Supplementary information

Experimental and related aspects

Synthesis of aminoclay:

The aminoclay was prepared by the method reported in the literature.[1] Typical synthesis involves room temperature drop wise addition of 3-aminopropyltriethoxysilane (1.3 mL, 5.85 mmol) to an ethanolic solution of magnesium chloride (0.84 g, 3.62 mmol) in ethanol (20 g). The white slurry obtained after 5 min was stirred overnight and the precipitate isolated by centrifugation was washed with ethanol (50 mL) and dried at 40 °C.

Synthesis of aminoclay stabilized Cu nanoparticles:

$CuSO_4.5H_2O$ was used as the metal precursor for Cu nanoparticles synthesis. The aminoclay-Cu nanoparticles composite was prepared as follows. The aminoclay was first exfoliated by dispersing 20 mg of clay in 2 mL millipore water by sonication. To this transparent clay suspension, 500 μL of 10 mM copper sulphate solution was added followed by the drop wise addition of 1 mL of 1 M hydrazine hydrate solution.

Synthesis of Cu chalcogenides from Cu-aminoclay nanoparticles:

(a) Synthesis of Cu_2S nanoparticles:

A known volume of freshly prepared Cu-aminoclay solution was mixed with an equal volume of 10 mM Na_2S solution followed by sonication for 5 minutes. The wine-red color of Cu-aminoclay solution changed in 5 minutes to greenish-brown colour indicative of formation of Cu_2S nanoparticles.

(b) Synthesis of $CuSe_2$ nanoparticles:

A known volume of freshly prepared Cu-aminoclay solution was mixed with an equal volume of 1 mM NaHSe solution followed by sonication for 5 minutes. The wine-red color of Cu-aminoclay solution changed in 5 minutes to dark orange-red colour due to the formation of $CuSe_2$ nanoparticles.

Estimation of undissociated hydrazine hydrate present in water and aminoclay:

20 mg of aminoclay was first exfoliated in 3 mL millipore water by sonication. 1mL of 1 M hydrazine hydrate was added to this aminoclay solution. In a separate vial 1mL of 1M hydrazine hydrate was added to 3 mL millipore water for comparison. Both the samples were kept for 8 days exposed to air. For the estimation of residual hydrazine hydrate present in pure water and aminoclay, the following quantitative titration was performed. Equal volumes of 0.05 M $K_3Fe(CN)_6$ solution and 0.05 M KOH solution were mixed in a conical flask and titrated against hydrazine hydrate to give light brown coloured solution as an end point. The reaction is shown below.[2]

$$4\ K_3Fe(CN)_6 + 4\ KOH + N_2H_4\ H_2O \longrightarrow 4\ K_4Fe(CN)_6 + N_2 + 5\ H_2O$$

Characterization techniques

For TEM analysis, the aqueous clay suspension was first precipitated by the addition of excess ethanol and then redispersed it in ethanol by sonication before drop casting on a carbon-coated copper grid. TEM images were recorded with a JEOL JEM 3010 instrument (Japan) operated at an accelerating voltage of 300 kV. UV-Vis absorption spectroscopic measurements were performed with Perkin-Elmer instruments Lambda 900 UV/Vis/NIR spectrometer. For XRD analysis, the Cu-aminoclay solution prepared was precipitated by the addition of excess ethanol which further on drying yields Cu powder.

