards silver is in agreement with the reported complexation of Au^{3+} ions. Liu et al. have shown that gold ions can complex effectively with cyclodextrin via second sphere co-ordi- nation.[8] They have used different gold salts for this experiment and showed that KAuBr$_4$ is the most efficient candidate for such complexation. Specificity of extraction

of gold by complexation with α-CD was demonstrated by extracting metal ions from an AuAg alloy using a mixture of conc. HBr and HNO$_3$.

5. Silver extraction is highly dependent on the purity of water. The extraction is highest in tap water and lowest in Millipore water (resistance 18.3 MΩ). Deionized water showed an intermediate effect. This happens mostly due to presence of different anions, such as carbonate, bicarbon- ate in regular tap water (see below for the anion effect).

6. Silver concentration increases with increase in solution temperature. From a temperature dependent study, we noticed that silver concentration was highest at 80°C. We carried out all the other experiments at 70°C to avoid excessive evaporation of water as we wanted to continue the experiment for longer time. Beyond 80°C, extraction was retarded. The probable cause could be cavitation on the silver surface by bubbles of water vapor at higher temperatures which cover the available silver surface and decrease the dissolution of silver.

The existence of Ag$^+$ in the form of complexes was confirmed by X-ray photoelectron spectroscopic studies by casting the material in the form of a thin film (Figure 3 B). The observed binding energy of 367.5 eV for Ag 3d$_{3/2}$ is close to that of Ag$^+$.[9]

The dissolution of silver ion was examined in presence of various anions and the data are presented in Figure 4 which reveals a correlation with the solubility of the corresponding silver salt. The salts were added separately in the solution prior to the addition of glucose and silver foil was immersed in it. Various anions commonly present in tap water, such as, nitrate, sulfate, carbonate, bicarbonate, phosphate, chloride, bromide, have been examined (all as sodium salts) and phosphate was found to be most effective among all. About 10 times and 7 times enhancement in dissolution were observed in presence of 50 ppm (optimized from a concen- tration dependent study of anion concentration keeping all other conditions same) phosphate and carbonate; respec- tively along with glucose (same concentration of glucose was used as mentioned before). Silver-leaching capacity may be
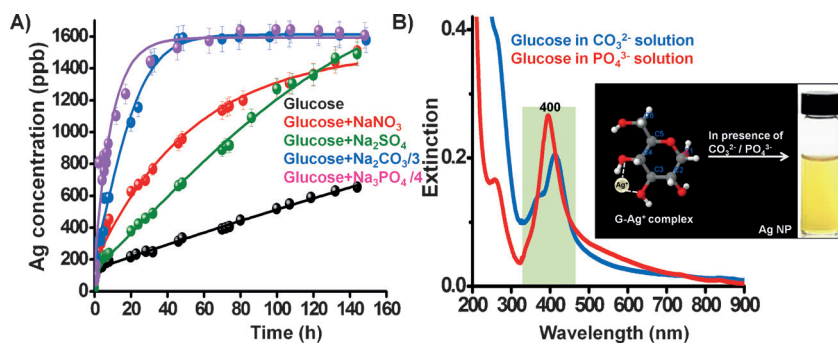
Figure 4. A) Effect of foreign anions on silver leaching from silver foil, in presence of glucose. In all cases, sodium salts of different anions namely, nitrate, sulfate, carbonate, and phosphate (50 ppm each, keeping glucose concentration the same) have been added. All of them enhance silver concentration in the solution while carbonate and phosphate have maximum enhancing capacity (4667 and 6554 ppb, respectively). The traces with carbonate and phosphate have been divided by 3 and 4, respectively. B) In presence of carbonate and phosphate, Ag nanoparticles form which was confirmed by UV/Vis spectroscopy with a characteristic plasmon band at 400 nm. Inset of (B) shows a schematic of the conversion of complexes into NPs and the photograph shows the product.

understood from the solubility of these silver salts in water, which are in the order, 32 and 6.5 mg L^{-1} for Ag$_2$CO$_3$ and Ag$_3$PO$_4$, respectively (see Table S1 for details). In all the cases, sodium salt of the respective anion was used.

In addition to the above, plasmonic nanoparticles were formed in presence of carbonate and phosphate which was confirmed from the characteristic plasmon band at 400 nm in the UV/Vis absorption spectrum of Ag nanoparticles (AgNPs) (Figure 4B). This appears due to the subsequent reduction of silver ions by glucose. Therefore, glucose has a dual role. Note that the anions alone (without glucose) have no significant effect in metal dissolution (see Figure S3). glucose can reduce Ag$^+$ as mentioned earlier.

