

## Supporting Information

### Remarkable Facet Selective Reduction of 4-Nitrophenol by Morphologically Tailored (111) Faceted Cu<sub>2</sub>O Nanocatalyst.

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**Analytical instruments.** Powder X-Ray diffraction (XRD) was investigated with a Philips PW-1710 X-ray diffractometer (40kV, 20 mA) using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the range of 5°-90° at a scanning rate of 0.5° min<sup>-1</sup>. For analysing the XRD data, JCPDS software was referred. Surface morphology was examined using field emission scanning electron microscopy (FESEM) with a supra, Carl Zeiss Pvt. Ltd. Elemental detection of the nanomaterials was done with an energy dispersive X-ray microanalyser (OXFORD ISI 3000 EDAX) attached to the scanning electron microscopy. For acquisition of further information on structural aspect, transmission electron microscopy (TEM) analysis was done with the help of Hitachi H-9000 NAR 2 transmission electron microscope, using accelerating voltage at 200 kV. Surface chemical analysis was analysed by X-Ray photoelectron spectroscopy, XPS (SPECS PHOIBOS 100 MCD energy analyser), in an ultra-high vacuum environment ( $1.9 \times 10^{-9}$  mbar) using Al K $\alpha$  anode (1486.6 eV). Pass energy of 40 eV for survey scan and 30 eV for high resolution scan have been used during acquisition of the XPS spectra. Fourier transform infrared (FTIR) studies were performed with a Thermo-Nicolet continuum FTIR microscope. High-resolution scans were recorded for comprehending the chemical

environment of the constituent elements present at the surface. Each scan was repeated 3 times in order to reduce the signal to noise ratio. UV-visible spectral analyses were done by means of SPECTRASCAN UV 2600 digital spectrophotometer (Chemito, INDIA). The surface charge of the as-synthesized nanoparticles was recorded through zeta potential measurement (Zetasizer 4, Malvern Instruments, UK). The point zero charge was evaluated using Sytonics Digital pH Meter 335.  $^1\text{H}$  NMR spectra were obtained with a Bruker DPX-400 MHz NMR instrument. The BET analysis providing the  $\text{N}_2$  adsorption–desorption isotherm was recorded at 77 K using Autosorb-iQ (Quantachrome Instruments).

**Chemicals.** All the chemicals used were of AR grade. Double distilled water was used throughout all the experiments. Copper (II) acetate monohydrate  $[\text{Cu}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}]$ , glucose, ethylene glycol (EG), acetic acid, nitroarenes, sodium borohydride ( $\text{NaBH}_4$ ), 4-nitrophenol, 2-nitrophenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, nitrobenzene, sodium chloride ( $\text{NaCl}$ ), sodium nitrite ( $\text{NaNO}_2$ ), sodium nitrate ( $\text{NaNO}_3$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) and formic acid (FA) were purchased from Sigma-Aldrich. Sodium hydroxide ( $\text{NaOH}$ ) was purchased from E-Merck. Glass apparatus were cleaned with aqua regia, water and dried before use.

