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A ternary nanocomposite Cu_2O-Cu-CuO: a catalyst for intriguing activity

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Supporting Information

Materials:

All the reagents were of AR grade. Copper acetate monohydrate [$Cu(CH_3COO)_2.H_2O$] and hydrazine hydrate ($N_2H_4.H_2O$; 80%) were purchased from E-Merck. $NaBH_4$ was purchased from Sigma-Aldrich. Glass apparatus were purchased from Blue Star India and they were properly cleaned with aqua regia, water and dried before use.

Analytical Instrument:

Powder X-ray diffraction (XRD) was done in a PW1710 diffractometer, a Philips, Holland,instrument. The XRD data were analyzed by using JCPDS software. Field emission scanning electron microscopy (FESEM) was performed with a supra 40, Carl ZeissPvt. Ltd. instrument.X-rayphotoelectron spectroscopy (XPS) analysis was carried out by a VG Scientific Escalab MK IIspectrometer equipped with a Mg Kr excitation source (1253.6 eV) and a five-channeltron detectionsystem.Transmission electron microscopy (TEM) was performed on a Hitachi H-9000 NARinstrument, Hitachi, using an accelerating voltage of 300 kV.Energy dispersive X-ray spectroscopic (EDX) analysis was obtained by an Oxford link andISIS 300 instruments.All UV-vis absorption spectra were recorded on SPECTRASCAN UV 2600 digitalspectrophotometer (Chemito, India).

Figure S1. FESEM images of Cu_2O (sample no. S2) at different magnifications (a,b).

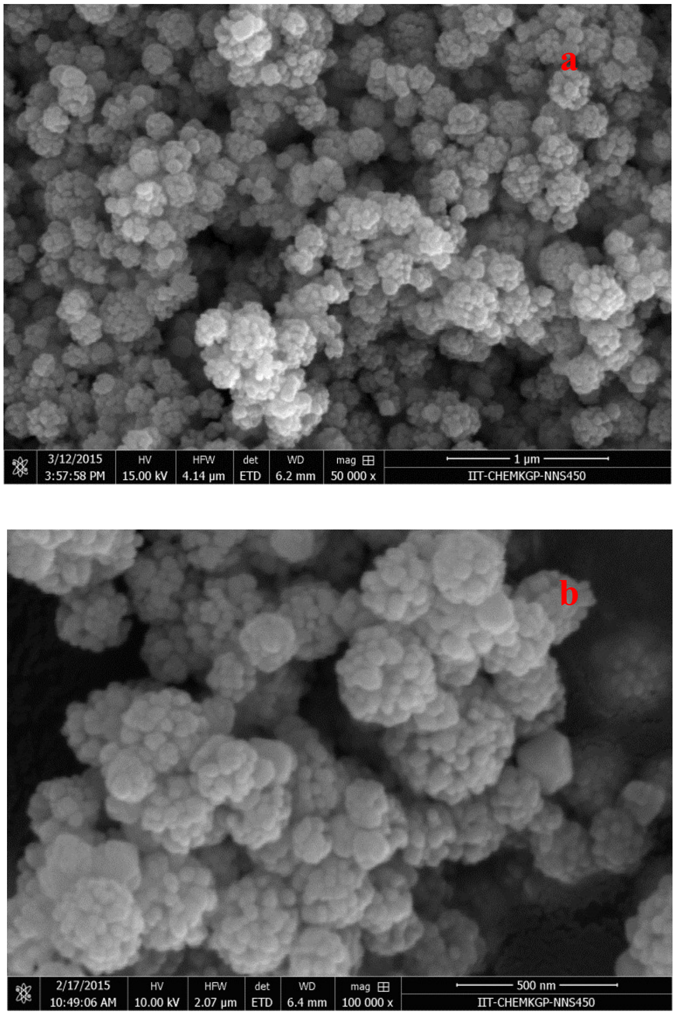


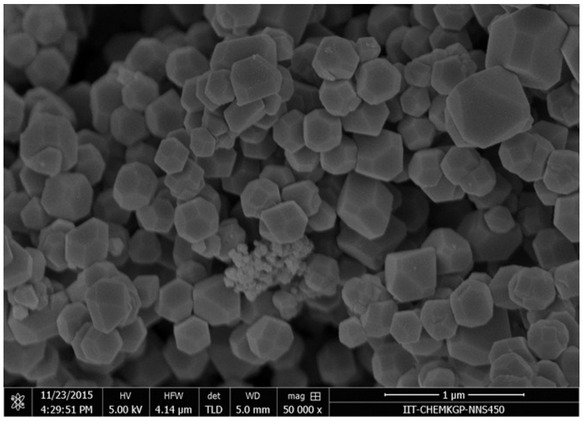
Figure S2. Characterization of Cu_2O and Cu NPs.