After confirming the role of counteranion in water, we have further extended the study to halides. Among the silver halides, AgF is soluble in water and the solubility decreases in the order, F$^-$ > Cl$^-$ > Br$^-$ > I$^-$. Same trend was found in dissolution where Ag concentration was maximum in presence of F$^-$ and minimum in presence of Br$^-$. However, in all such cases, the Ag$^+$ concentration was much below that with G (see Table 1 for details).

We have also studied a wide range of pH (pH 3 to 8) to check its effect in the extraction (see Figure S4). Acidic pH was maintained using acetic acid and sodium bicarbonate and sodium hydroxide (pH 8) was used to maintain basic condition in water. At slightly acidic condition (pH 6), silver concentration was found to be higher (1368 ppb after 48 h) than the neutral condition. But as we increase the acidity, silver concentration gradually decreases. When basic pH was maintained using sodium bicarbonate (NaHCO$_3$), high concentration of silver (3888 ppb after 48 h) was recorded in solution. At the same time, silver extraction was retarded (50 ppb after 48 h) in presence of sodium hydroxide (pH 8), may be due to the hydrolysis of G at that condition. So not only pH but also the counter ion has important role in deciding the silver concentration in solution. Larger pH variation was not examined as in both these extremes, sugars will hydrolyze.

Presence of inorganic fertilizers in the soil can have some effect on the dissolution of insoluble compounds in water. To check whether presence of such species can alter silver concentration, we have performed four sets of extractions with two common fertilizers urea and NPK (a mixture of urea, phosphate and potassium in the ratio, 10:26:26), with and without glucose) and found that very high concentration of silver comes out when urea was used in presence of glucose. About 20 ppm of silver was observed in the solution of 1:1 glucose:urea (molar) mixture. About 1 ppm of silver was found when 40 mM of urea alone was used. Urea can produce ammonia in solution which can interact with the silver ion coming in the solution and form a stable silver-amine complex. This complex can subsequently interact with glucose and enhance the extraction. NPK does not enhance silver leaching to the same extent like urea. About 9 ppm of silver was observed in presence of glucose and NPK. This study suggests that fertilizers can have an effect in extracting noble metals in ionic form from their
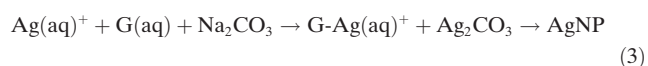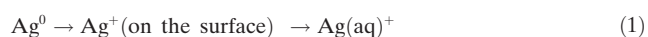
Table 1: Extraction of silver at different conditions.[a]

Entry	Sample	Max. Ag conc. [ppb]
1	MilliQ water	80
2	DI water (DIW)	140
3	G in DIW	656
4	G in tap water	4100
5	Sucrose in DIW	120
6	Maltotriose in DIW	990
7	α-CD in DIW	460
8	β-CD in DIW	300
9	γ-CD in DIW	120
10	DIW + CO$_3^{2-}$	66
11	DIW + PO$_4^{3-}$	144
12	G + NO$_3^-$ in DIW	1409
13	G + SO$_4^{2-}$ in DIW	1591
14	G + CO$_3^{2-}$ in DIW	4667
15	G + HCO$_3^-$ in DIW	3888
16	G + PO$_4^{3-}$ in DIW	6554
17	G + F$^-$ in DIW	167
18	G + Cl$^-$ in DIW	101
19	G + Br$^-$ in DIW	42
20	G in DIW at pH 3	718
21	G in DIW at pH 5	607
22	G in DIW at pH 6	1369
23	G in DIW at pH 8	60
24	Silver mirror in G in DIW	1037 (with stirring)
		561 (without stirring)
25	Silver mirror in G + CO$_3^{2-}$ in DIW	3701
26	Silver mirror in G + PO$_4^{3-}$ in DIW	4752
27	Urea in DIW	987
28	NPK in DIW	519
29	G + Urea in DIW	15888
30	G + NPK in DIW	8541

[a] All the experiments were repeated three times and average data are listed. Typical standard deviation among measurements is ±2.

sources in soil causing heavy metal toxicity, which may be bio-amplified through agriculture.