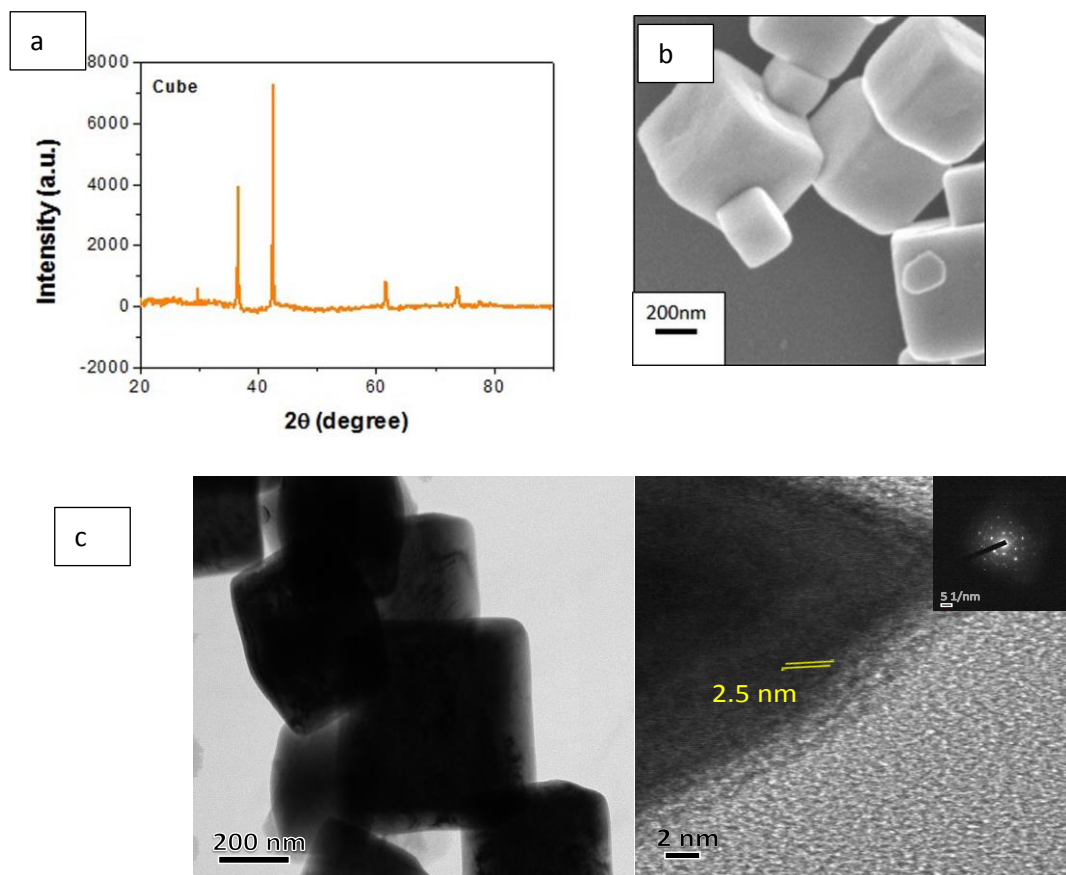


Figure S1. (a) XRD pattern and (b) FESEM image (c) TEM and HRTEM analysis of cubic  $\text{Cu}_2\text{O}$  nanoparticle.

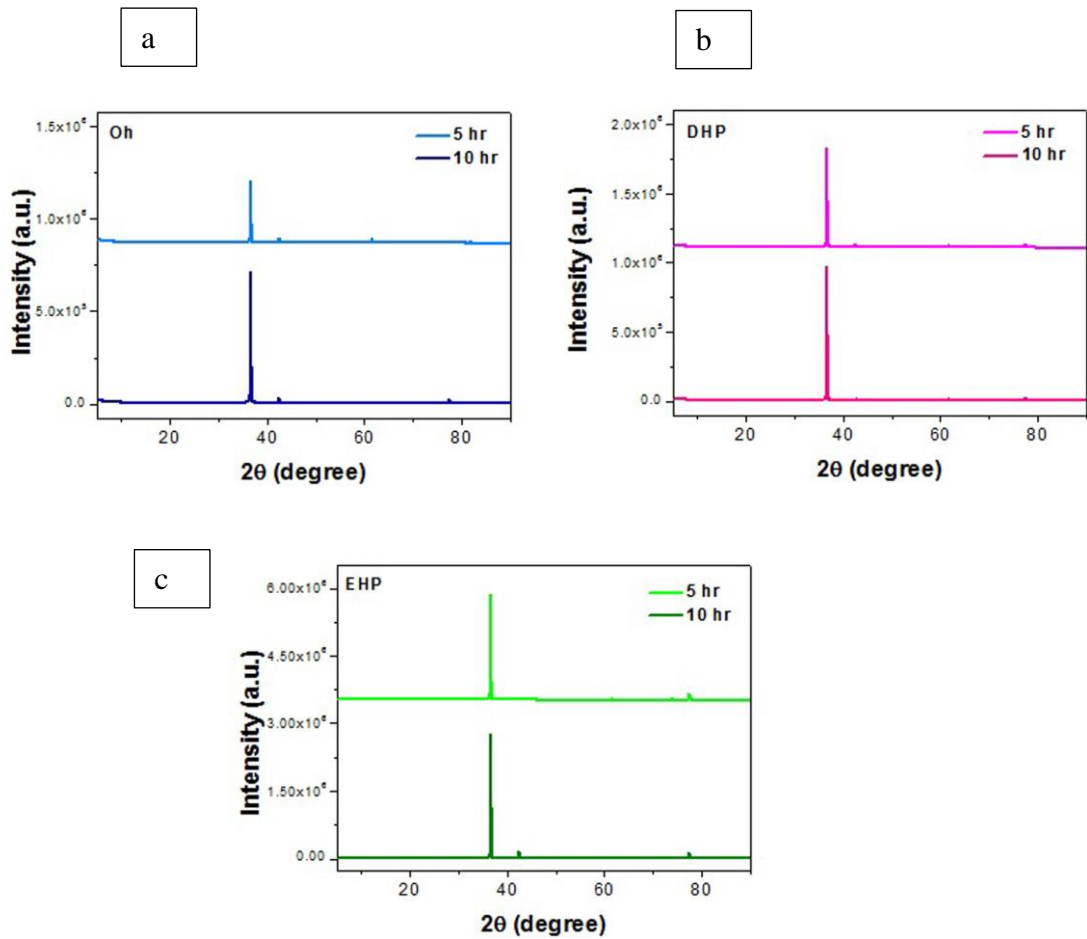
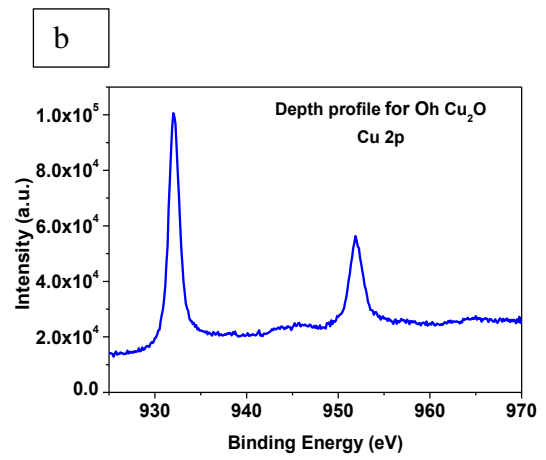
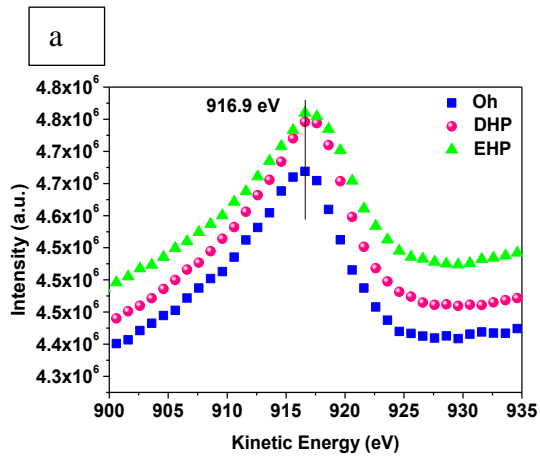


Figure S2. XRD of (a) Oh, (b) DHP and (c) EHP Cu<sub>2</sub>O in 5hr and 10hr of growth progress.