Figure S2a. FESEM and XRD of Cu_2O NPs prepared from $Cu(OAc)_2$ (0.25 mmol) and $NaBH_4$ or ascorbic acid at room temperature .

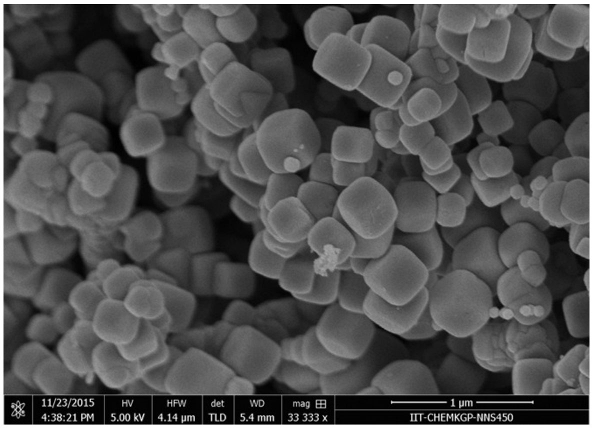
Reducing agent	Amount (mmol)	Particle size (nm)	Composition	Stirring Time (min)
N_2H_4	0.33	50-100	Cu_2O(S1)	30
$NaBH_4$	0.10	300-600 nm	Cu_2O(A)	70
Ascorbic acid (+ 200 mg NaOH)	0.33	200-500 nm	Cu_2O(B)	45

Volume of total aqueous solution = 20 mL

FFESEM images:

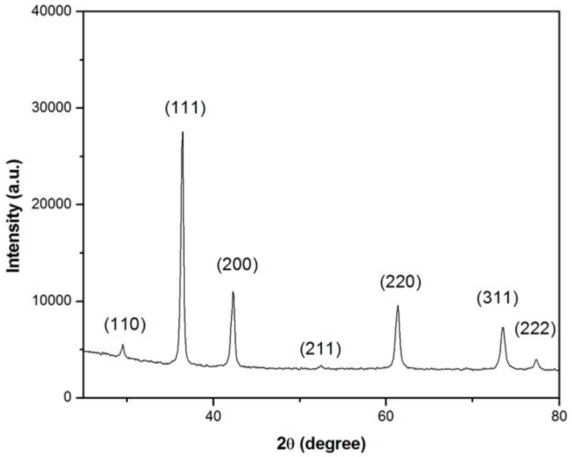


Cu_2O(A)

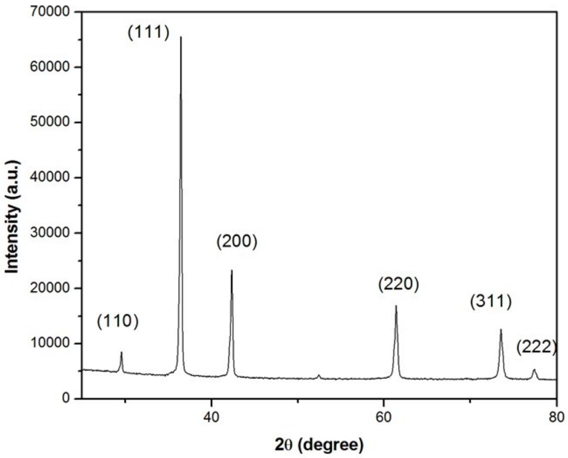


Cu_2O(B)

XRD spectra (matched well with JCPDS Card No. 05-0667):



Cu_2O(A)



Cu_2O(B)

Figure S2b. FESEM (a) and EDX (b) of Cu NPs (sample no.S3).

