Electronic Supplementary Information

Development of novel inorganic-organic hybrid nanocomposites as recyclable adsorbent and catalyst

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Materials:

All chemicals were used as received. Halloysite nanotubes, gold(III) chloride trihydrate (≥99.9%), silver nitrate (99.9999%), (3-mercaptopropyl) trimethoxysilane (MPTMS, 97%), 1-octadecene, and oleylamine (70%) were purchased from Sigma-Aldrich. Toluene was obtained from Merck, India and *o*-nitrobenzoic acid (*o*-NBA) was from Alfa Aesar. Mercury acetate, lead nitrate, and cadmium acetate were received from Sisco Research Laboratory, India.

Adsorption Studies:

To study the adsorption of heavy metals ions from aqueous solution using Mod-HNTs at room temperature, Hg(II) solution was taken in beaker along with Mod-HNTs and then the solution was stirred on a magnetic stirrer up to a desired time. After the adsorption of Hg(II) ions by Mod-HNTs, the solution was filtered and the unbound Hg(II) ions present in the filtrate was estimated by a complexing agent, diphenylthiocarbazone (dithizone) which forms a complex with Hg(II) ions. The time-dependent absorption spectra of mercury-dithizone comples have been studied using a UV-Visible spectrophotometer in a standard quartz cuvette of 1 cm path length. Keeping all the experimental condition the same, we have also studied the adsorption kinetics of other metal ions, like Cd(II) and Pb(II) ions present in the aqueous solution.

Catalytic Reaction:

To study the catalytic efficiency of these nanocomposites, reduction of *o*-NBA has been chosen as a model reaction. In a standard quartz cuvette of 1 cm path length, 0.02 g of metal/HNTs nanocomposites was taken along with 2.7 mL of aqueous solution of *o*-NBA (0.1 mM). Aqueous solution $NaBH_4$ (0.3 mL of 0.1M) was added to the reaction mixture and time dependent absorption spectra were recorded using a UV-Visible spectrophotometer at ~25 °C.

Characterization:

Powder X-ray diffraction (XRD) data were collected on a PANalytical X-PERT PRO powder diffractometer using Cu Kα radiation with 45 kV beam voltage and 40 mA beam current. Fourier transform infrared (FTIR) spectra were recorded using JASCO FT/IR 6300. Thermogravimetric analyses (TG) were performed on a Perkin Elmer DAIMOND TG/DTA instruments. Sulphur concentration in the surface modified HNTs has been estimated by ELTRA CS-800 Double Dual Range Carbon/Sulphur analyzer. The morphology of the halloysite nanotubes was characterized using transmission electron microscopy (TEM: FEI TECNAI G2 F20-ST) operating at 200 kV after drop casting a drop of solution on a carbon coated copper grid and field emission scanning electron microscopy (FESEM: FEI QUANTA FEG 250). High resolution transmission electron microscopy (HR-TEM) and Energy dispersive X-ray spectroscopy (EDS) have been done in the above mentioned TEM operating at 200 kV.

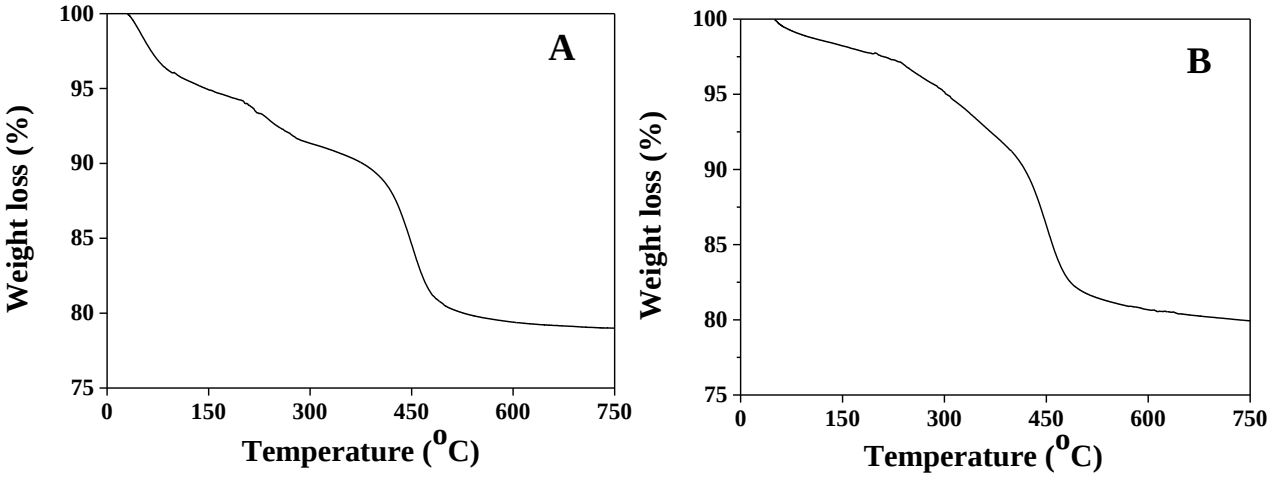

Fig. S1 Thermogravimetric analysis (TGA) data of (A) HNTs and (B) surface modified HNTs measured under nitrogen from room temperature to 750°C.

