

**Electronic supplementary information**

**Influence of Ni on enhanced catalytic activity of Cu/Co<sub>3</sub>O<sub>4</sub> towards  
reduction of nitroaromatic compounds: studies on the reduction  
kinetics**

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## **Experimental section**

### ***Materials***

Cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), copper chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), 4-nitrophenol (4-NP), and urea ( $\text{CO}(\text{NH}_2)_2$ ) were purchased from Merck, India. Sodium borohydride ( $\text{NaBH}_4$ ) was purchased from SRL Chemicals, India. Cetyltrimethylammonium bromide (CTAB) was purchased from RANKEM, India. Various nitroaromatics, viz., 4-nitroaniline (4-NA), 3-nitroaniline (3-NA), 2-nitroaniline (2-NA) and 4-nitrotoluene (4-NT) were purchased from G. S. Chemical, India. Distilled water was employed throughout the all experiments. All reagents were used as received without further purification.

### ***Synthesis of unsupported Ni, Cu and CuNi catalysts***

In a typical synthetic procedure, to a 2.5 mL aqueous solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.072 g, 0.304 mmol) and cetyltrimethylammonium bromide (CTAB; 0.105 g, 0.288 mmol), obtained by subsequent sonication and stirring for 15 min, 1.5 mL aqueous solution of  $\text{NaBH}_4$  (0.020 g, 0.526 mmol) was added dropwise. The contents of the flask were vigorously shaken for 5 min, resulting the generation of Ni catalyst as a black suspension, which was collected by centrifugation and dried under vacuum at 55 °C for 24 h.

To synthesize Cu catalyst, to a 2.5 mL aqueous solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.052 g, 0.304 mmol) and CTAB (0.105 g, 0.288 mmol), obtained by subsequent sonication and stirring for 15 min, 1.5 mL aqueous solution of  $\text{NaBH}_4$  (0.020 g, 0.526 mmol) was added dropwise. The contents of the flask were vigorously shaken for 5 min, resulting the generation of Cu catalyst as a brown suspension, which was collected by centrifugation and dried under vacuum at 55 °C for 24 h.

In a similar synthetic procedure, to a 2.5 mL aqueous solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.036 g, 0.152 mmol),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.026 g, 0.152 mmol) and CTAB (0.105 g, 0.288 mmol), obtained by subsequent sonication and stirring for 15 min, 1.5 mL aqueous solution of  $\text{NaBH}_4$  (0.020 g, 0.526 mmol) was added dropwise. The contents of the flask were vigorously shaken for 5 min, resulting the generation of CuNi catalyst as a bluish suspension, which was collected by centrifugation and dried under vacuum at 55 °C for 24 h. Thus obtained Ni, Cu and CuNi catalysts were used for characterizations and catalytic reduction experiments.

### ***Synthesis of $\text{Co}_3\text{O}_4$ support***

To synthesize cobalt oxide, 0.9517 g of cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) and 2.4024 g of urea ( $\text{CO}(\text{NH}_2)_2$ ) were dissolved in 40 mL of distilled water separately to form homogeneous solutions, respectively. The urea solution was then added dropwise to the cobalt chloride solution under vigorous stirring. The mixture was then transferred to a 150 mL teflon-lined stainless-steel autoclave, which was sealed and heated to 120 °C and kept at that temperature for 6 h. After the autoclave was cooled to room temperature, the resulting pink precipitate was separated by centrifugation, washed three times with distilled water, and dried in oven at 80 °C overnight. The dried product was then calcined at 400 °C for 4 h in air atmosphere. The final black powders were then obtained. Thus obtained cobalt oxide was used for characterization and as support material for metal catalysts.

### ***Synthesis of $\text{Co}_3\text{O}_4$ supported Ni, Cu and CuNi catalysts***

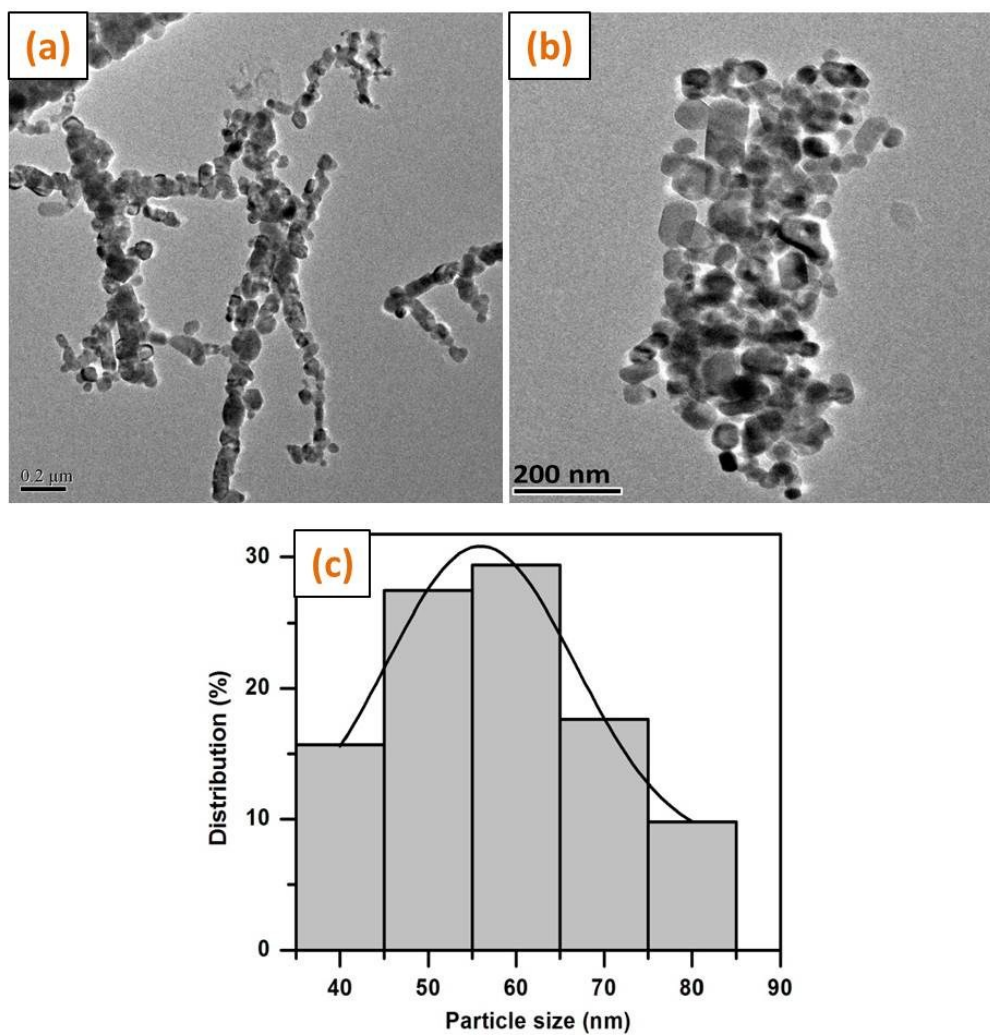
To a suspension of cobalt oxide particles (0.25 g) dispersed in distilled water (50 mL), a 1 mL solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.028 g, 0.118 mmol,) and CTAB (0.041 g, 0.112 mmol), obtained by

subsequent sonication and stirring for 30 min, was added dropwise a 0.6 mL aqueous solution of  $\text{NaBH}_4$  (0.0077 g, 0.203 mmol). The contents of the flask was vigorously shaken for 10 min, resulting the generation of cobalt oxide supported Ni nanocatalyst as a black suspension, which was collected by centrifugation and dried under vacuum at 55 °C for 24 h.