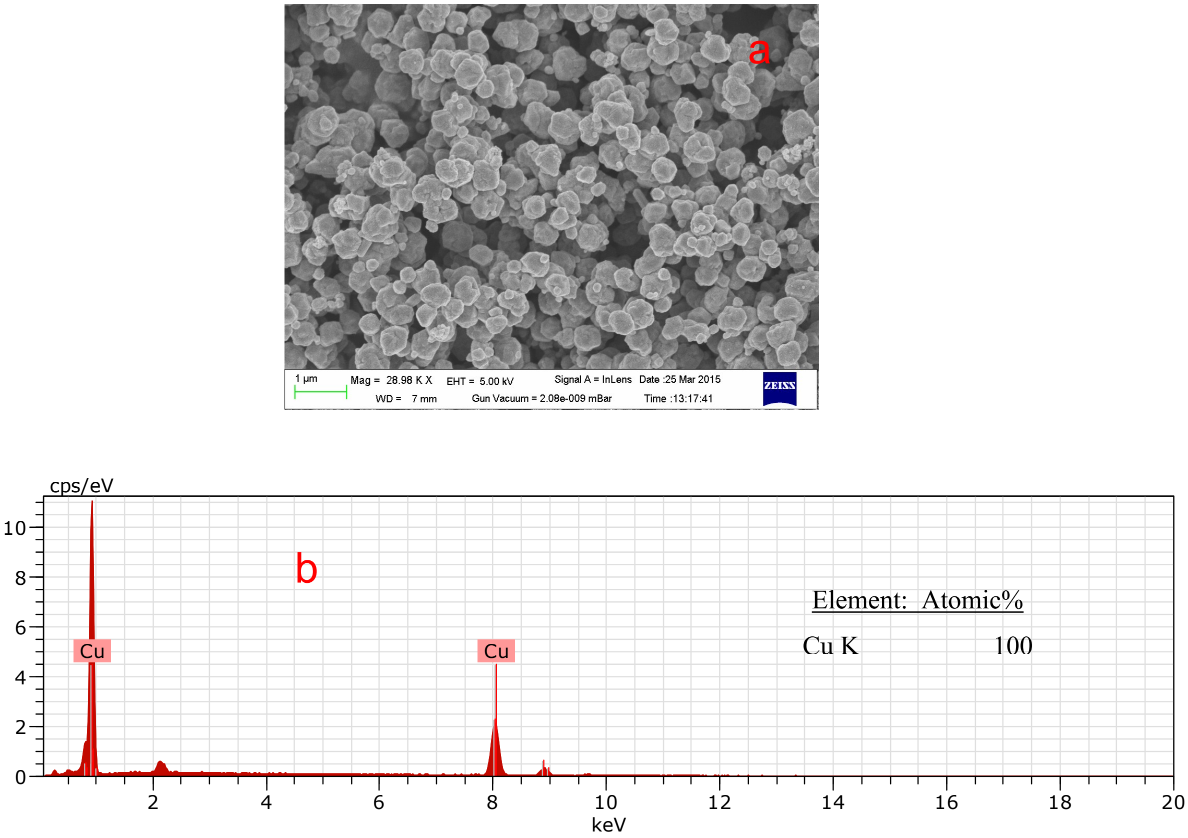


Figure S2c. DRS spectra of Cu_2O (S1) and Cu(S3).

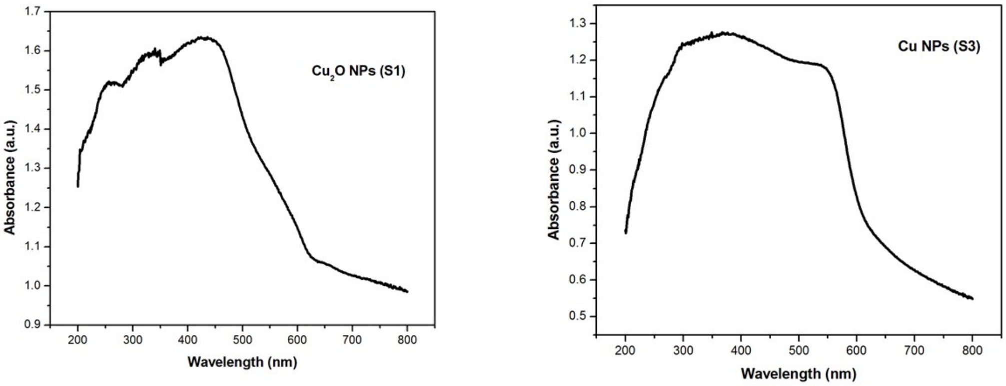
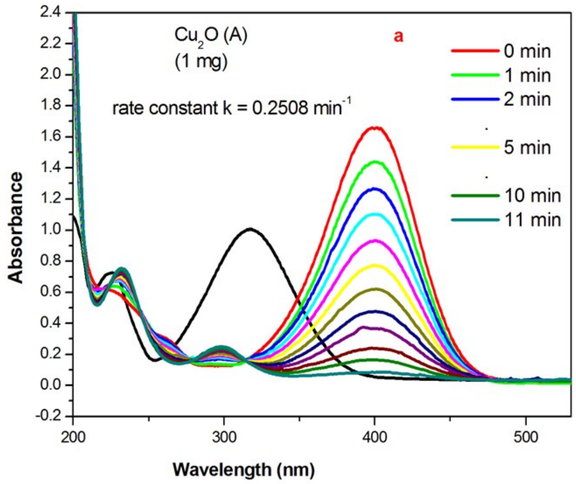