Figures S3. (a) The Auger spectral analysis of the as-synthesized Cu<sub>2</sub>O after surface cleaning. (b) Depth profile of Oh Cu<sub>2</sub>O nanocatalyst after surface sputtering for Cu 2p.

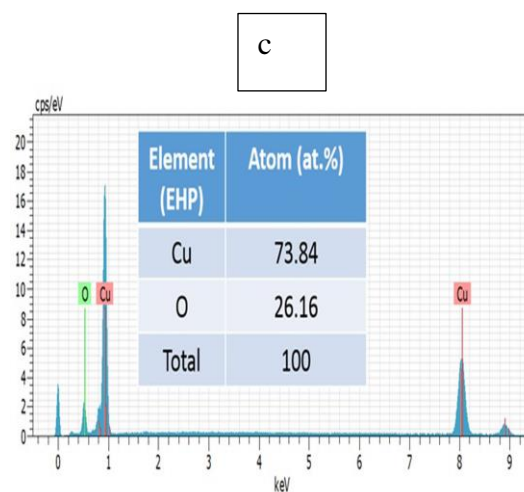
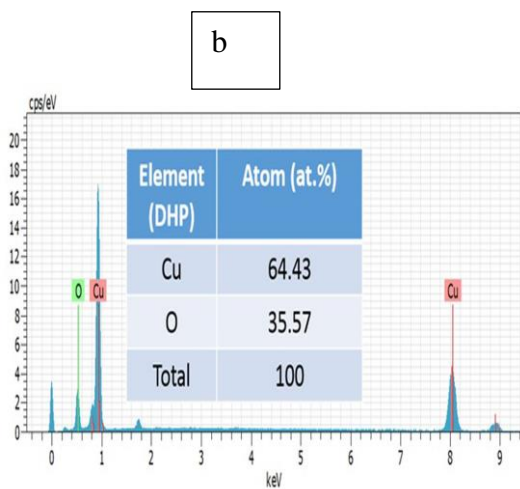
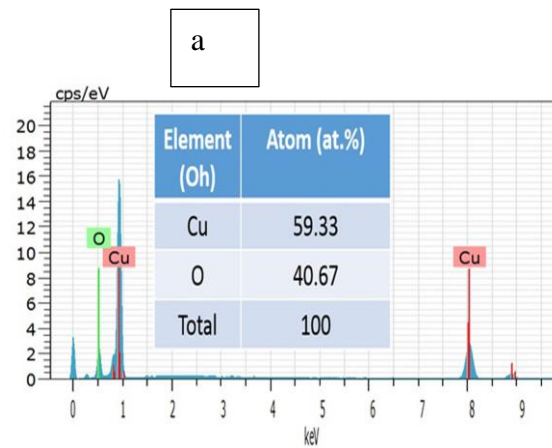
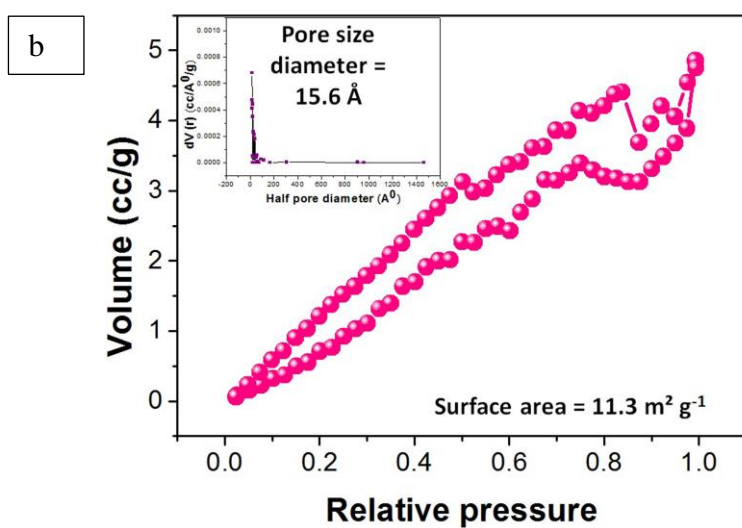
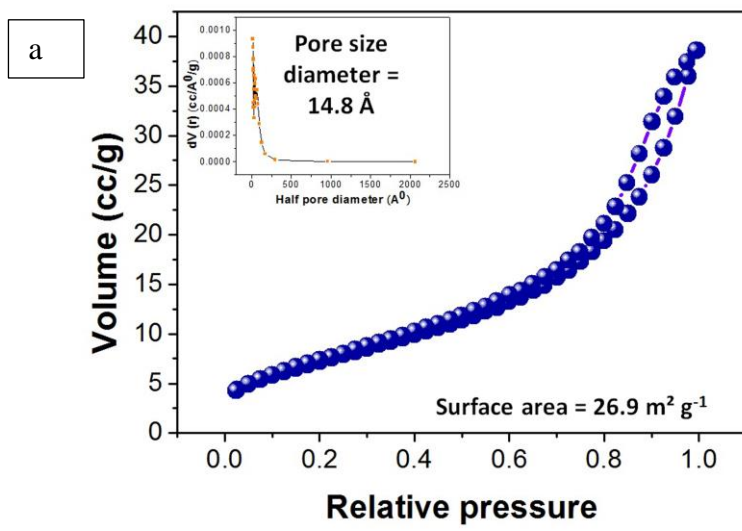


Figure S4. EDX Analysis for the as-prepared Cu<sub>2</sub>O nanocatalyst (a) Oh, (b) DHP and (c) EHP.