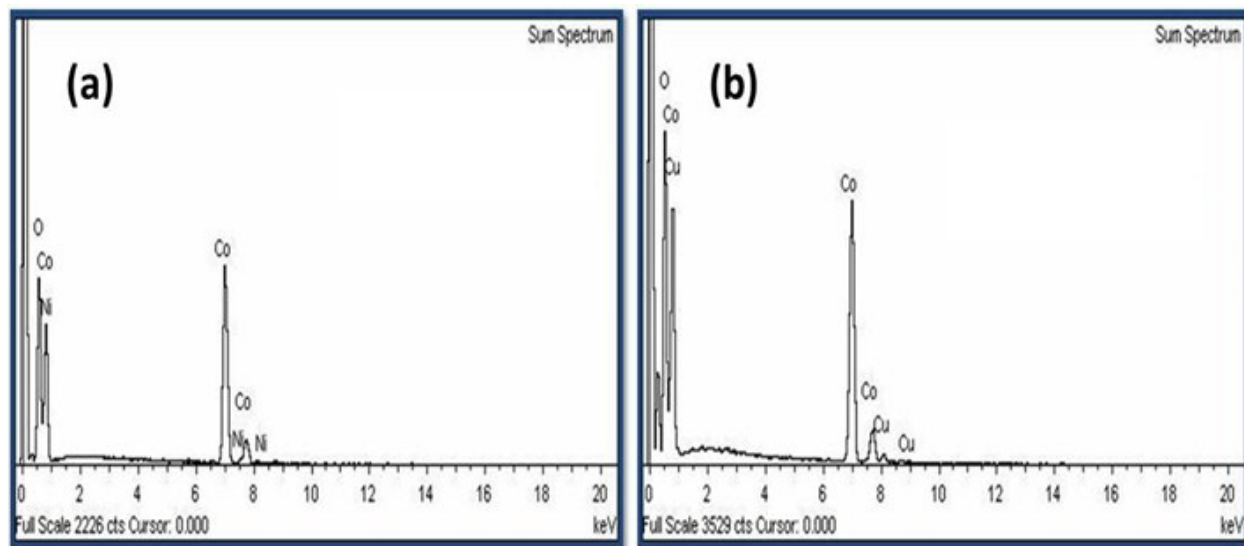
To synthesize  $\text{Cu/Co}_3\text{O}_4$ , to a suspension of cobalt oxide particles (0.25 g) dispersed in distilled water (50 mL), a 1.83 mL solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.038 g, 0.222 mmol) and CTAB (0.077 g, 0.211 mmol), obtained by subsequent sonication and stirring for 30 min, was added dropwise a 1.1 mL aqueous solution of  $\text{NaBH}_4$  (0.0146 g, 0.384 mmol). The contents of the flask was vigorously shaken for 10 min, resulting the generation of cobalt oxide supported Cu nanocatalyst as a black suspension, which was collected by centrifugation and dried under vacuum at 55 °C for 24 h.

In an identical synthetic procedure, to a suspension of cobalt oxide particles (0.25 g) dispersed in distilled water (50 mL), a 1.5 mL solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.014 g, 0.059 mmol)  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.019 g, 0.111 mmol) and CTAB (0.06 g, 0.161 mmol), obtained by subsequent sonication and stirring for 30 min, was added dropwise a 0.8 mL aqueous solution of  $\text{NaBH}_4$  (0.011 g, 0.289 mmol). The contents of the flask was vigorously shaken for 10 min, resulting the generation of oxide supported Cu-Ni nanocatalyst as a black suspension, which was collected by centrifugation and dried under vacuum at 55 °C for 24 h. Thus obtained supported Ni, Cu and CuNi catalysts were used for characterization and catalytic reduction experiments.

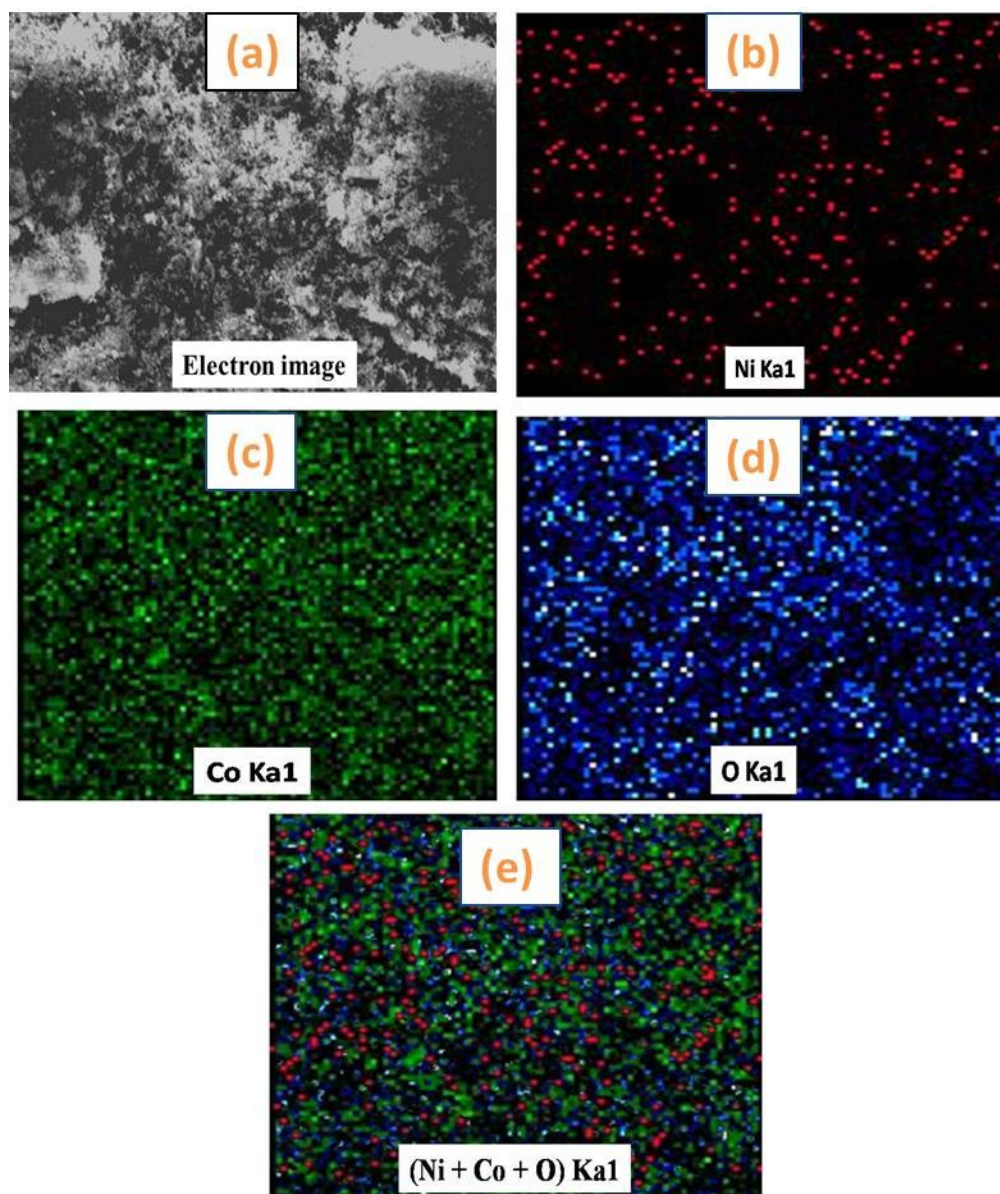
**Fig. S1** Typical (a, b) TEM images and (c) size distribution histogram of  $\text{Co}_3\text{O}_4$  nanostructure.