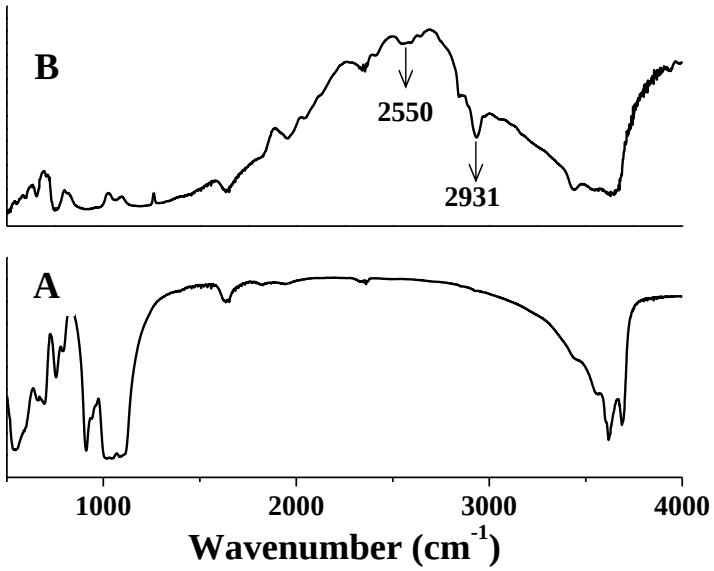

Fig. S2 FTIR spectra of (A) HNTs and (B) surface modified HNTs by (3-mercaptopropyl) trimethoxysilane.

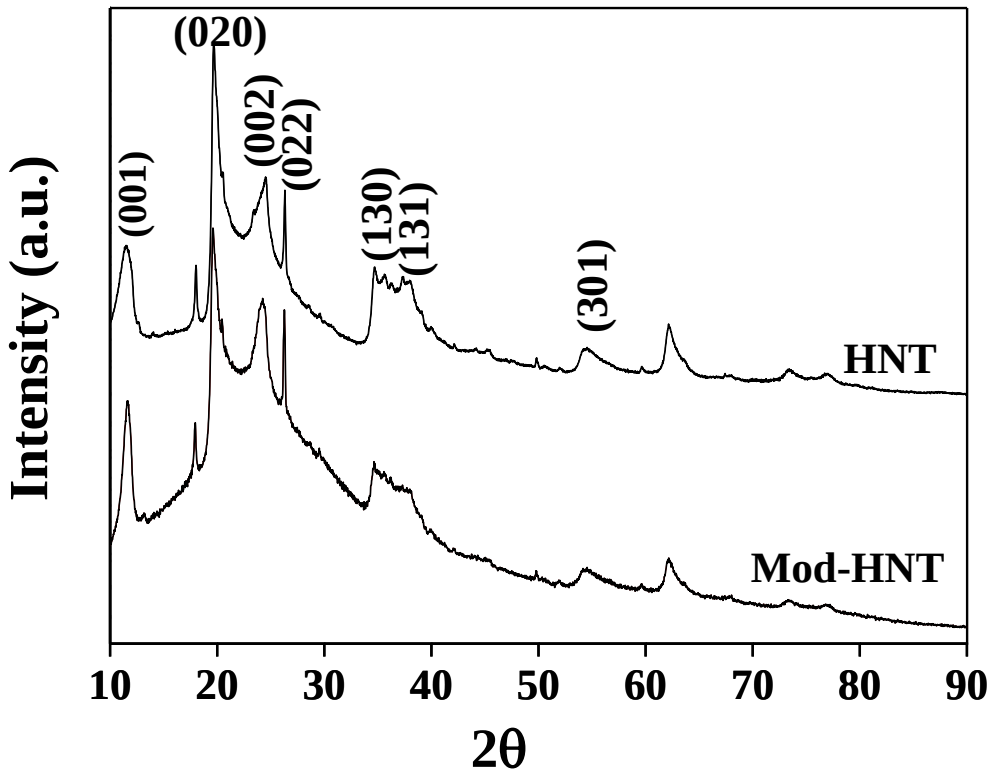

Fig. S3 XRD patterns of HNTs before and after surface modification.

