

Surface-assisted electron transfer reaction and stabilization of reduced state



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ABSTRACT

The present study aims to probe the effect of silver nanoparticles (AgNPs) on the sorption behaviour of boroaluminosilicate glass (BASG). Firstly, BASG was loaded with AgNPs and benzotriazole (BT) and the glass exhibited surface-enhanced Raman spectrum of BT. The loaded BASG was equilibrated with copper (II) chloride solution and was investigated using ICP-AES, Raman spectroscopy, and luminescence measurements. It was observed that the glass matrix along with the sorbed copper ions showed luminescence, with a broad peak centered at ~ 400 nm, indicating the presence of copper ions in the Cu (I) state. However, in the absence of AgNPs, the glass matrix containing BT and sorbed copper ions failed to show luminescence implying that the copper ions are in the Cu (II) state. The glass matrix containing copper ions in addition to AgNPs and BT gave an enhanced Raman peak at 240 cm^{-1} (corresponding to Ag-Cl stretch with overlapping Ag-N stretch mode) and a shift of peak from 1022 (inplane trigonal ring breathing mode) to 1040 cm^{-1} and a broadening of the ring stretching modes at 1390 and 1575 cm^{-1} . All these observations could be attributed to the interaction of copper ions with BT and the simultaneous uptake of chloride ions along with copper. The studies suggest that both AgNPs and copper ions bind to the nitrogen atoms of BT and form a nanoarray like assembly AgNPs-BT-Cu which facilitates the diffusion/tunnelling of electrons from AgNPs to Cu (II) ions resulting in the reduction of Cu (II) to Cu (I).

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1. Introduction

Metal nanoparticles have unique optical, magnetic, electronic and catalytic properties as compared to the bulk metal [1] and have become a subject of interest in the field of physics, chemistry, biology and medicine. They find applications in sensors, catalysis, drug delivery, etc. [1–3]. It is known that excitation of localized surface plasmon resonance (LSPR) associated with the noble metal nanoparticles gives rise to enhanced electromagnetic field which leads to surface-enhanced Raman scattering (SERS) of the adsorbates attached on or near the nanoparticles [4–13]. Apart from its high sensitivity, another aspect of SERS is its potential to probe the interaction between various adsorbates and metallic surfaces [14–17].

Recently, the combination of plasmonic and catalytic properties of metallic nanoparticles has given rise to plasmon-mediated photocatalysis of the molecules attached to the metal nanostructures

and probed by SERS [18]. The elevated fields at the surface of the nanoparticles yield a great number of energetic charge-carriers (electron–hole pairs), which can induce photochemical transformations either through localized heating of the nanostructure or by attachment of energetic charge-carriers to the reactants adsorbed on the surface of the nanostructures [19,20]. Reports have also shown that the thermal electrons generated on the surface of the nanoparticles can also induce catalytic reactions [21]. SERS studies have shown that charge transfer occurs between nanoparticles interconnected with functionalised molecule [22].

In the last few years, nanocomposite glasses containing metal or semiconductor nanoparticles in glass matrix have become an object of interest due to their promising utilisation in optoelectronics and photonics [23–27]. Silver nanoparticles (AgNPs) embedded in glass containing rare earth are known to improve the photoluminescence properties of rare earth ions [28]. Various mechanisms such as the effect of surface plasmon resonance of the AgNPs and energy transfer between small silver particles and rare earth ions have been proposed [28].

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In the light of the various applications exhibited by metal nanoparticles, we tried to probe the nature of the sorbed copper ions in borosilicate glass (BASG), loaded with AgNPs and benzotriazole (BT). The use of BASG as room temperature sorbents for the removal of various inorganic and organic species have been reported earlier [29,30]. BT has found several applications in the field of corrosion of metals and has been widely used in the surface treatment of materials as corrosion inhibitors. The resistance to corrosion of metals in the presence of BT has been attributed to the formation of a stable film of metal-BT polymeric complex [31–35]. In the present study, BASG was loaded with AgNPs followed by BT. The modified glass matrix was characterised by Raman spectroscopic measurement. Further, the unmodified and modified glass matrix was equilibrated with copper (II) ions and was studied using Raman, ICP-AES and luminescence measurements. It is known that sorption of copper ions occurs in borosilicate glass [36]. Copper ions are also known to form complex with BT and hence thought interesting to probe its sorption by BASG loaded with AgNPs and BT.

2. Experimental

2.1. Materials

Formamide (UV spectroscopy grade) was obtained from Spectrochem, India and the remaining chemicals used in the studies were obtained from the Aldrich Chemical Co. USA. Solutions were made using water filtered by a Millipore Milli-Q system having a resistivity of 18.0 megaohm/cm.

2.2. Preparation and characterisation of BASG samples

BASG was prepared by conventional melt quench method from reagent grade SiO_2 , H_3BO_3 , Al_2O_3 , NaNO_3 and KNO_3 at 1400–1500 °C in platinum crucibles to get glass powders with chemical composition of $[(\text{Na}_2\text{O})_{0.22}(\text{K}_2\text{O})_{0.029}(\text{B}_2\text{O}_3)_{0.05}(\text{Al}_2\text{O}_3)_{0.011}(\text{SiO}_2)_{0.69}]$ and size distribution of 180–212 μm . A part of the glass powder sample was loaded with BT by equilibrating a known weight of glass (~1 g) with 10 mL of 0.01 M BT for an hour to obtain the BT loaded glass and is referred as BASG-BT. Another part of the BASG sample was mixed with silver nitrate salt (~0.1 g) and 20 mL formamide with continuous stirring for an hour. This was to ensure almost complete reduction of Ag^+ ions by formamide [37] as well as the incorporation of AgNPs in BASG. The solution was centrifuged and the AgNPs loaded BASG was separated out. The glass sample was filtered off, washed, dried well and equilibrated with 10 mL of 0.01 M BT for an hour and the sample obtained is referred as BASG-AgNPs-BT. The untreated glass sample is referred in the manuscript as UN-BASG.