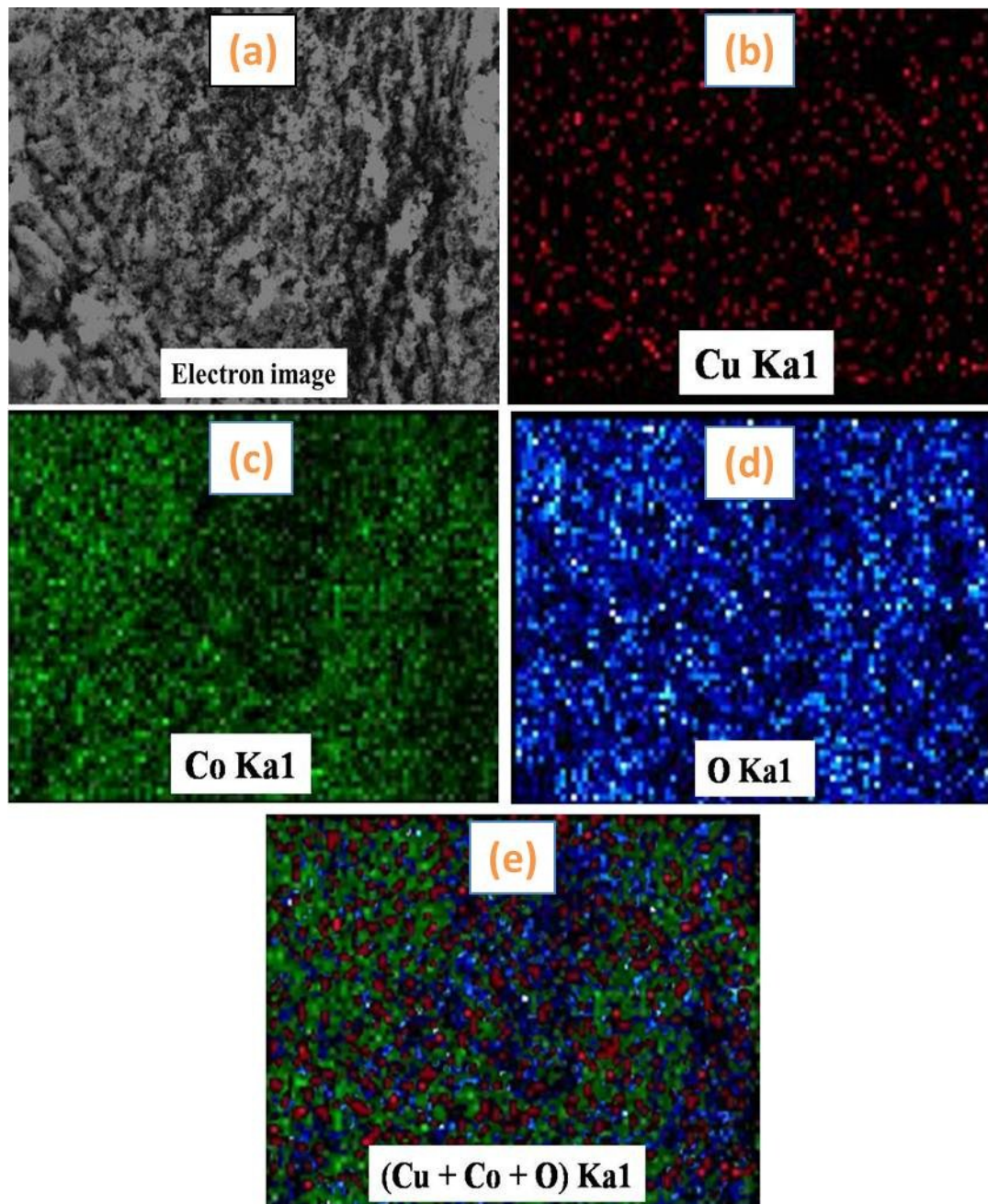
**Fig. S2** EDX patterns of (a) Ni/Co<sub>3</sub>O<sub>4</sub> and (b) Cu/Co<sub>3</sub>O<sub>4</sub>, respectively.



