Wonderful nanoconfinement effect on redox reaction equilibrium

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1. Description of porous matrices.

The Amberlite XAD-4 spherical beads used in the present work were purchased from Sigma-Aldrich. These beads are based on highly crosslinked macroreticular polystyrene (av. pore size of 10 nm). The distribution of pore size as obtained from FE-SEM characterization is given in Figure S1. The silica gel particles (63-200 μm) used in the present study was also purchased from Sigma-Aldrich and is of average pore size 4 nm and ~0.68 cm³g⁻¹ pore volume.

Preconditioning of XAD-4 beads: The XAD-4 beads were soaked overnight in methanol and washed thoroughly with 2 mol L⁻¹ HNO₃ and water to remove any chemical impurities.
2. Choice of redox reactions.

In order to study the nanoconfinement effect on redox reactions, two types of redox reactions were chosen primarily in the present study. The first type of reactions belongs to the category which in general requires very high temperature. Such redox reactions include polyol reduction of noble metal ions to form noble metal nanoparticles,\textsuperscript{1} borohydride reduction of Pt ions to form Pt nanoparticles etc. First attempt was made to perform those reactions at ambient condition (room temperature or at a temperature lower than it usually demands). The second type of reaction belongs to the category of metal nanoparticles mediated catalysis. Influence of nanoconfinement effect on AgNPs catalysed reduction of para nitrophenol with excess of NaBH\textsubscript{4} was studied.

In addition to the above two types of reaction, redox decomposition reaction of silver-citrate complex for the synthesis of silver nanoparticles under the condition of citrate/Ag\textsuperscript{+} >>1 was also
studied in nanoporous silica gel particles. The reaction was already studied in ion-exchange films and XAD-4 beads as can be seen in our earlier publication\textsuperscript{2}. In this work, the same reaction was performed in silica gel particles (pore size 4 nm) in order to see the matrix dependence of nanoconfinement effect.

3. Experimental Section.

3.1. Reaction steps.

3.1.1. Reduction of noble metal ions with ethylene glycol (EG) at ambient temperature.

For the synthesis of different noble metal nanoparticles (i) 20 mg of AgNO\textsubscript{3} (S. D. Fine Chem Ltd., 99.9 \% Ag), (ii) 47.3 mg of HAuCl\textsubscript{4} (Pravat Chemicals, India, 50 \% Au) and (iii) 58.4 mg of H\textsubscript{2}PtCl\textsubscript{6}.xH\textsubscript{2}O (S. D. Fine Chem Ltd., 40 \% Pt) was dissolved in 10 mL of deionised water (18 MΩ/cm, purified by model Quantum\textsuperscript{TM} from Millipore, Mumbai, India) seperately in three different beaker. To each of the precursor solution 10 mL of ethylene glycol (EG) was added. The final concentration of precursor ions in each system was 6 mM. In each of the beaker 1.5 g of preconditioned XAD-4 beads were added. The solutions in the beaker then kept in dark for 48 h under stirring condition (300 rpm) at room temperature and atmospheric pressure. Faint colour characteristic of the respective metal nanoparticles was appeared in the XAD-4 beads with time. It is worthy to mention that no colour typical of noble metal nanoparticles was observed in the bulk reaction solutions. For gold, there was initially a light yellow colur in the bulk solution due to the presence of unreduced AuCl\textsuperscript{4} ions, whereas with time the solution turned to colourless. Finally the beads were filtered out of the reaction solution, washed thoroughly with deionised water and dried. FE-SEM characterisation of the beads was done in order to see the formation of noble metal nanoparticles. The EG reduction of H\textsubscript{2}PtCl\textsubscript{6} was carried out also in higher
temperature (80 °C) keeping all other parameters constant in order to see the temperature dependence of the reaction rate. In that case, the reaction was continued for 6 h. The constant temperature was maintained using a water bath.

3.1.2. Reduction of PtCl$_6^{2-}$ with sodium borohydride (NaBH$_4$) at 80 °C.

20 mg of H$_2$PtCl$_6$.xH$_2$O (S. D. Fine Chem Ltd., 40 % Pt) was mixed with 20 mL freshly prepared aqueous solution of sodium borohydride (0.2 mol L$^{-1}$) at room temperature. 2 g of preconditioned XAD-4 beads were added into it. The mixed solution was then kept at 80 °C for 6 h under continuous stirring (300 rpm). The beads were found to change their colour from colourless to gray with time at a faster rate. On the other hand the bulk solution remained almost colourless even after 6 h of reduction, showing the slow reduction at bulk.