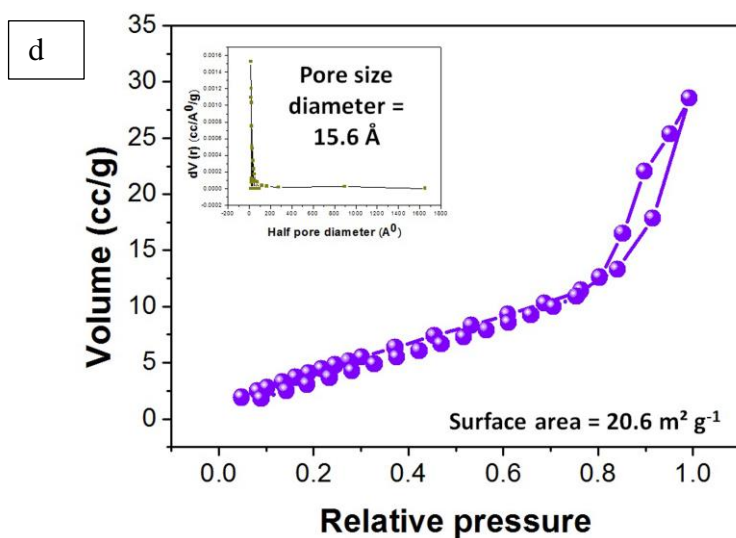
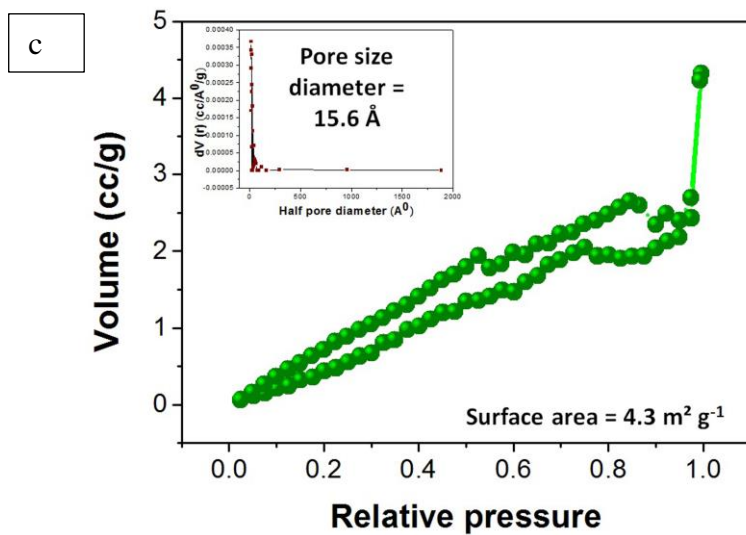


Figure S5. BET analysis for (a) Oh, (b) DHP, (c) EHP and (d) cube (inset: pore size diameter for respective morphology).

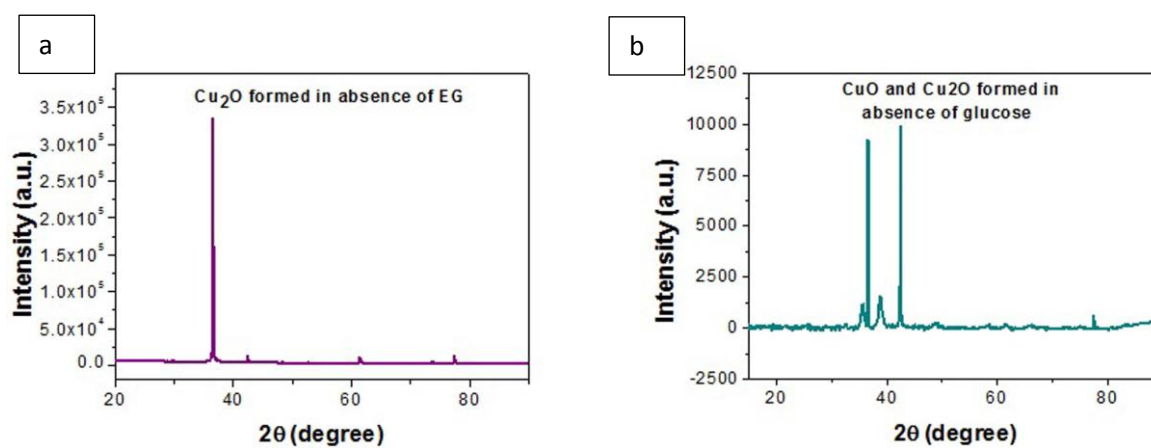


Figure S6. XRD pattern in presence of (a) only glucose without EG producing  $\text{Cu}_2\text{O}$  (JCPDS file no. 77-0199), (b) only EG without glucose producing  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  (JCPDS file no. 77-0199 and 80-1916).