**Fig. S3** (a) Electron image of Ni/Co<sub>3</sub>O<sub>4</sub>; EDS maps of (b) Ni, (c) Co, (d) O and (e) (Ni+Co+O).

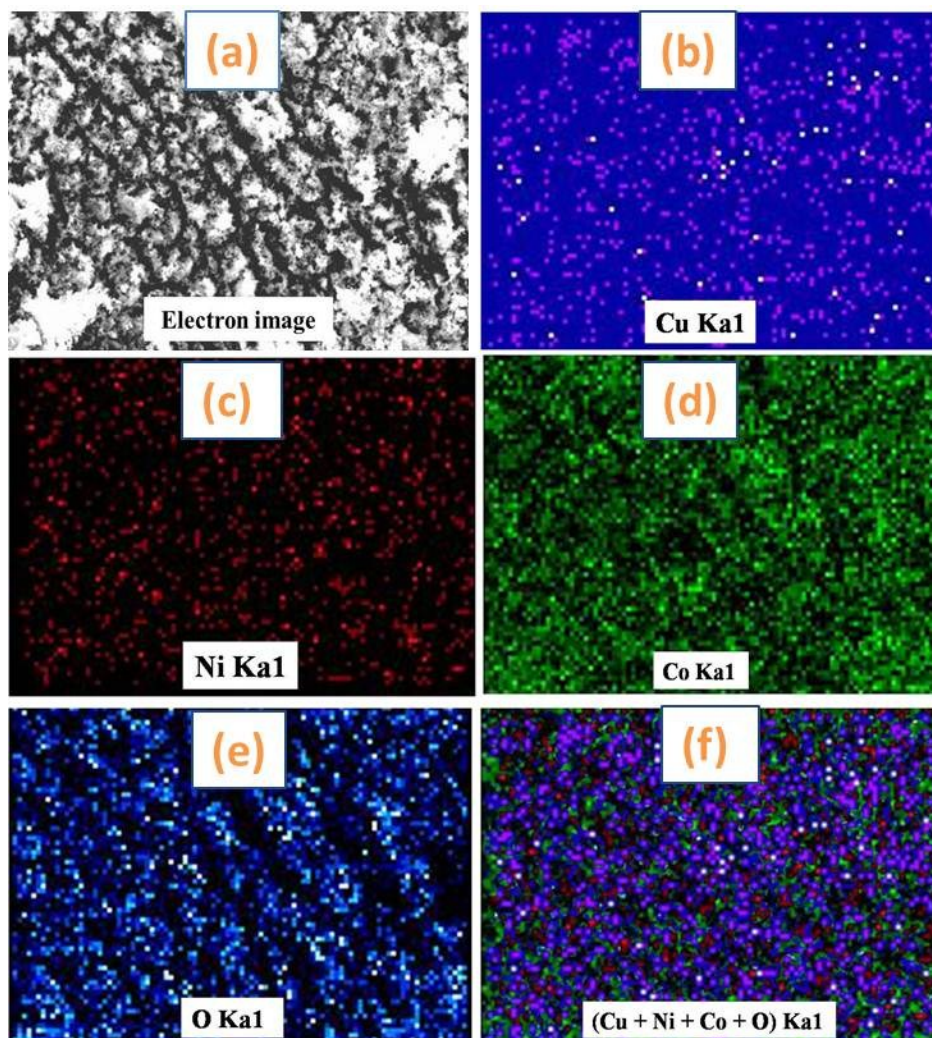


**Fig. S4** (a) Electron image of Cu/Co<sub>3</sub>O<sub>4</sub>; EDS maps of (b) Cu, (c) Co, (d) O and (e) (Cu+Co+O).

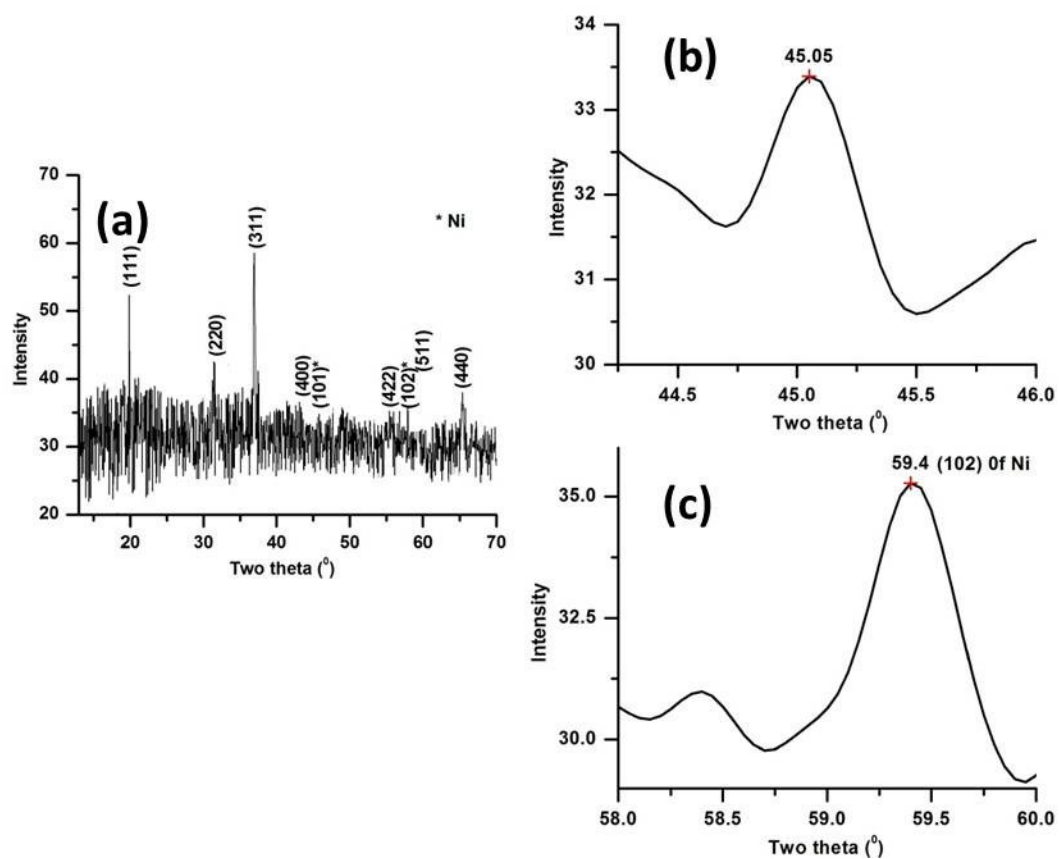




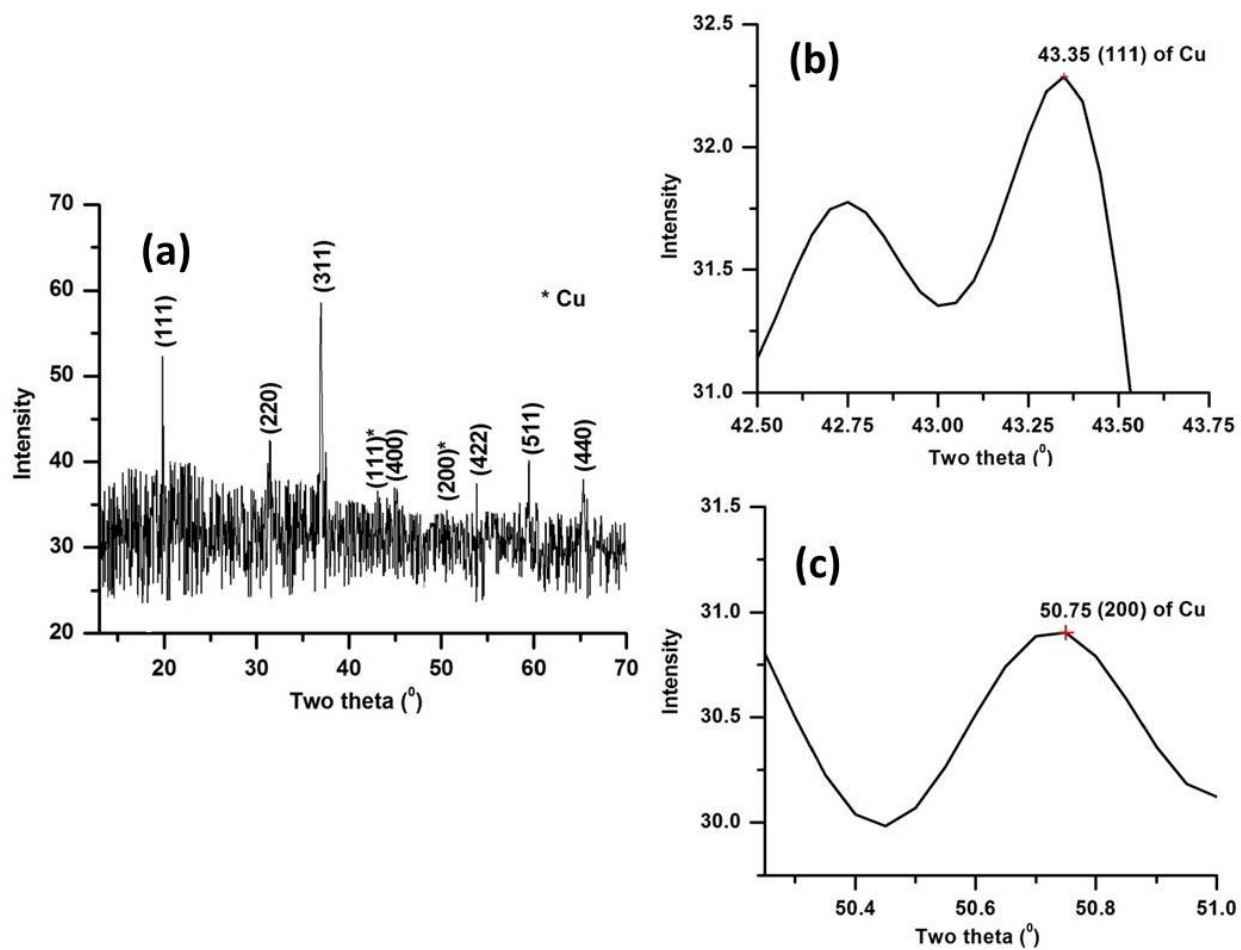
**Fig. S5** (a) Electron image of CuNi/Co<sub>3</sub>O<sub>4</sub>; EDS maps of (b) Cu, (c) Ni (d) Co, (e) O and (f) (Cu+Ni+Co+O).