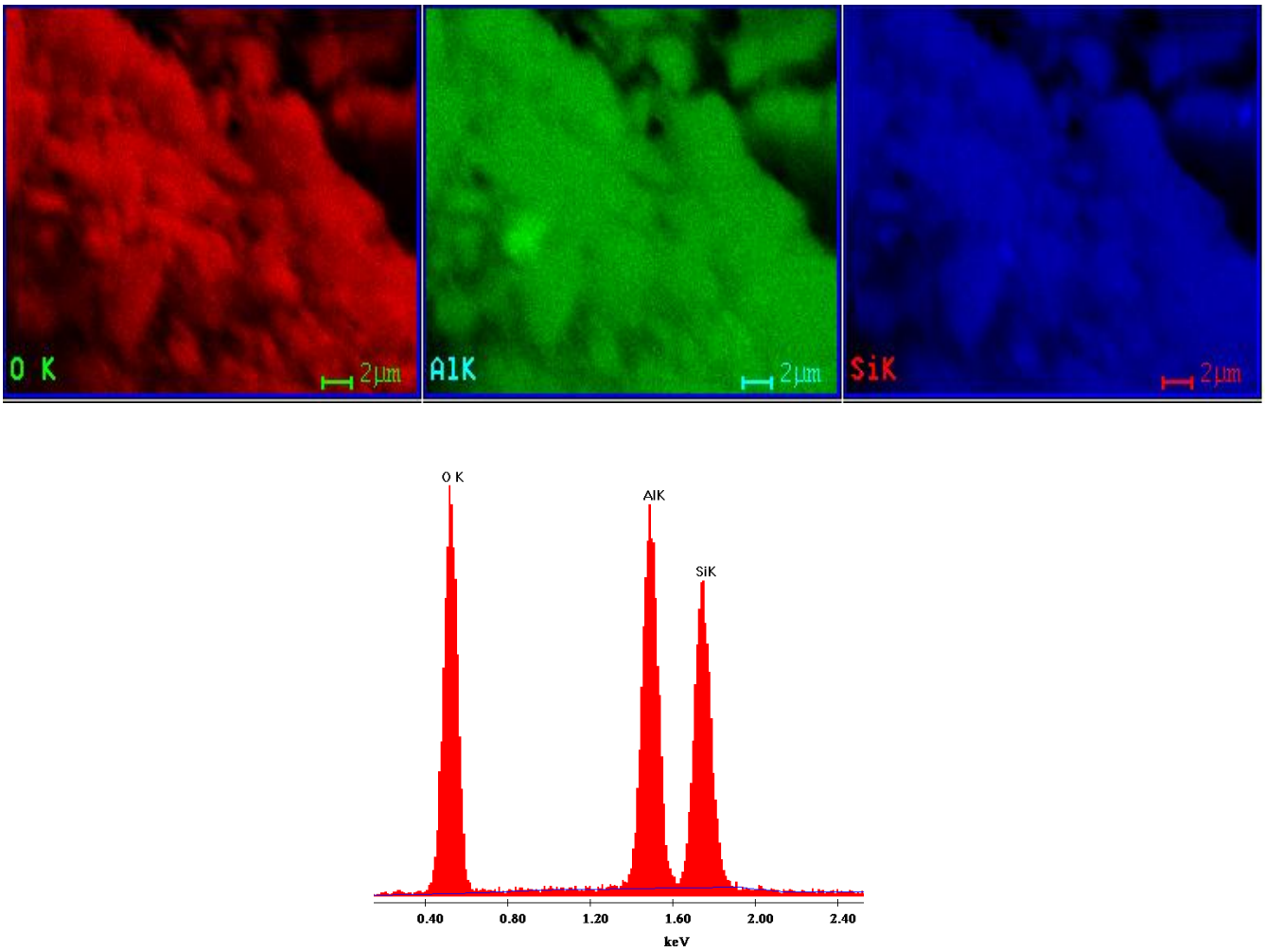

Fig. S4 Element mapping by scanning electron microscopy and corresponding EDS spectrum of pure HNTs.