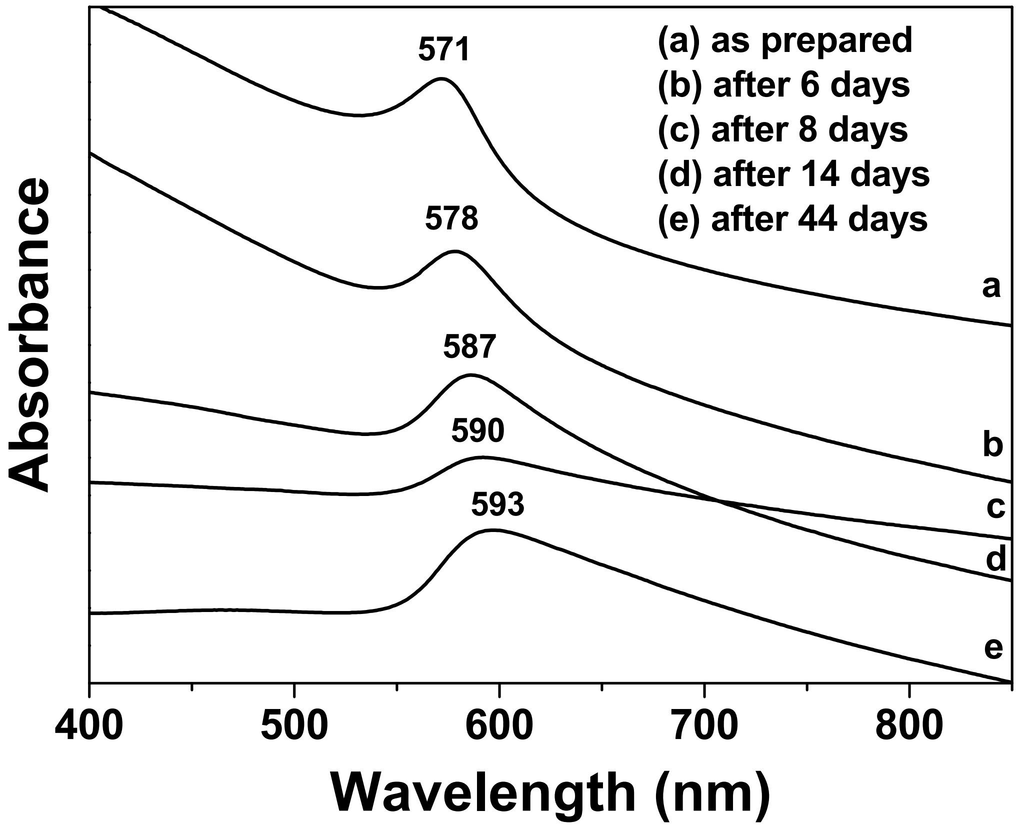

Fig. S1. UV-Vis spectra of Cu-aminoclay solution aged at different time intervals.

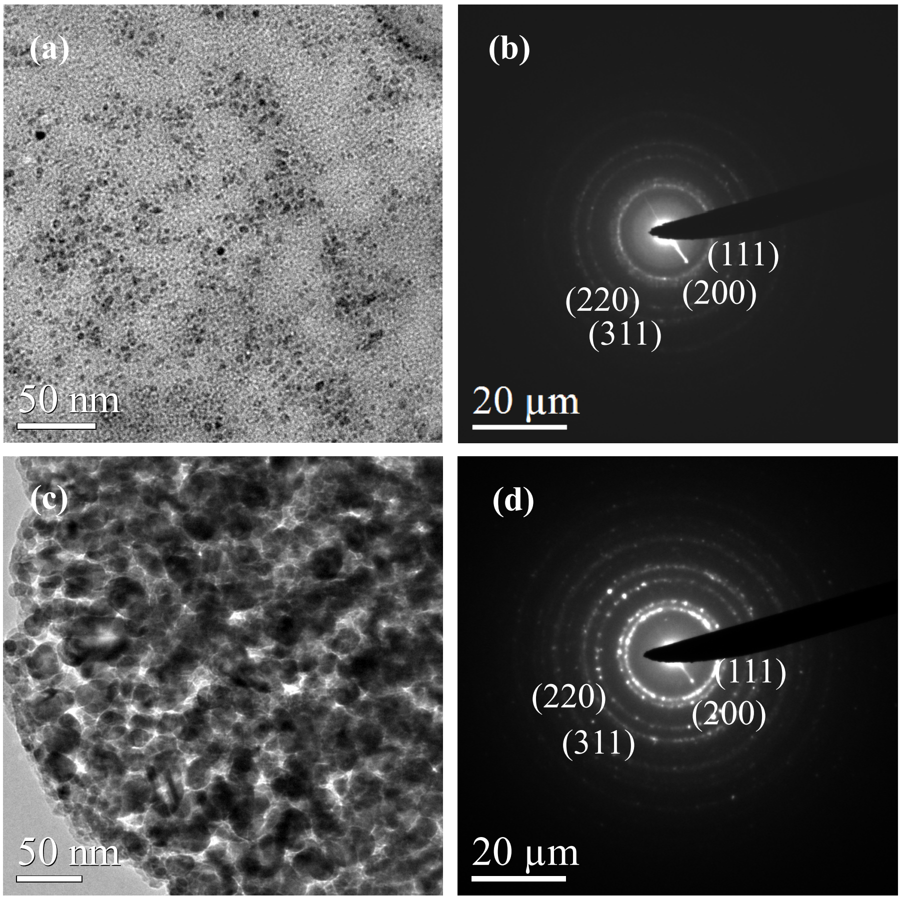

Fig. S2. TEM images of (a) freshly prepared Cu-aminoclay solution, (b) corresponding electron diffraction pattern, (c) Cu-aminoclay solution aged for 14 days, (d) corresponding electron diffraction pattern.