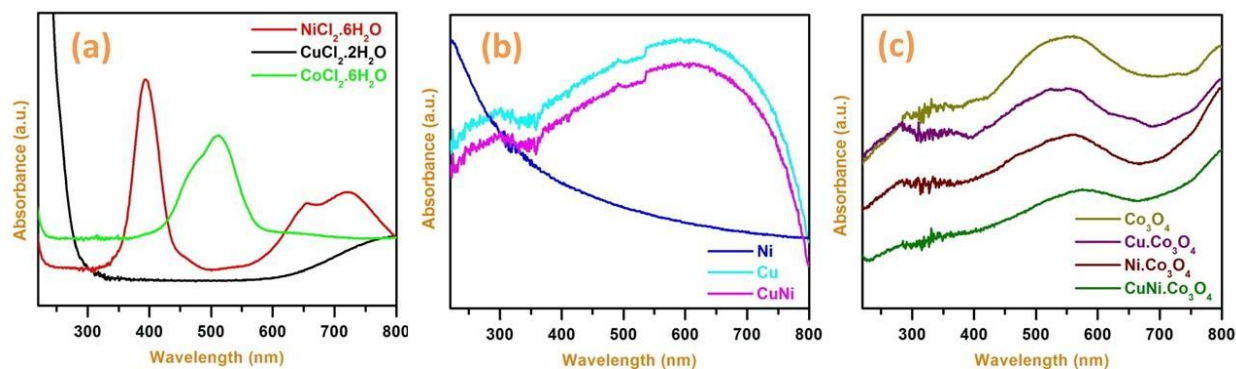
**Fig. S6** X-ray powder diffraction patterns of (a) Ni/Co<sub>3</sub>O<sub>4</sub> and (b, c) expanded X-ray powder diffraction patterns of Ni/Co<sub>3</sub>O<sub>4</sub> at different 2θ (°) values, respectively.



**Fig. S7** X-ray powder diffraction patterns of (a) Cu/Co<sub>3</sub>O<sub>4</sub> and (b, c) expanded X-ray powder diffraction patterns of Cu/Co<sub>3</sub>O<sub>4</sub> at different 2θ (°) values, respectively.



**Fig. S8** UV-visible spectra of reference compounds and as synthesized catalysts.



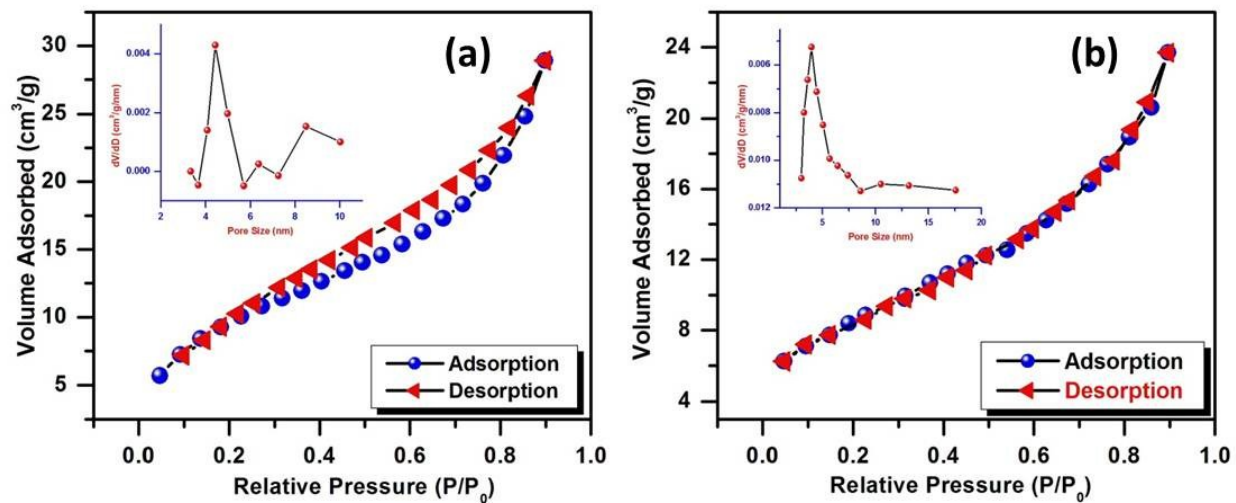
The valence state of the metal and metallic alloy catalysts are investigated by UV-visible spectroscopic analysis along with reference compounds and are presented Fig. S8. The spectrum of NiCl<sub>2</sub>·6H<sub>2</sub>O solution, a Ni(II) complex, are expected to exhibit three absorption bands corresponding to the transitions,  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  in the UV-visible region. The transition  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  is located in the UV region was not recorded. The absorption peaks were observed in the wavelength range 350–800 nm corresponding to  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  transitions as shown in Fig. S8(a). The  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  transition band in the 550–800 nm splits to a peak at 722 nm along with a shoulder at 655 nm which are due to spin–orbit coupling that mixes the  ${}^3T_{1g}(F)$  and  ${}^1E_g$  states.<sup>S1</sup> However, UV-visible spectral analyses of unsupported Ni catalyst show the absence of absorption peaks in the 200–800 nm range. This observation confirms that the valence state of Ni is Ni(0). Again, the spectrum of CuCl<sub>2</sub>·2H<sub>2</sub>O solution, a Cu(II) complex, does not shows any peaks in the UV-visible region. However, UV-visible spectral analyses of unsupported Cu catalyst are expected to exhibit absorption band corresponding to the SPR (surface plasmon resonance) in the visible region of the spectrum.<sup>S2</sup> From the figure (Fig. S8b), it is observed that unsupported Cu catalyst shows SPR (surface

plasmon resonance) band in the visible region of the spectrum. This observation confirms that the valence state of Cu is Cu(0). Moreover, for unsupported CuNi catalyst we have found similar UV-visible pattern as that of unsupported Cu catalyst. It confirms that the metallic nature of Cu & Ni in CuNi. The UV-Vis absorption spectrum of the cobalt oxide sample shows that there are two absorption maxima one of these is in the UV region and one in visible region. The absorption peaks observed around 350 nm is attributed to  $O^{2-} \rightarrow Co^{2+}$  and the peak in the visible region (~600 nm) is due to  $O^{2-} \rightarrow Co^{3+}$  charge transfer transitions.<sup>S3</sup> The UV-visible absorption spectra of Cu/Co<sub>3</sub>O<sub>4</sub>, Ni/Co<sub>3</sub>O<sub>4</sub>, CuNi/Co<sub>3</sub>O<sub>4</sub> are plotted in Fig. S16c. All the compounds exhibit almost similar patterns as that for Co<sub>3</sub>O<sub>4</sub>. No other distinguishable peaks for Ni(II) & Cu(II) are observed. This confirms the metallic states of Cu and Ni in the respective samples