Figure S3. UV-vis spectra of 4-nitrophenol reduction using (a) Cu_2O NPs (A) and (b) Cu_2ONPs (B).



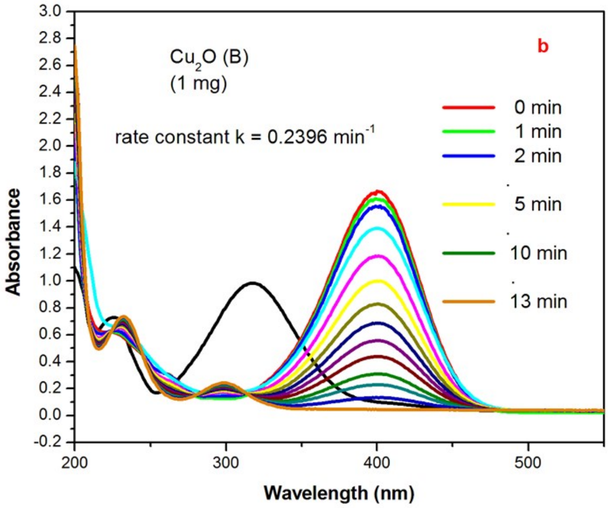
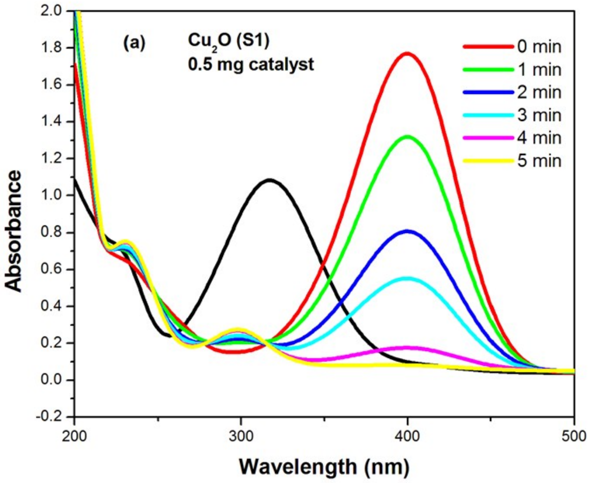


Figure S4. UV-vis spectra of 4-nitrophenol reduction using (a) 0.5 mg and (b) 1.5 mg of Cu_2O NPs (S1).



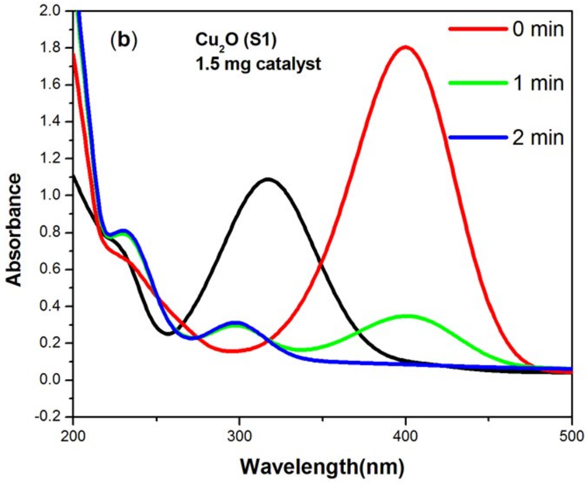


Table S1. Recycling after use of Cu_2O NPs (S1) in first cycle and Cu NPs (S3) for 4-nitrophenol reduction.