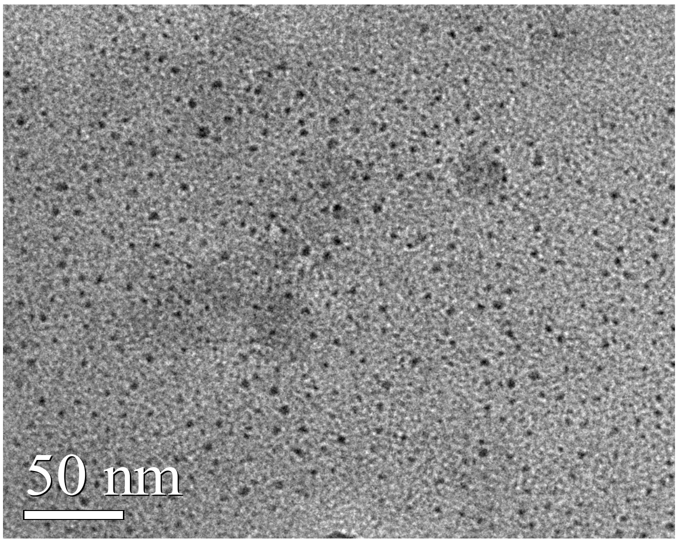

Fig. S3 (a).TEM image of Cu powder (obtained by precipitating freshly prepared Cu-aminoclay solution) kept in air for two months.

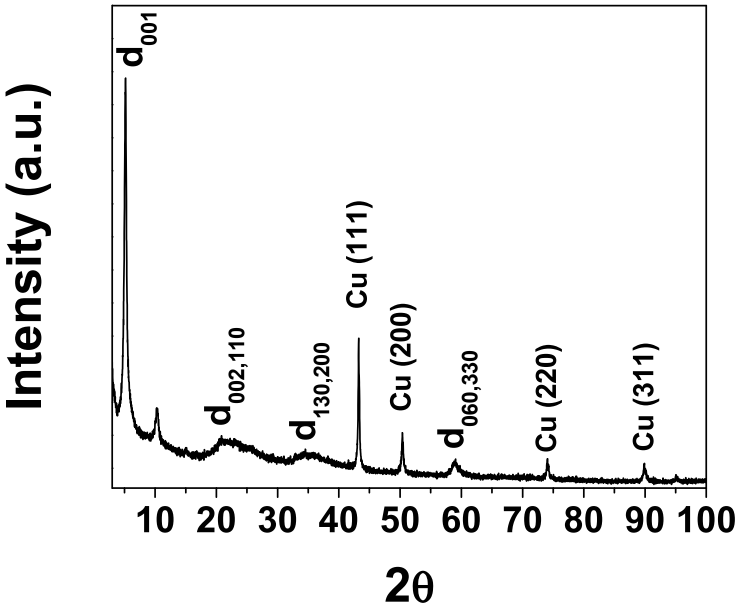

Fig. S3 (b). Wide angle XRD pattern of Cu-aminoclay composite kept in air for two months. Low-angle reflection with d_{001} spacing of 1.7 nm corresponding to the bilayer arrangement of propylamino groups of aminoclay. The in-plane reflections with $d_{020\ 110}$ = 0.42 nm, $d_{130\ 200}$ = 0.26 nm and d_{060} = 0.156 nm are associated with clay.[3]

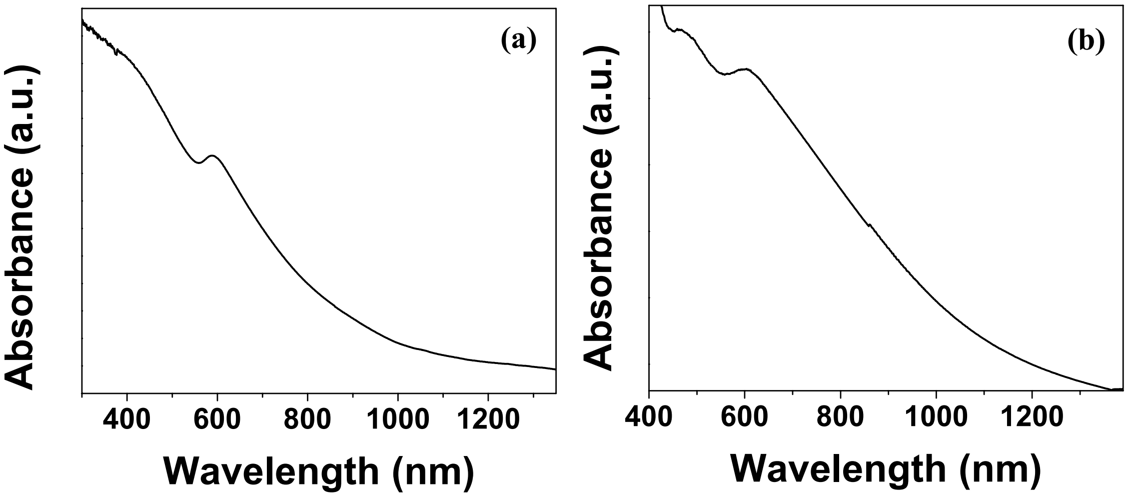

Fig.S4. UV-Vis spectrum of Cu chalcogenides in aminoclay solution kept for 3 days (a) Cu_2S-aminoclay solution, (b) $CuSe_2$-aminoclay solution (both the cases copper plasmon band is seen).