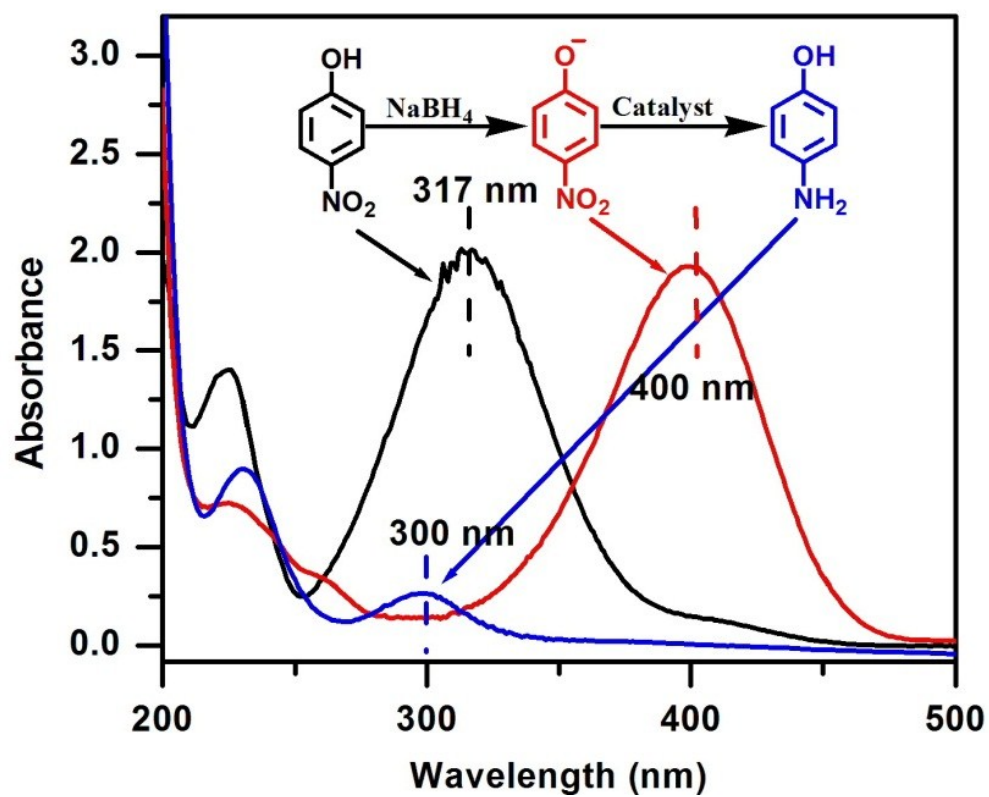
### Supporting references

- S1) W. Liu, A. Migdisov and A. Williams-Jones, *Geochim. Cosmochim. Acta*, 2012, **94**, 276–290.
- S2) M. S. Usman, N. A. Ibrahim, K. Shameli, N. Zainuddin and W. M. Z. W. Yunus, *Molecules*, 2012, **17**, 14928–14936.
- S3) K. Deori and S. Deka, *CrystEngComm*, 2013, **15**, 8465–8474.

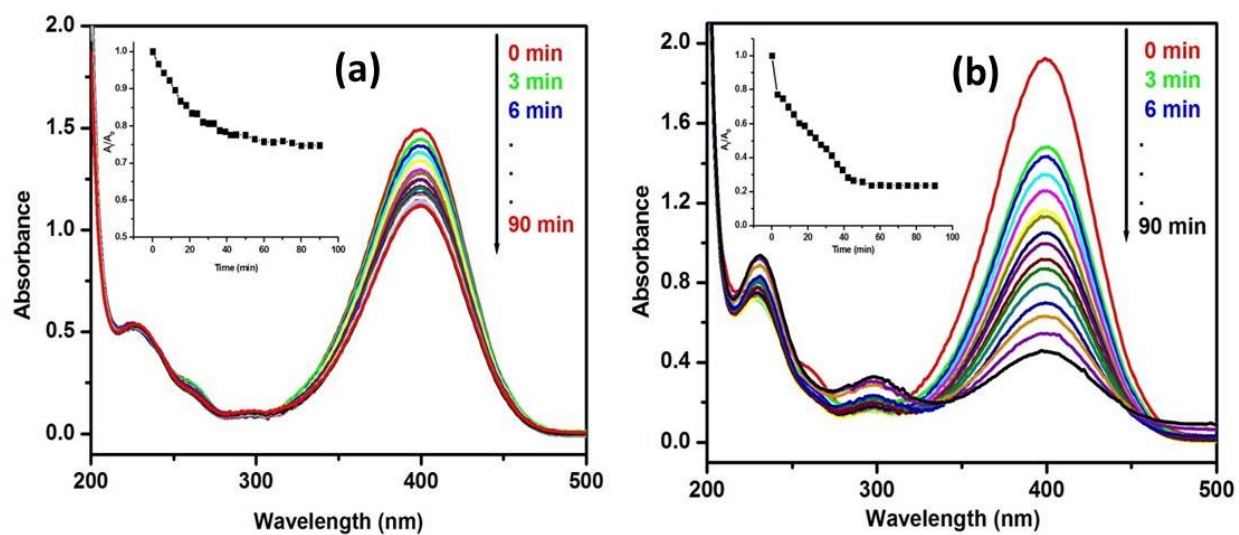
**Fig. S9** N<sub>2</sub> adsorption-desorption isotherms of (a) Ni/Co<sub>3</sub>O<sub>4</sub> and (b) Cu/Co<sub>3</sub>O<sub>4</sub>; insets corresponding pore size distribution curves.



**Fig. S10** UV–visible absorption spectra of 4-nitrophenol before (black line) and after (red line) adding  $\text{NaBH}_4$  and 4-aminophenol (blue line).