All the three glasses UN-BASG, BASG-BT and BASG-AgNPs -BT were then used for the uptake of Cu (II) ions. The solution of Cu (II) ions was prepared by dissolving suitable amount of copper chloride in dilute HCl. Weighed amounts of the above three glass samples were equilibrated with 10 mL of 0.01 M Cu (II) ion solution for 6 h and the concentration left behind in solution after equilibration was determined using Jobin-Yvon JY 2000 Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES). The uptake efficiency was calculated for all the glass samples. Errors in the uptake capacity have been calculated by duplicate measurements. The copper sorbed glass samples will be addressed as UN-BASG- Cu^{2+} , BASG-BT- Cu^{2+} and BASG-AgNPs-BT- Cu^{2+} in the text.

Raman spectra of the glass samples were recorded using 532 nm line from a diode pumped Nd^{3+} :YAG laser. The laser power used for the Raman measurements was 25 mW. The Raman scattered light was collected at the back-scattered geometry and detected using a CCD based home-built monochromator [38].

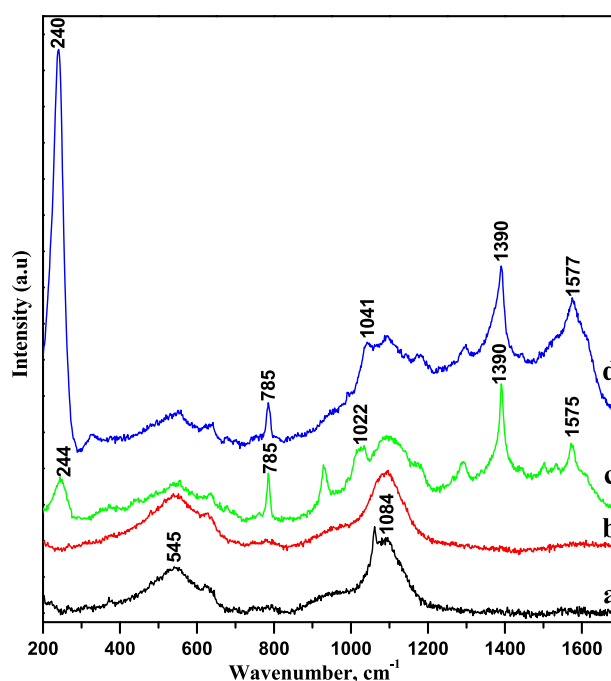


Fig. 1. Raman spectra of a) UN-BASG b) BASG-BT c) BASG-AgNPs-BT d) BASG-AgNPs-BT- Cu^{2+} .

Luminescence measurements were carried out at room temperature with a resolution of 3 nm and $\lambda_{\text{exc}} = 280$ nm, using Edinburgh instrument (FLSP-920) having excitation source 450 W Xe lamp.

3. Results and discussion

3.1. Raman spectroscopic studies of BASG samples UN-BASG, BASG-BT and BASG-AgNPs-BT

Fig. 1a corresponds to the Raman spectrum of UN-BASG while Fig. 1b corresponds to that of BASG-BT. Both the Raman spectra of BASG-BT and UN-BASG showed only the features of glass although BT was present in the BASG-BT. The Raman spectra have two major bands at ~ 541 cm^{-1} and ~ 1096 cm^{-1} . The 1096 cm^{-1} band is indicative of $=\text{SiO}$ units (Q_3 species: SiO_4 units with one nonbridging oxygen), whereas the 541 cm^{-1} band is associated with vibrations of the bridging oxygen in the Si-O-Si linkages of the glass [39]. Fig. 1c shows the Raman spectrum of BASG-AgNPs-BT. The presence of AgNPs along with BT in the glass matrix made all the difference, giving rise to SERS spectrum of BT as shown in Fig. 1c. The vibrational bands of BT ride on the Raman peaks of glass. The spectral region >1200 cm^{-1} is free from glass signatures as seen in Fig. 1c. The spectral features appear similar and match with our earlier SERS studies of BT in silver sol [12,40]. BT is known to interact with AgNPs through the nitrogen atoms of the triazole ring of BT. The peaks at 1390 and 1022 cm^{-1} is attributed to the triazole ring stretching mode and inplane triangular ring breathing mode, respectively. The appearance of the band at 244 cm^{-1} in the SERS spectrum is attributed to the Ag-N stretch which gives a direct evidence for AgNPs-BT interaction through the N atoms of the triazole ring. The observed peaks at 1575 and 785 cm^{-1} is due to C-C stretches of benzene.

3.2. Studies on copper ions sorbed glass samples

The uptake of copper ions was measured for the unmodified glass UN-BASG and modified glass samples (BASG-BT and BASG-AgNPs-BT). It was seen that upon modification, the uptake of cop-

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