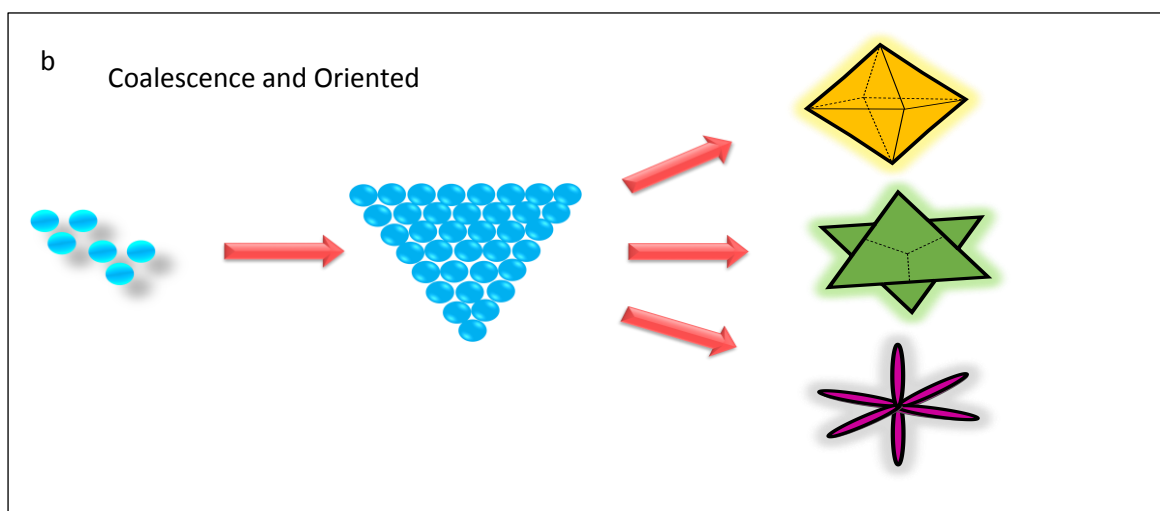
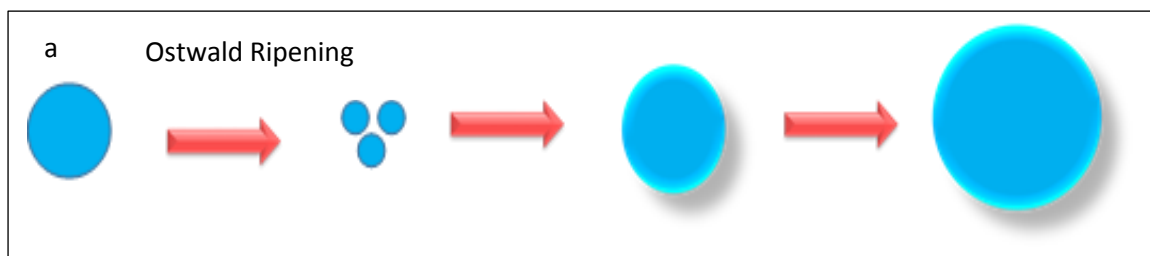


Figure S7. Pictorial representation of growth mechanism: (a) Ostwald ripening, (b) coalescence and oriented attachment.

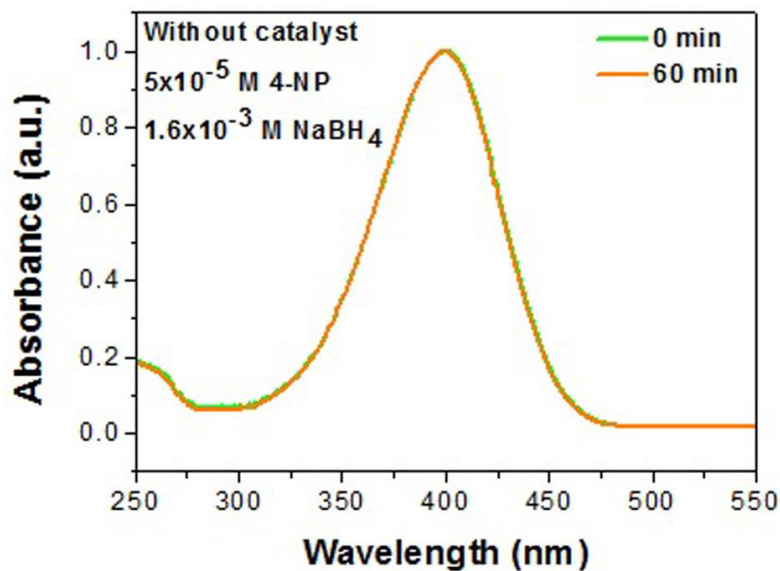


Figure S8. Absorption spectrum of 4-nitrophenol reduction reaction in absence of catalyst