All these studies point to an ionic reaction in which silver ions come into the solution and subsequently get stabilized by the carbohydrate present in the medium. For further confirmation of this hypothesis, we have modified the silver surface. A new and polished silver foil was used for this study. The surface of the foil was wiped with very dilute nitric acid for mild oxidation of the silver surface. This modified silver foil was dipped in glucose containing water and heated at 70 °C for 2 h. About 2 ppm of silver was observed just after 2 h. Without wiping with dilute HNO_3, the silver concentration was 0.7 ppm after 7 days. This study confirms our claim of ionic reactions. On the basis of the above studies and observations, the process can be written as follows [Eq. (1)–(3)]:

$$Ag^0 \rightarrow Ag^+(\text{on the surface}) \ \rightarrow Ag(aq)^+ \tag{1}$$

$$Ag(aq)^+ + G(aq) \rightarrow \text{G-Ag}(aq)^+ \tag{2}$$

$$Ag(aq)^+ + G(aq) + Na_2CO_3 \rightarrow \text{G-Ag}(aq)^+ + Ag_2CO_3 \rightarrow \text{AgNP} \tag{3}$$

As the G-Ag(aq)$^+$ complex is stable, more silver comes into the solution. The effect of silver dissolution in various conditions is summarized in Table 1. Oxidation of silver appears to be facilitated by dissolved oxygen as an Ar purged solution shows only 530 ppb Ag under identical conditions (in contrast to 656 ppb for exposed solution). There is no effect of ambient light in this reaction as similar Ag concentration was seen for a reaction done in dark (687 ppb).

Enhanced dissolution of silver in presence of ions suggests increased chemical affinity of the metal with glucose in presence of these ions. This was proven by isothermal titration calorimetric (ITC) experiments. In a typical ITC measurement, 1 mM glucose solution was titrated against 10 mM of $AgNO_3$ (20 mM in presence of carbonate and phosphate) and the heat change was recorded. The data were converted to a sigmoidal curve and from fitting the data we derive the thermodynamic parameters, N, K, ΔH, ΔS, ΔG which represent the number of binding sites, rate of reaction, reaction enthalpy, entropy and Gibb's free energy, respectively. The temperature for the experiment was 343 K. The data suggest nearly 1:1 complex formation of G with Ag$^+$ (Figure S5A), in the glucose versus $AgNO_3$ titration. Fractional binding sites are due to the presence of different aggregates (G-Ag$^+$, 2G-Ag$^+$, etc. as discussed in the ESI MS of the complex and in Figure S2) which also interact with Ag$^+$ in the reaction conditions. Negative ΔH, ΔG and positive ΔS suggest that the reaction is thermodynamically favorable and mostly enthalpy driven. In presence of carbonate (Figure S5B) and phosphate (Figure S5C), the rate of reaction increased and also the heat change. Entropy remained almost the same and hence the reaction is enthalpy driven. All the data are summarized in Figure S5D. The data confirm that ionic silver present in water forms complexes with glucose and the dissolution strongly depends on the solubility of the species in water. Owing to its high chemical affinity in

presence of anions as suggested by the thermochemical values, larger dissolution occurs.

Etching of silver by glucose leads to microscopically roughened surface (Figure S6B). This nanoscale roughening creates SERS-active substrates which can detect crystal violet (cv) up to 10^{-7} M with an enhancement factor of 5×10^8 (calculated from Raman intensity, see Figure S6, S7, and Table S2 for details). This substrate can be used for the detection of biomolecules such as DNA and biomarkers.[10]

In summary, a green and efficient method for extracting silver from the bulk metal, by simple use of carbohydrates is presented. Presence of specific anions can enhance the extraction. Glucose-induced corrosion of bulk silver can lead to microscopic roughness of the surface which can be used for the detection of analytes at ultralow concentrations by SERS. We believe that this method can contribute to new processes in extractive metallurgy of noble metals. There is alarming growth of heavy-metal poisoning and there is a belief that use of fertilizers may be responsible, at least partially. The extraction of ions from minerals can be enhanced by chemical fertilizers and this could present a problem of bioamplification by agriculture.

Experimental Section

Experimental details: At optimized condition, 1 g of sugar was added to 200 mL of DI water in a Teflon beaker. A 6 cm × 6 cm (3 gm in mass) silver foil was immersed in that solution and heated at 70 °C. Equal volumes of solution were taken out at selected times and analyzed by ICP MS. The total volume was made up by adding equal volume of the stock solution (1 g sugar/200 mL). The foil was thoroughly washed with DI water and dried before Raman experiments. Experimental details and instrumentation used are presented in Supporting Information.

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