Entry	**Catalyst used in 1st Cycle**	**Cycle No**	**Time(min)**	**Rate constant (min^{-1})**
1	Cu_2O (S1)	1st	3	0.9407
2		2nd	6	0.5196
3		3rd	10	0.3004
4		4th	14	0.2499
5		5th	16	0.2348
6	Cu	1st	9	0.3105
7		2nd	24	0.1276

Figure S5

Figure S5a. UV-vis spectra of 4-nitrophenol reduction in 2nd to 5th cycles (Recycling after use of Cu_2O NPs (S1) in the First Cycle).

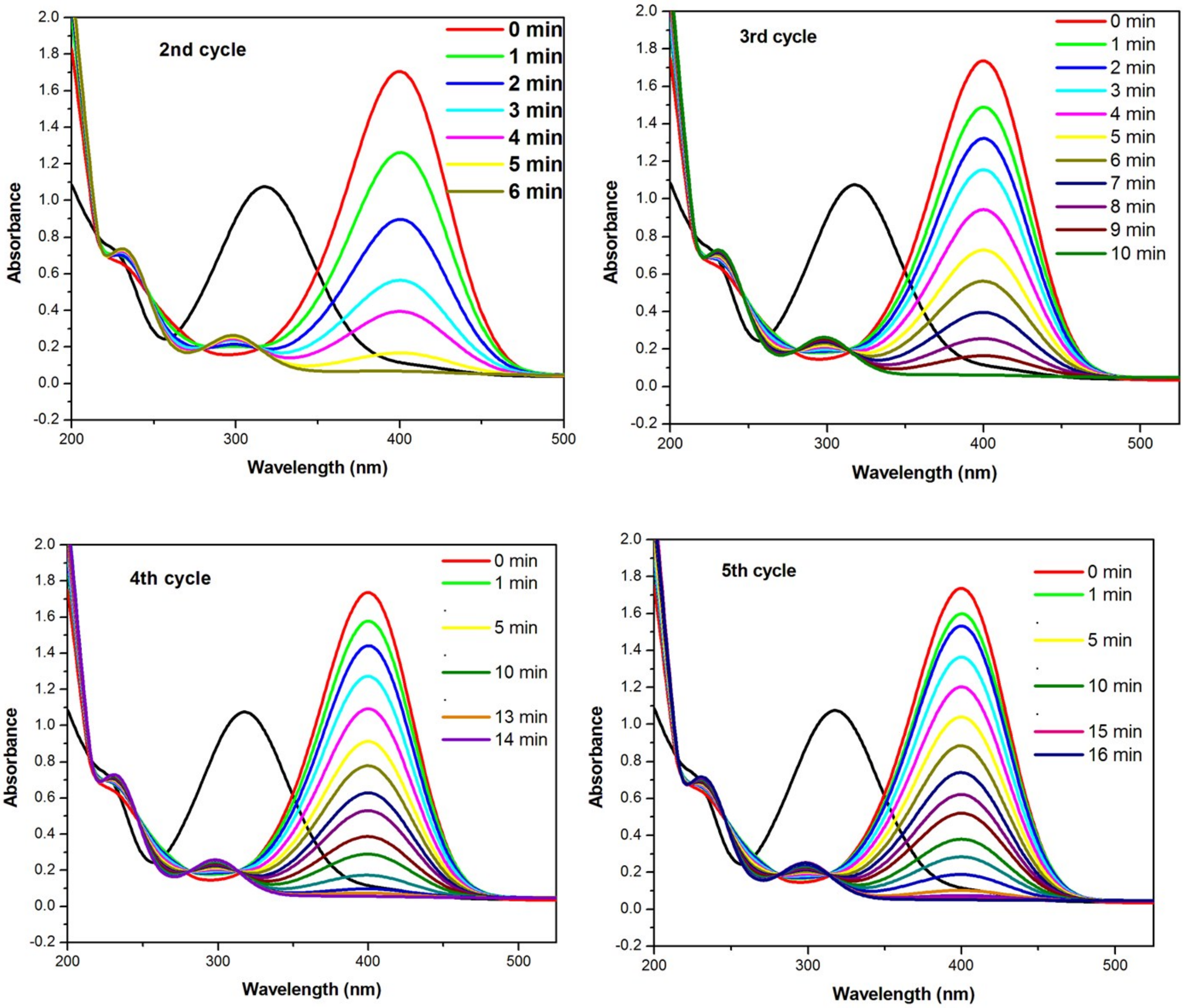


Figure S5b. UV-vis spectrum of 4-nitrophenol reduction in 2nd cycle (recycling of Cu NPs (S3) after use in first cycle).