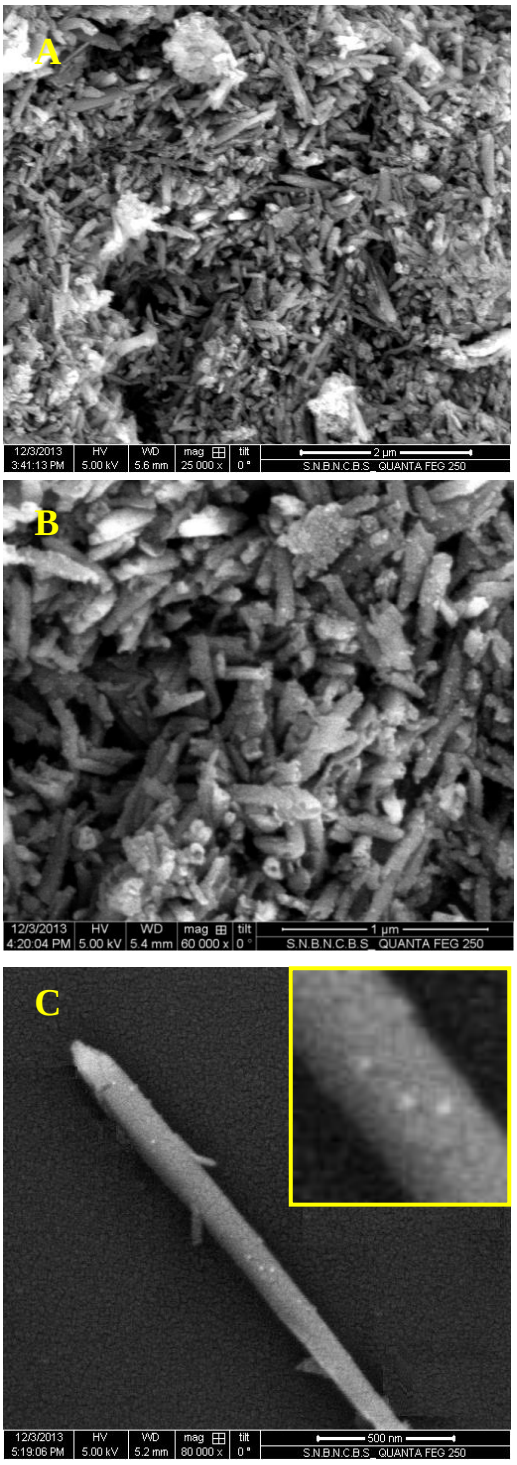

Fig. S5 FESEM images of Au/HNTs nanocomposites at different magnification obtained by the immobilization of preformed Au NPs on modified HNTs surfaces.

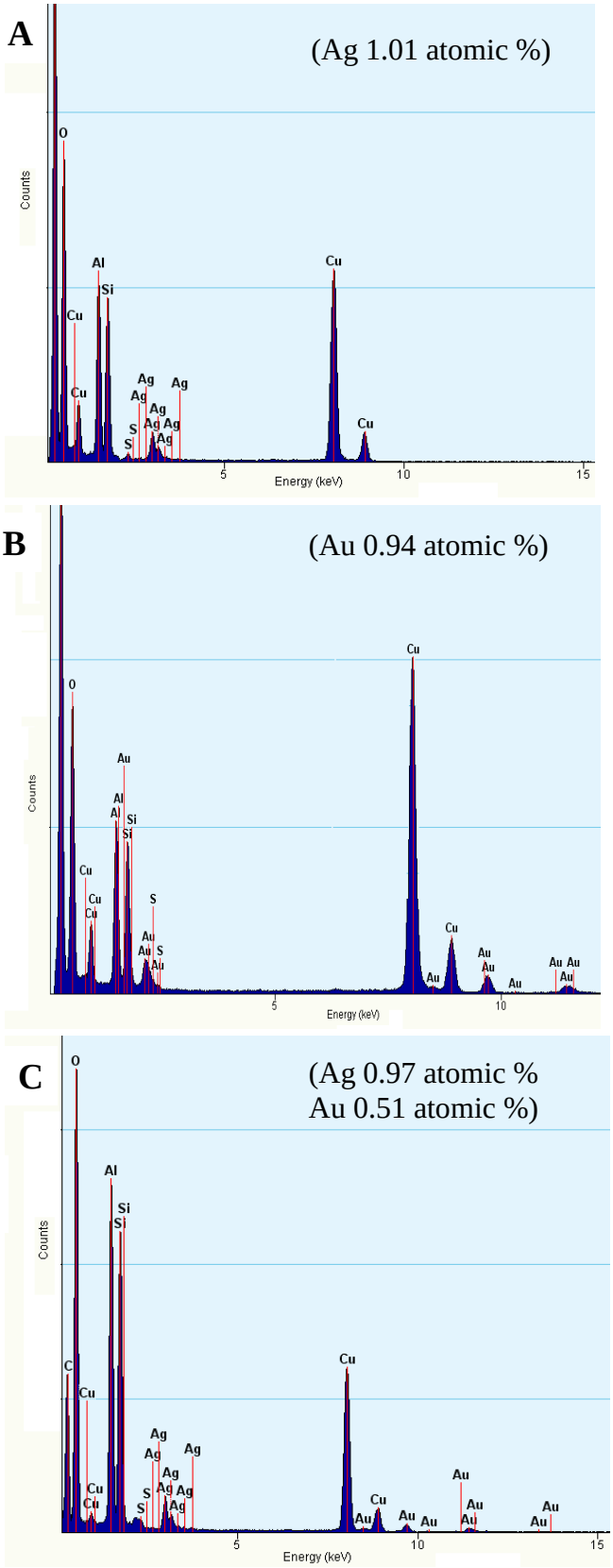

Fig. S6 EDS spectra of (A) Ag/HNTs, (B) Au/HNTs, and (C) AuAg/HNTs nanocomposites demonstrating the presence of respective nanoparticles.