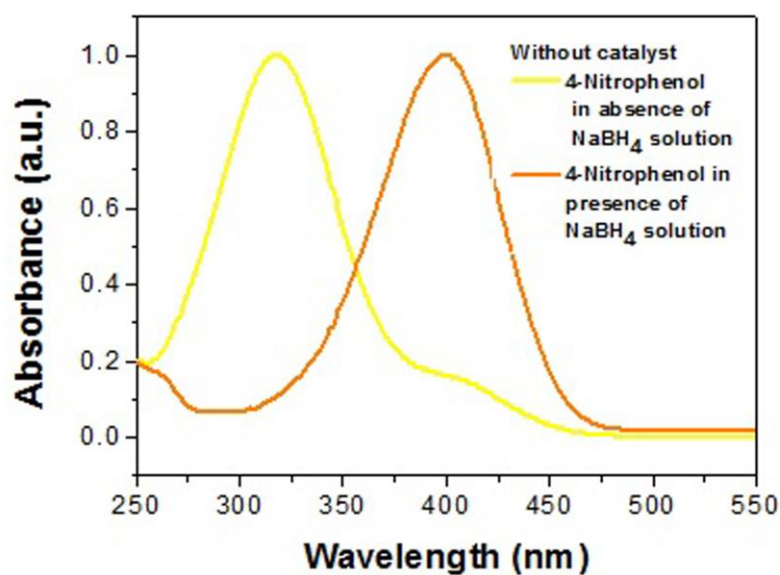


Figure S9. Absorption spectrum of 4-nitrophenol solution in presence and absence of  $\text{NaBH}_4$  solution.

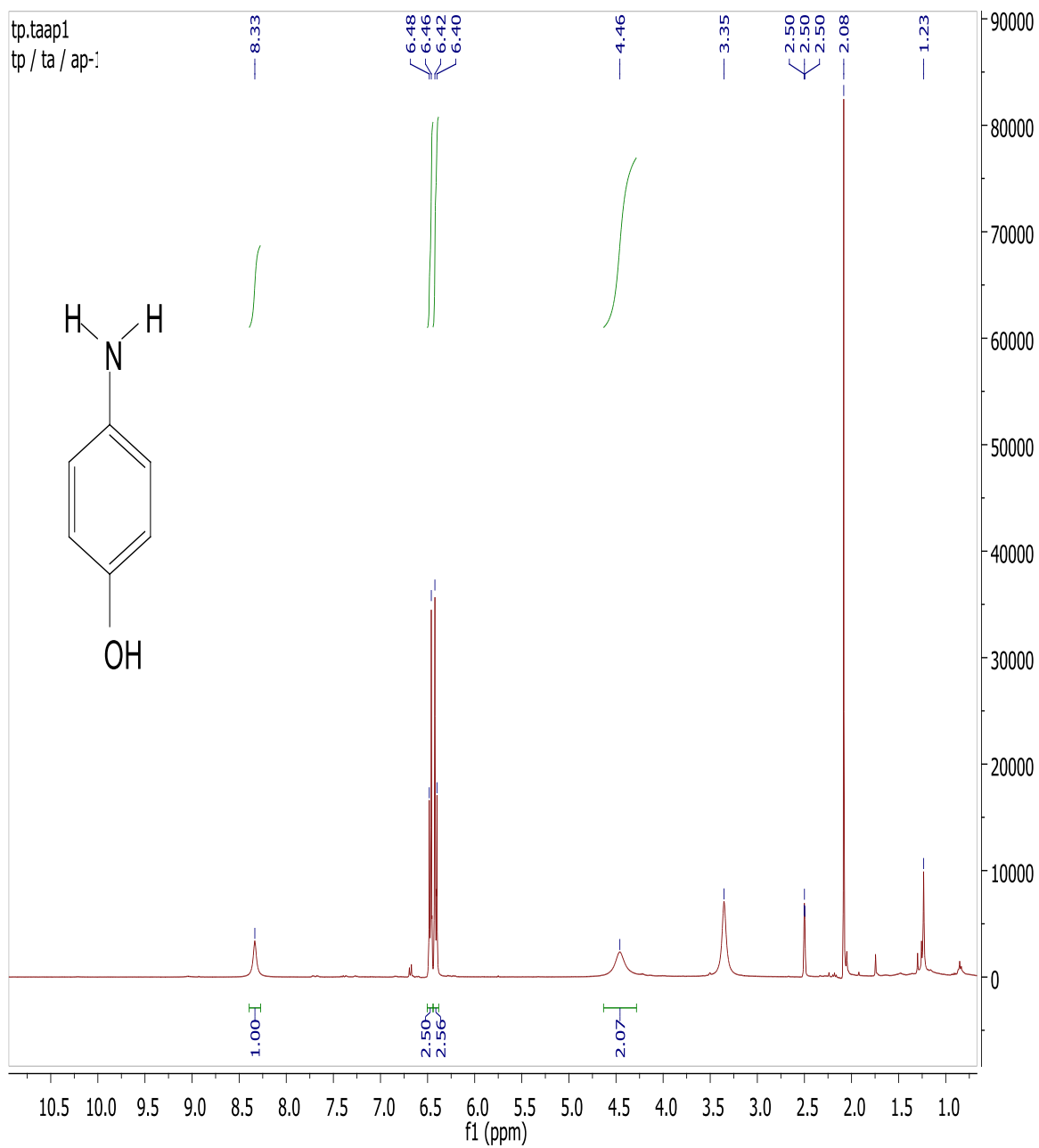


Figure S10. <sup>1</sup>H NMR data for product of catalysed 4-NP reduction. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz): δ 8.33 (s, 1H), 6.48-6.46 (d, 2H, J = 8 Hz), 6.42-6.40 (d, 2H, J = 8 Hz), 4.46 (s, 2H).