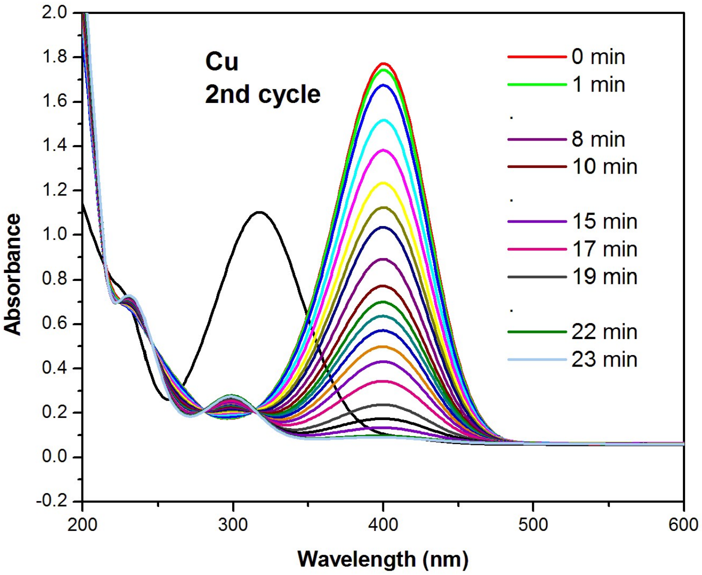
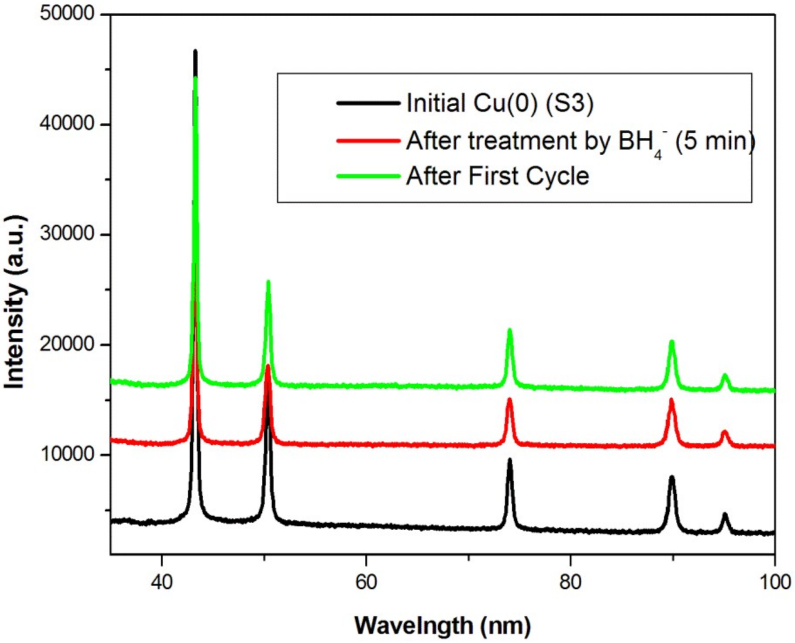


Figure S6. XRD of Cu NPs (S3), after $NaBH_4$ treatment, and after first cycle (all matched well with JCPDS# 04-0836)



Cu NPs (S3) treatment by $NaBH_4$: 1.0 mg of Cu NPs was taken in centrifuge tube and suspended in 3 mL water. Then 300 µL of $NaBH_4$ (5×10^{-2} M) was added and kept for 5 min. Then centrifugation was performed immediately with washing by water for several times, finally by ethanol. Then the product was dried and characterized (Matched well with JCPDS# 04-0836).

Figure S7. Characterization of Cu_2O-Cu-CuO obtained after first cycle use of Cu_2O NPs on 4-nitrophenol reduction.