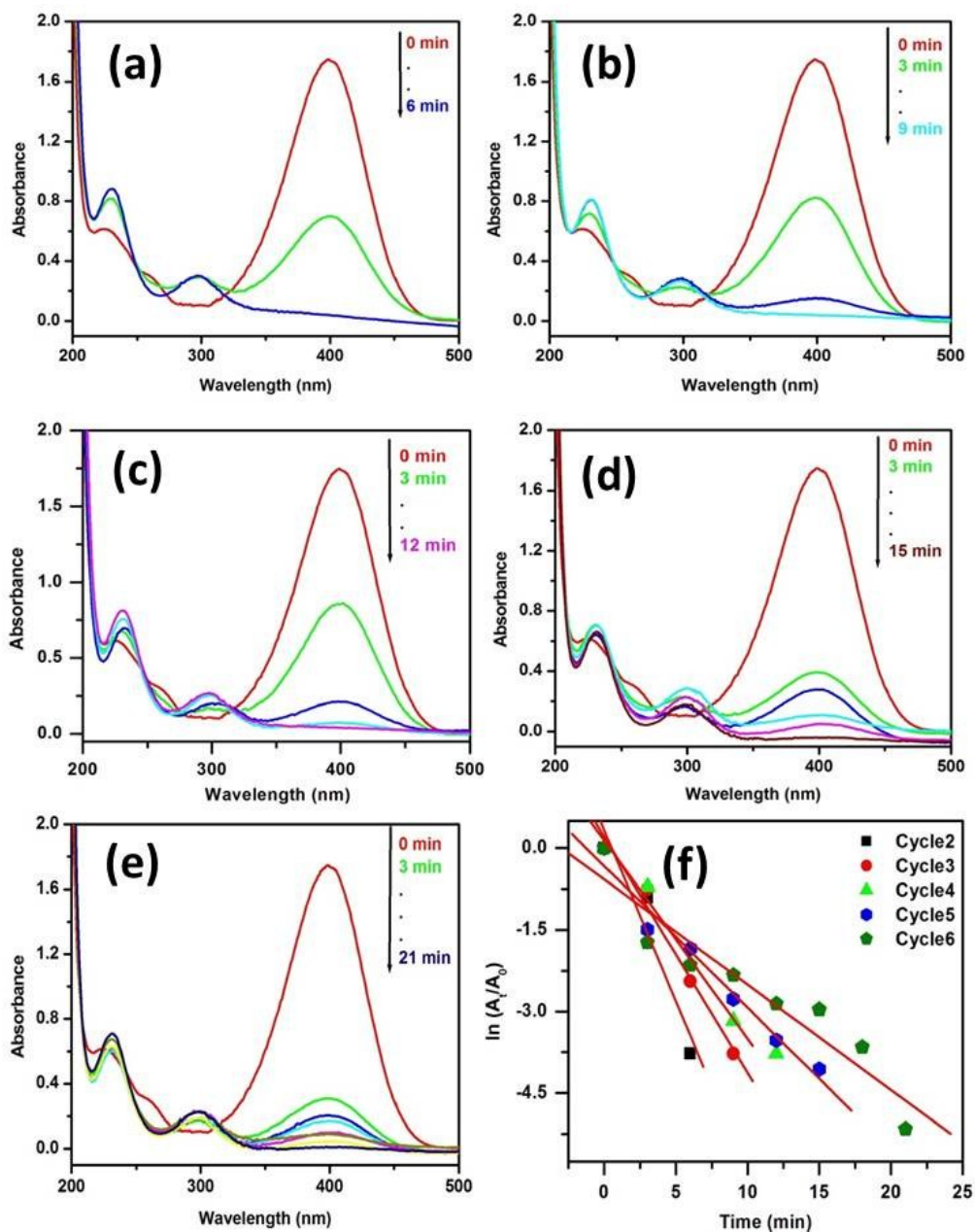


**Fig. S11** (a) Time-dependent UV-visible absorption spectra of the reaction solution of 4-NP reduction without catalyst and (b) with 2 mg of  $\text{Co}_3\text{O}_4$ ; insets: plots of  $A_t/A_0$  against the reaction time. Condition:  $[\text{NaBH}_4] = 20 \text{ mmol/L}$ .

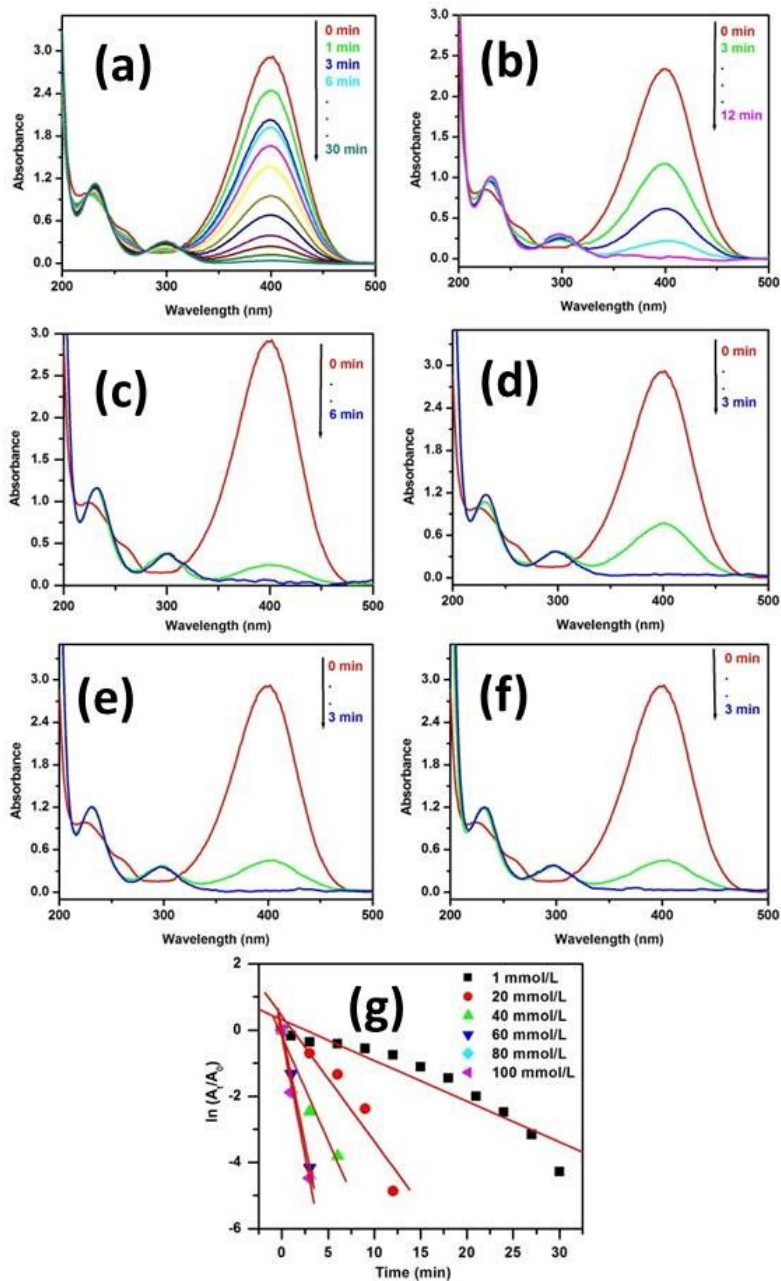




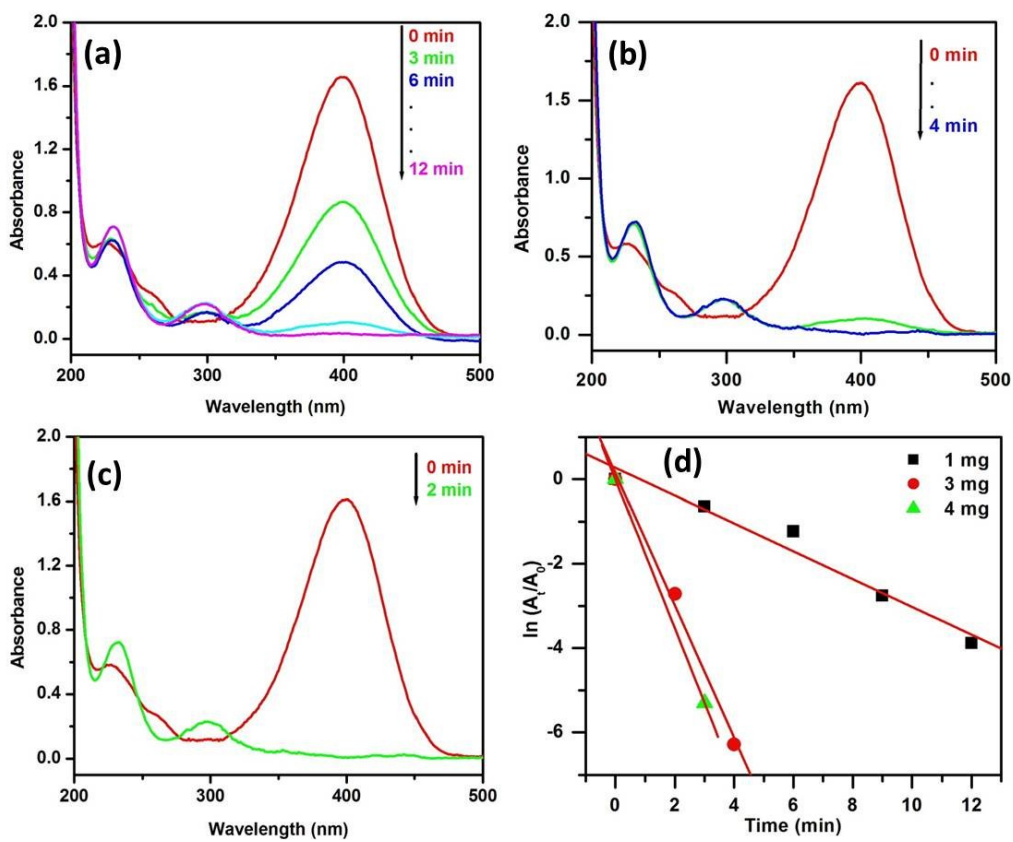
**Fig. S12** Time dependent absorption spectra for the catalytic reduction of 4-NP by  $\text{NaBH}_4$  in presence of  $\text{CuNi}/\text{Co}_3\text{O}_4$  for (a) cycle 2, (b) cycle 3, (c) cycle 4, (d) cycle 5, (e) cycle 6 and (f) the plots of  $\ln(A_t/A_0)$  against reaction time derived from absorption spectra presented in above for the various cycles . Conditions:  $[\text{4-NP}] = 0.2 \text{ mmol/L}$ ,  $[\text{NaBH}_4] = 20 \text{ mmol/L}$ , Catalyst dose =  $2.0 \text{ mg}$ .