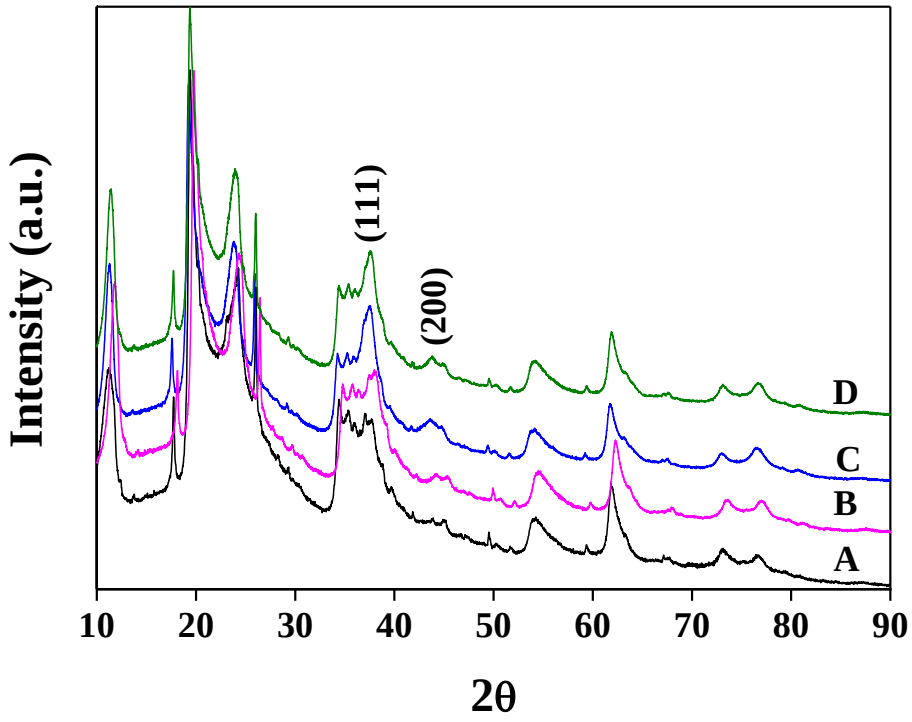

Fig. S7 XRD patterns of of (A) modified HNTs, (B) Ag/HNTs, (C) Au/HNTs, and (D) AuAg/HNTs nanocomposites.