Figure S7a. Digital image

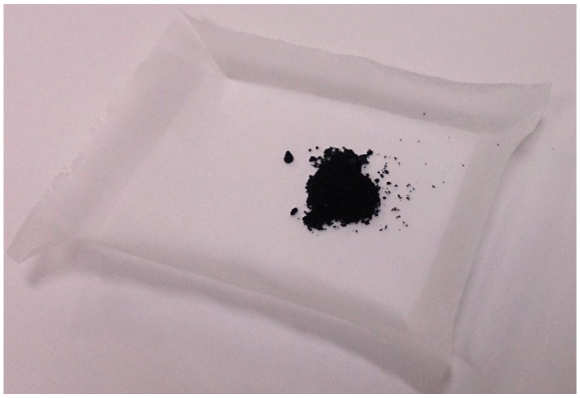


Figure S7b. XRD spectrum

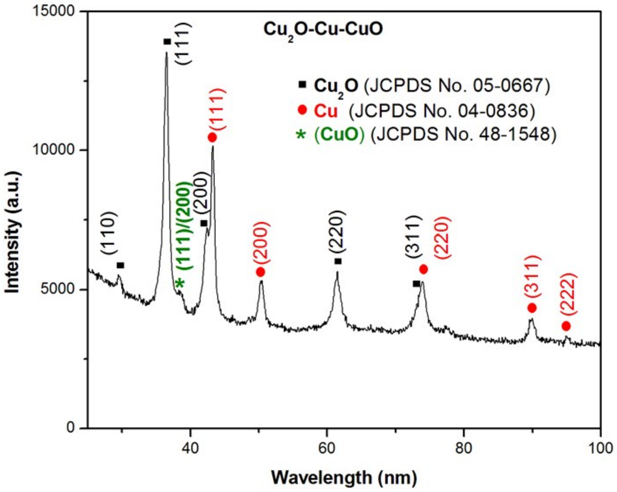


Figure S7c.TEM Images

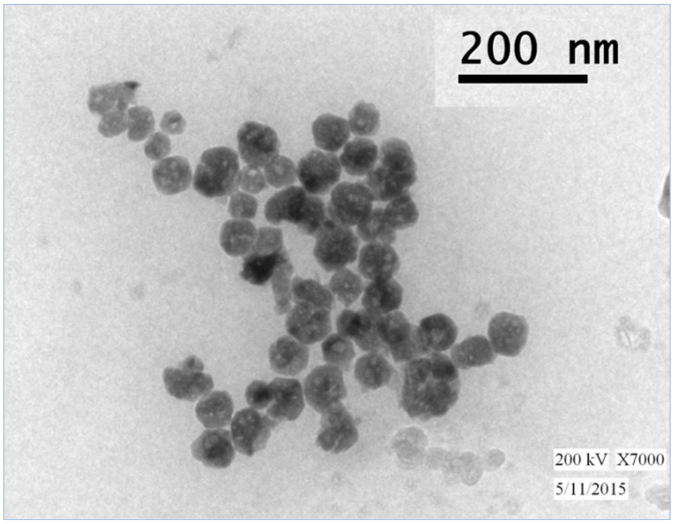


Figure S7d. SAED Image

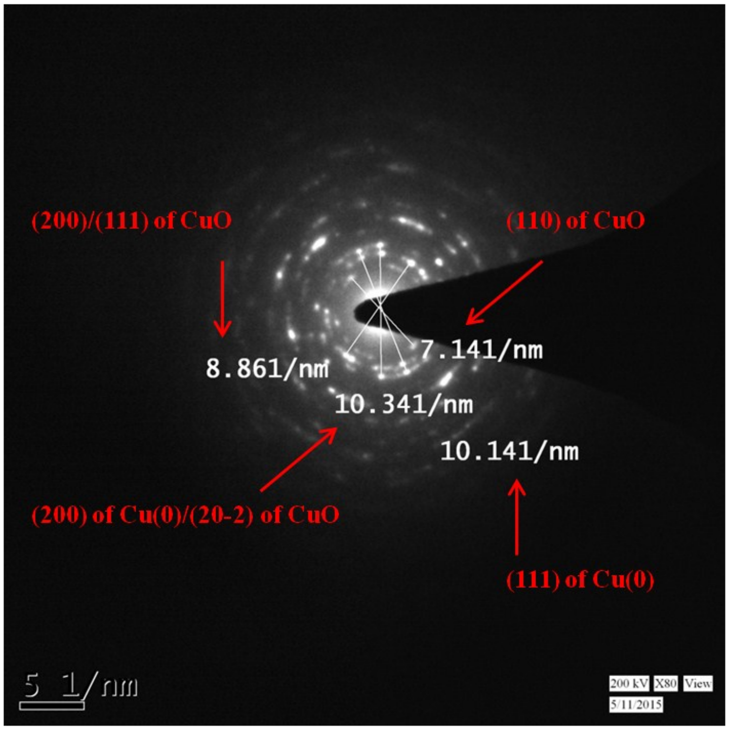


Figure S8.