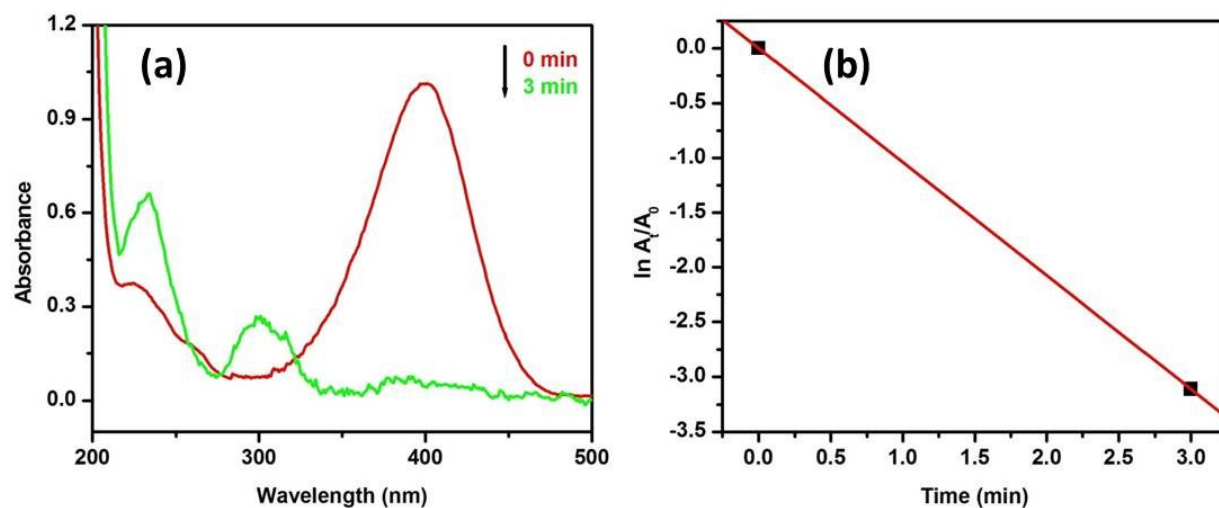
**Fig. S13** Time dependent absorption spectra for the catalytic reduction of 4-NP in presence of CuNi/Co<sub>3</sub>O<sub>4</sub> by (a) 1, (b) 20, (c) 40, (d) 60, (e) 80 and (f) 100 mmol/L of [NaBH<sub>4</sub>] and (g) the plots of  $\ln(A_t/A_0)$  against reaction time derived from absorption spectra presented in above for the various [NaBH<sub>4</sub>]. Conditions: [4-NP] = 0.2 mmol/L and catalyst dose = 2.0 mg.



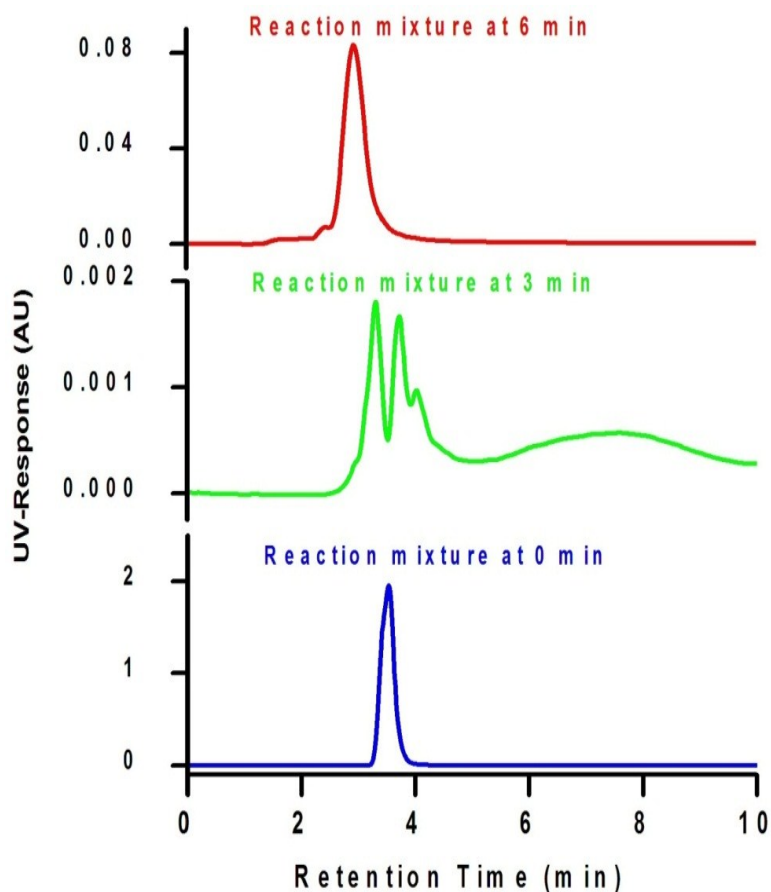
**Fig. S14** Time dependent absorption spectra for the catalytic reduction of 4-NP by NaBH<sub>4</sub> in presence of (a) 1.0 mg , (b) 3.0 mg, (c) 4.0 mg of CuNi/Co<sub>3</sub>O<sub>4</sub> and (d) the plots of ln (A<sub>t</sub>/A<sub>0</sub>) against reaction time derived from absorption spectra for various catalyst dosage. Conditions: [4-NP] = 0.2 mmol/L and [NaBH<sub>4</sub>] = 20 mmol/L.



**Fig. S15** Time dependent absorption spectra for the catalytic reduction of 4-NP by NaBH<sub>4</sub> in presence of CuNi/Co<sub>3</sub>O<sub>4</sub> for (a) 0.1 mmol/L of [4-NP] and (c) the plots of ln (A<sub>t</sub>/A<sub>0</sub>) against reaction time derived from absorption spectra presented in above. Conditions: [NaBH<sub>4</sub>] = 20 mmol/L and catalyst dose = 2.0 mg.



**Fig. S16** HPLC chromatograms of reaction mixture (a) initially, (b) at 3 min and (c) at 6 min of the catalytic reduction of 4-NP by NaBH<sub>4</sub> in presence CuNi/Co<sub>3</sub>O<sub>4</sub>. Conditions: [4-NP] = 0.2 mmol/L, [NaBH<sub>4</sub>] = 20 mmol/L and amount of CuNi/Co<sub>3</sub>O<sub>4</sub> = 2.0 mg.



**High-performance liquid chromatography (HPLC) Analysis:** For the HPLC analysis, the mobile phase used a solution consisting of 50% methanol and 50% of acetonitrile (1%). A standard of 0.003 g/L of 4-NP and 4-AP was prepared by using distilled water. The sample volume was 20  $\mu$ L, the flow rate was 1.0 mL/min and detection was affected at a C18 column (5  $\mu$ m, 4.6 mm  $\times$  250 mm) and wavelength 290 nm, the wavelength was found to be the optimum for simultaneous detection of 4-NP and 4-AP. The analyses were performed at ambient temperature allowing 10 min equilibration after the start of pumping mobile phase through the column.

**Fig. S17** FTIR spectra of (a) the commercial 4-AP (black line) and (b) the product of the reduction of 4-NP (red line).