Reduction of p-nitro phenol:

The light yellow colour of p-nitrophenol changes to yellow-green upon mixing of sodium borohydride solution. The intensity which was quantitatively monitored using UV-Vis spectrophotometer with a time gap of 20 seconds in a scanning range of 200-700 nm at room temperature of 25 ^{0}C with scan speed of 250 nm per minute.

The reduction of p-nitrophenol was monitored using UV-Vis absorption spectroscopy. 1 mL of 15mM $NaBH_4$ (aqueous solution) was mixed with 1.7 mL of 0.2 mM 4-nitrophenol (aqueous solution) in a quartz cell. The light yellow colour of p-nitrophenol changes to yellow-green upon mixing of sodium borohydride solution. The reduction of p-nitrophenol to p-aminophenol was very slow in presence of $NaBH_4$ alone (without the aid of Cu nanoparticles). Aqueous p-nitro phenol shows a peak centred around 317 nm, which on addition of $NaBH_4$ red-shifted to 401nm. In the absence of copper nanoparticles this peak remains unaltered. Addition of 100 μL of Cu-aminoclay solution to the above mixture gradually decolourises the solution due to the formation of p-aminophenol (S-5(a)). The decrease in intensity of the peak at 401 nm was monitored for the reduction of p-nitro phenol (or the increase in intensity of the peak at 300 nm corresponding to p-aminophenol) using UV-Vis absorption spectroscopy. The rate constant was calculated by measuring the absorbance (at 401 nm) at regular intervals of every 20 sec. The rate constant derived by plotting $\ln(A_{max})$ vs. time was around $2*10^{-3}$ sec^{-1} which follows first order kinetics. (S-5(b)). This value is comparable to other nanoparticle catalysts used for the reduction of p-nitrophenol in the presence of $NaBH_4$.[4]

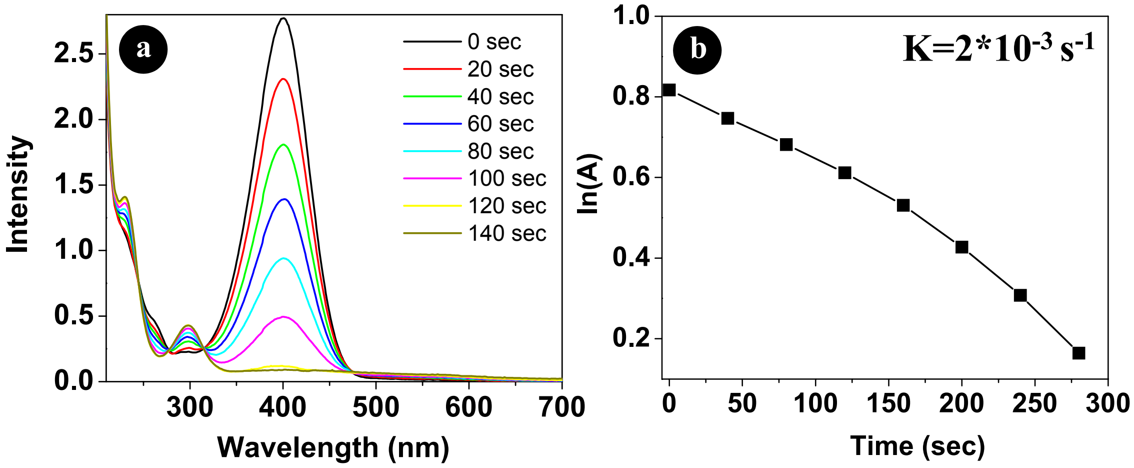

Fig. S5. (a) UV/Vis absorption spectra for the reduction of 0.2 mM p-nitrophenol by 15 mM $NaBH_4$ in the presence of Cu-aminoclay solution ; (b) Plot of ln (A) vs time for the reduction of p-nitrophenol.

References

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(3) S. L. Burkett, A. Press and S. Mann, *Chem. Mater.,* 1997, **9***,* 1071.

(4) N. Pradhan, A. Pal and T. Pal, *Langmuir.,* 2001, **17***,* 1800; S. Kundu, S. Lau and H. Liang, *J. Phys. Chem. C.,* 2009, **113***,* 5150; J. Liu, G. Qin, P. Raveendran and Y. Ikushima, *Chem. Eur. J.*, 2006, **12**, 2131.