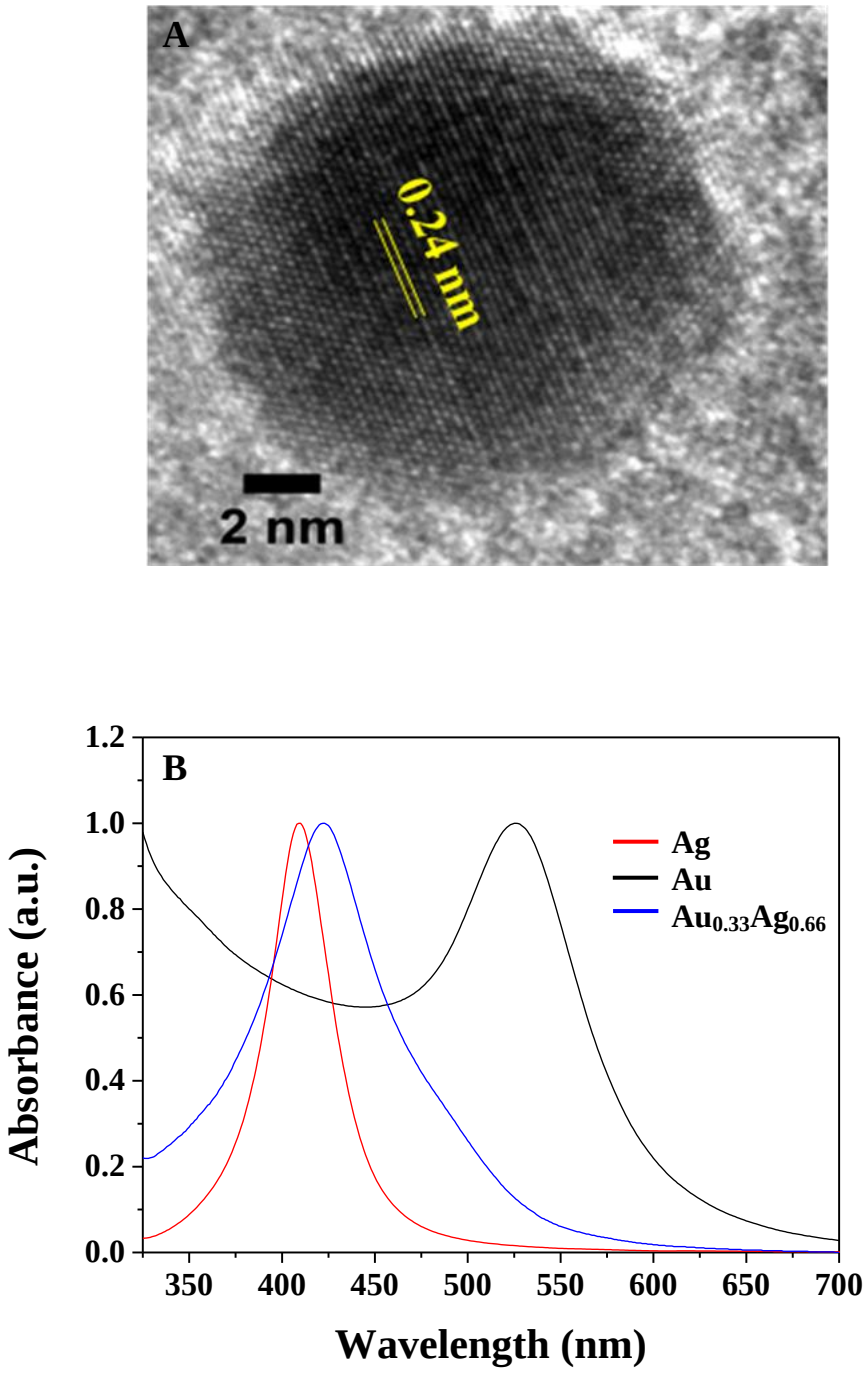

Fig. S8 HRTEM images of (A) $Au_{0.33}Ag_{0.66}$ NPs and (B) UV-Visible absorption spectra of Ag, Au, and $Au_{0.33}Ag_{0.66}$ NPs.