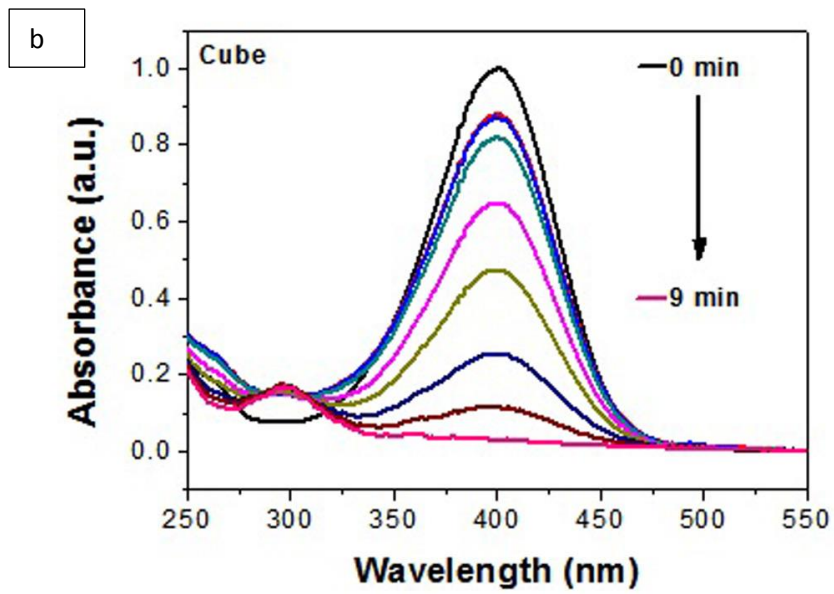
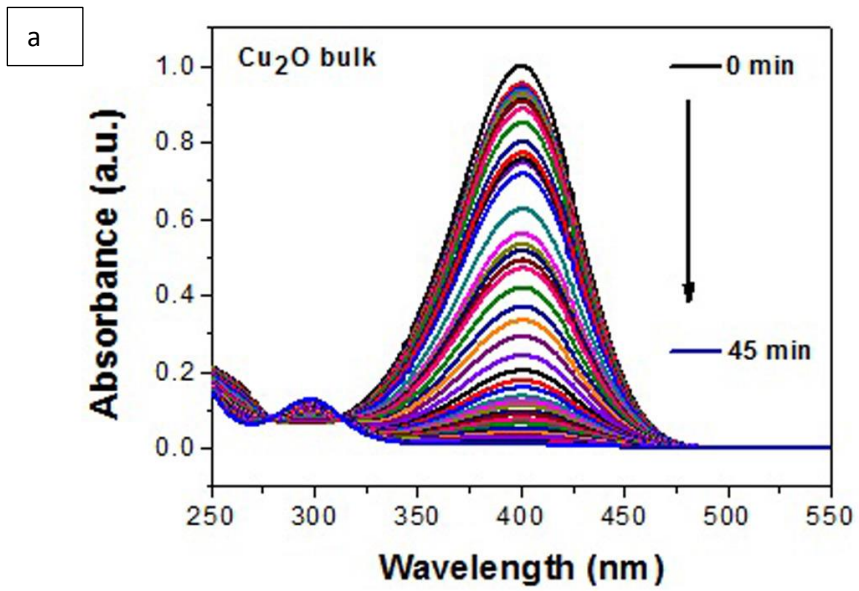


Figure S11. Absorption spectra of 4-nitrophenol reduction solution in presence of  $\text{NaBH}_4$  with (a) bulk  $\text{Cu}_2\text{O}$  and (b) cube  $\text{Cu}_2\text{O}$  having (100) facet.

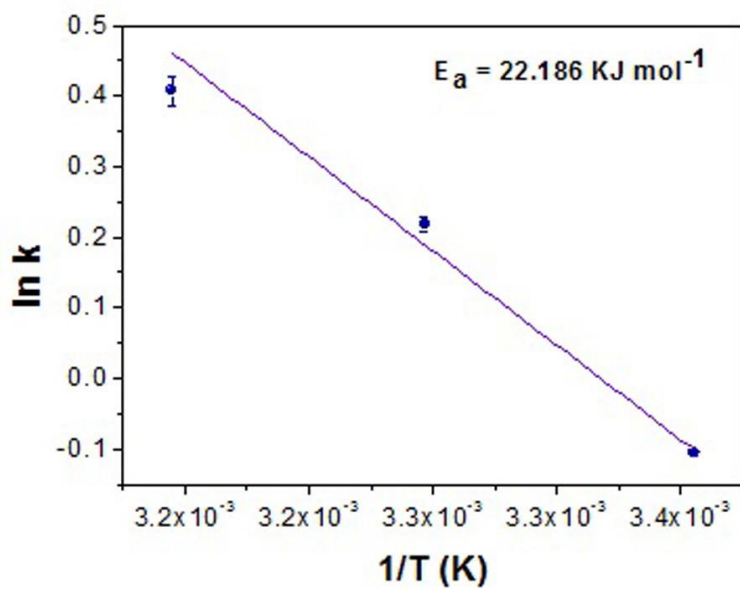


Figure S12. Activation energy of 4-nitrophenol reduction reaction with Oh  $\text{Cu}_2\text{O}$  nanocatalyst.