3.1.3. Catalytic reduction of para nitrophenol.

The catalytic reduction of para nitrophenol (PNP) with sodium borohydride (NaBH$_4$) in presence of noble metal nanoparticles was used as a model reaction in the present study in order to see the nanoconfinement effect on catalysis reactions which involves electron transfer. This reaction was performed in a standard quartz cell with path length of 1 cm. For the kinetic measurements 100 μl of PNP solution (2 mM) was taken in the quartz cuvette followed by addition of 1.8 mL of deionised water. To that cuvette, 100 mg of silver nanoparticles incorporated XAD-4 beads (prepared by EG reduction of Ag$^+$ ions at room temperature) was added. Finally 200 μl of freshly prepared NaBH$_4$ solution (0.1 mol L$^{-1}$) was added into the reaction mixture in cuvette. The addition of NaBH$_4$ led to a colour change from light-yellow to yellow-green. The cuvette was immediately placed in a portable UV-VIS spectrophotometer (K-MAC, Korea) and the UV-VIS
absorption spectra were recorded with a time interval of 1 min in the scanning range of 200-700 nm at room temperature (25 °C). While recording the spectra the spectrophotometer was placed on a stirr plate. A microstir bar was added to the cuvette for continuous stirring of the reaction solution. The stirring rate was fixed at 300 rpm.

3.1.4. Redox decomposition reaction of silver-citrate complex in nanoporous silica gel particles.

20 mg of AgNO₃ salt was dissolved in 20 mL aqueous solution of tri-sodium citrate (0.2 mol L⁻¹) resulting in the formation of soluble anionic silver-citrate complex as discussed in our earlier publication.² To that solution 2 g of silica gel powder (Sigma Aldrich) was added and the reaction mixture was kept at 75 °C for 3.5 h under stirring condition. The white silica gel particles were found to be brown with time keeping the bulk silver-citrate solution colourless.

3.2. Characterisation.

3.2.1. Microscopy.

Field emission scanning electron microscopy (FE-SEM) was carried out for the surface of the XAD-4 beads and the silica particles with and without noble metal nanoparticles. For some of the samples FE-SEM was done for the interior of the beads. In order to observe the interior, the spherical beads were ground carefully with SiC sandpaper followed by polishing with diamond suspensions. Finally the beads were made conductive by gold coating prior to microscopy.

4. FE-SEM images.
Figure S2. FE-SEM images (secondary electrons mode) of the surface of a XAD-4 bead after treating with an aqueous solution of EG and AgNO$_3$ (Section 3.1.1). Clusters of bright spherical objects near the nanoscale crevices represent the silver nanoparticles.
Figure S3. FE-SEM images (secondary electrons mode) of the surface of a XAD-4 bead after treating with an aqueous solution of EG and AuCl$_4^-$ (Section 3.1.1). Clusters of bright spherical objects near the nanoscale crevices represent the gold nanoparticles.
Figure S4. FE-SEM images (secondary electrons mode) of the surface of a XAD-4 bead after treating with an aqueous solution of EG and PtCl$_6^{2-}$ (Section 3.1.1). Clusters of bright spherical objects near the nanoscale crevices represent the platinum nanoparticles.
Figure S5. FE-SEM images of the interior of a XAD-4 bead after treating in a solution of PtCl$_6^{2-}$ and sodium borohydride (NaBH$_4$) at 80 °C (Section 3.1.2) in secondary electrons imaging mode for topography (a, c) and in backscattered electron imaging mode for elemental mapping (b). The bright spots represent the platinum nanoparticle formed via BH$_4^-$ reduction in nanoconfinement.
5. ICP-AES study for the quantification of silver loading in XAD-4 beads.

In order to quantify the silver loaded per unit mass of the XAD-4 beads after room temperature EG reduction of Ag$^+$ ions, known quantity of AgNPs incorporated XAD beads were digested in 6M HNO$_3$ for 20 h to dissolve the silver in the beads. Dissolution of silver was confirmed by the decolouration of the beads. The HNO$_3$ solution was then evaporated under IR lamp carefully. The dried sample was then made upto 5 mL with millipore water. The concentration of silver was determined using ICP-AES technique. As known mass of AgNPs incorporated XAD beads were digested, the silver loading per unit mass of XAD beads were obtained and was found to be 0.143 mg per g of XAD-4 beads.

6. Time resolved UV-VIS spectrophotometry during silver nanoparticles catalysed BH$_4^-$ reduction of para nitrophenol in nanoconfinement.
Figure S6. UV-Vis spectra obtained as a function of time during reduction of para-nitrophenolate anions (PNP) to para-aminophenol (PAP) with BH₄⁻ ions in presence of poly(styrene) beads containing silver nanoparticles.

References.