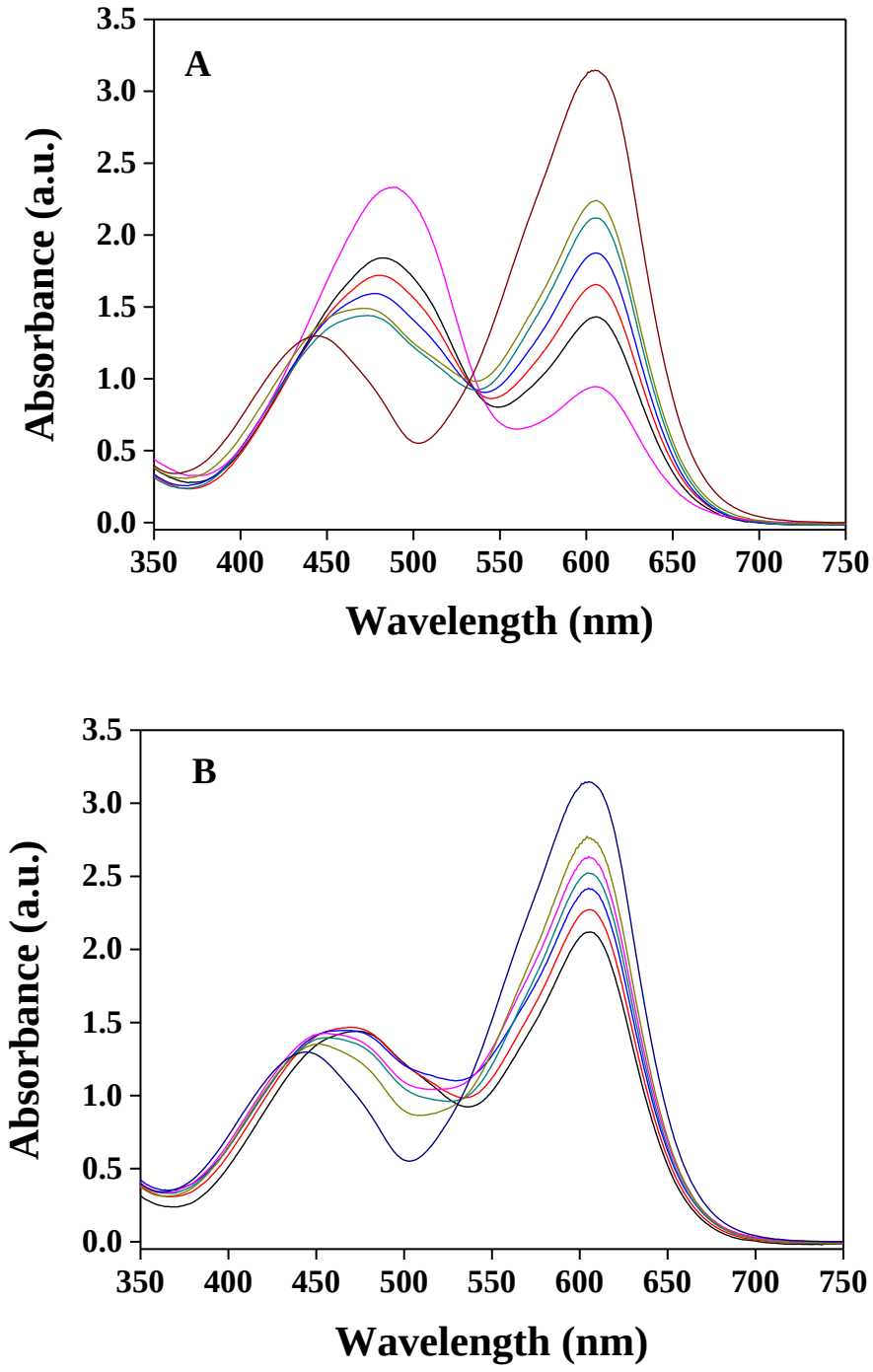

Fig. S9 UV-Visible spectra of Hg(II)-diphenylthiocarbazone complex for unbound Hg(II) ions present in the solution after the adsorption of Hg(II) ions by Mod-HNTs at an intervals of (A) 2 min and (B) 10 min respectively.

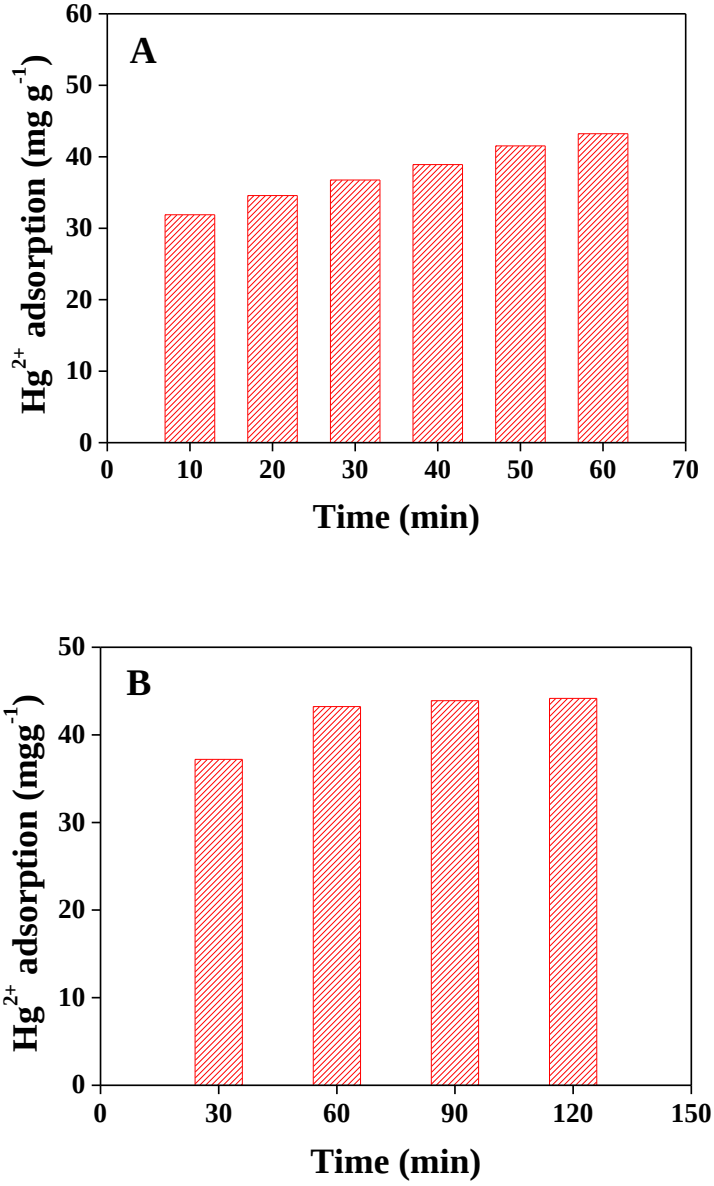

Fig. S10 Adsorption of Hg(II) ions from the aqueous solution (200 mg/L) by modified HNTs as a function of time, at an interval of (A) 10 min and (B) 30 min, indicating adsorption of Hg(II) increases with time and finally reaches to a maximum 1h after the addition of the above adsorbent.