UV-vis spectrum of 4-nitrophenol reduction using 1.0 mg Cu_2O-Cu-CuO (prepared from Cu_2O (S1) by $NaBH_4$ treatment for 2 min.)

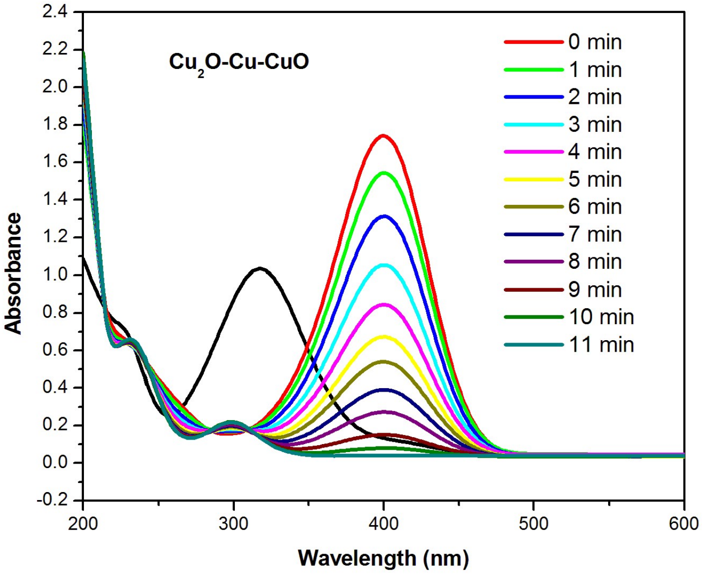
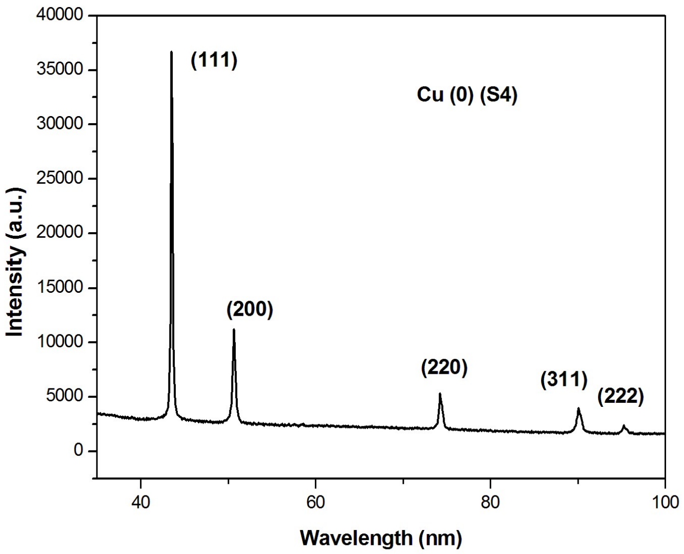


Figure S9.

(a) XRD of Cu(0) (S4) (Matched well with JCPDS# 04-0836).



(b) UV-vis spectrum of 4-nitrophenol reduction using 1.0 mg Cu(0) (S4)

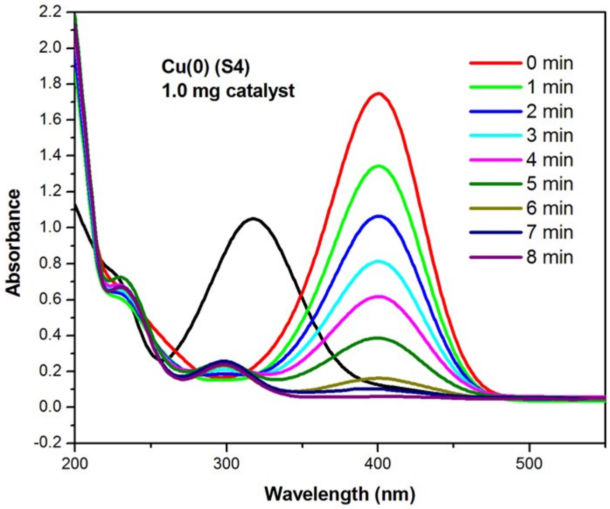


Figure S10.UV-vis spectra of nitroarenes reduction.