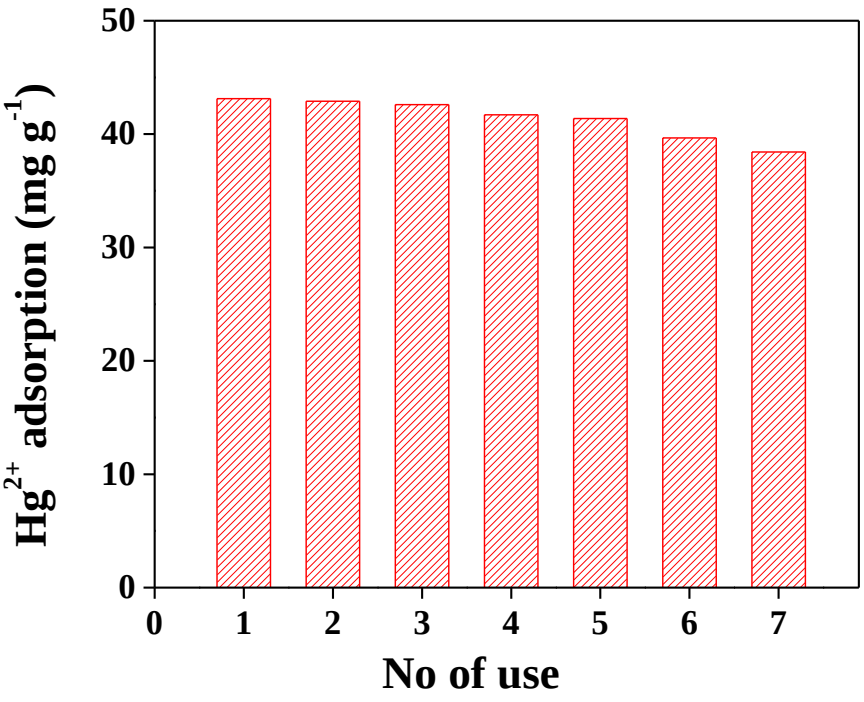

Fig. S11 Adsorption efficiency of Mod-HNTs for Hg(II) ions from the aqueous solution (200 mg/L) using the same batch of surface modified HNTs.

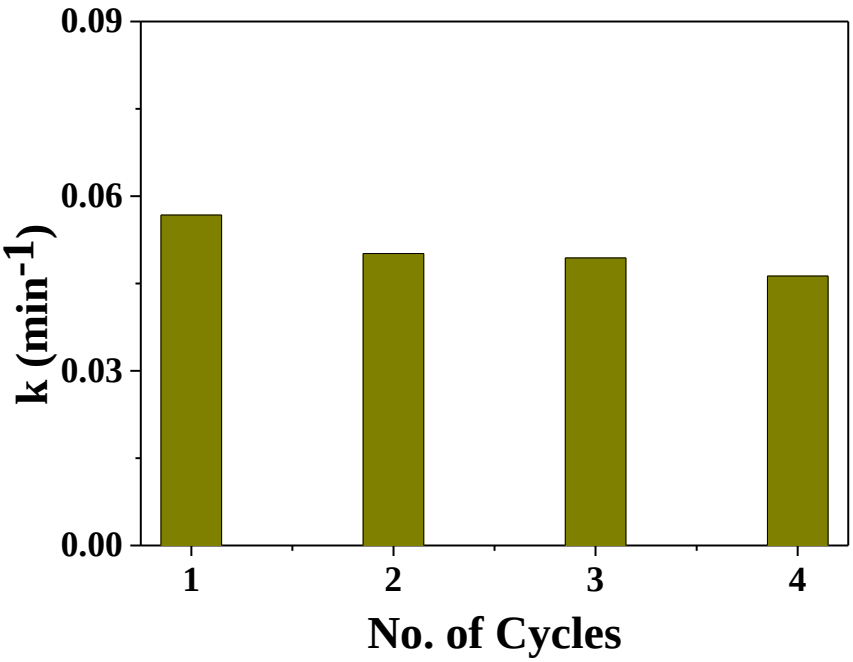

Fig. S12 Reaction rate constant (k) for the reduction of *o*-NBA over a number of cycles using the same batch of Ag/HNTs nanocomposites demonstrating stability and recyclability of the nanocomposite catalyst.