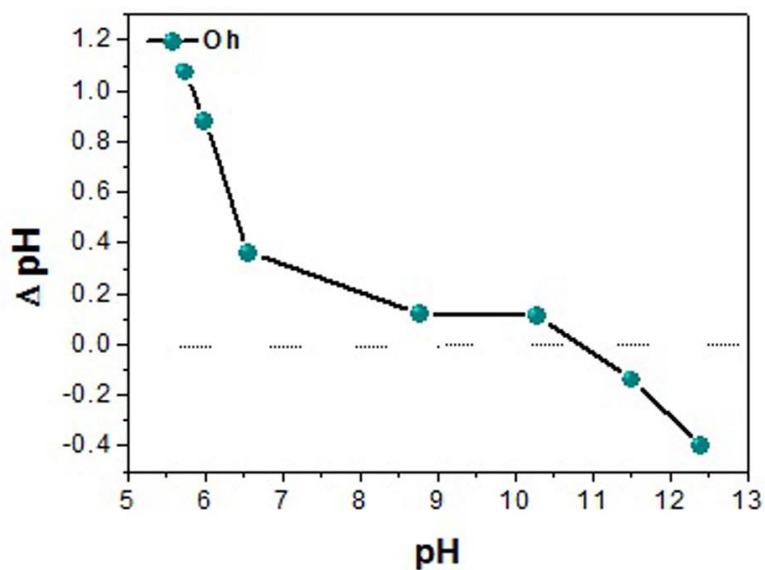


Figure S13. Point of Zero Charge (PZC) of Oh Cu<sub>2</sub>O nanocatalyst.

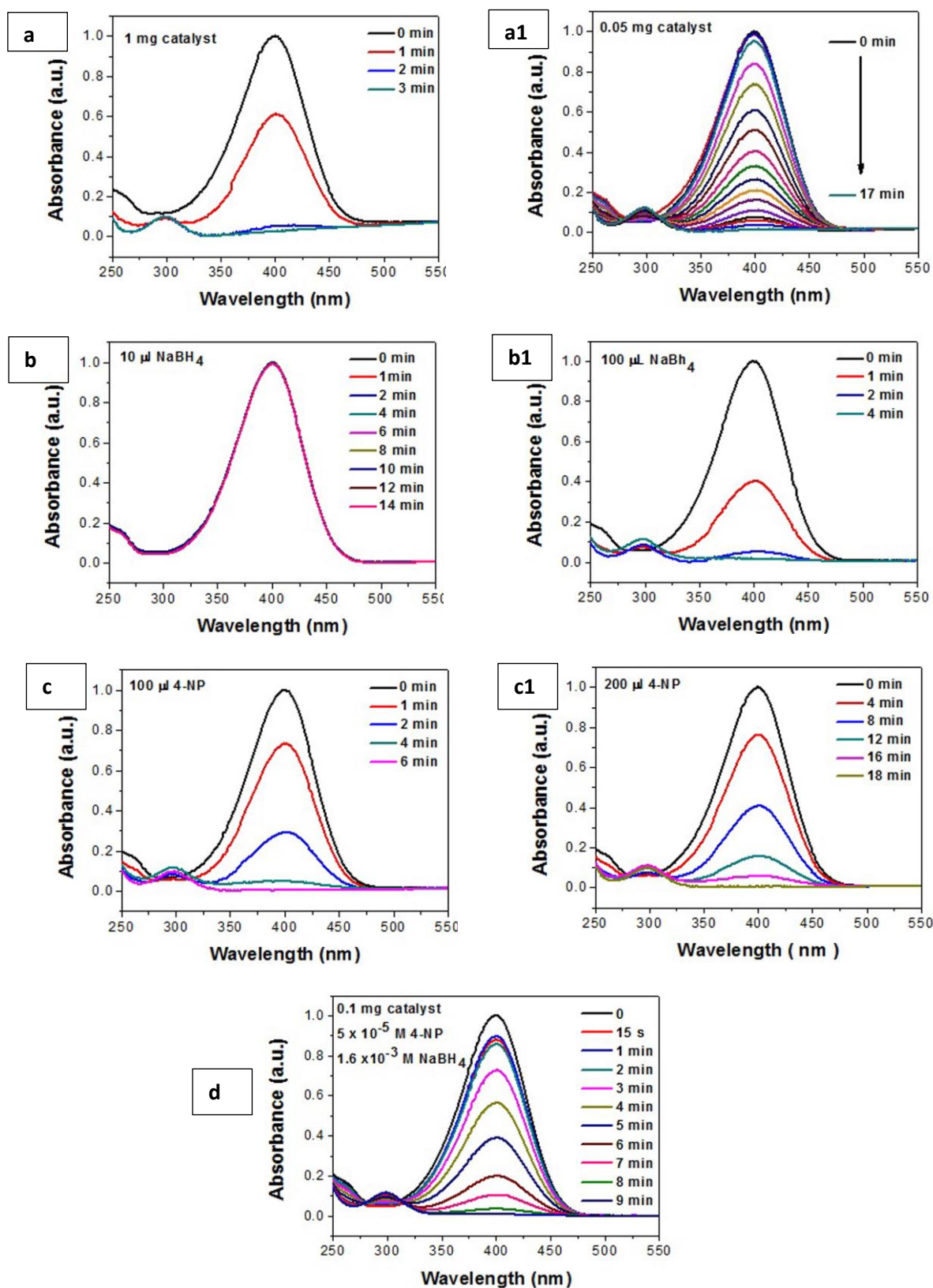


Figure S14. UV-visible absorption spectra of 4-nitrophenol reduction parameters. (a, a1) varying catalyst amount (b, b1) varying NaBH<sub>4</sub> concentration (c, c1) varying 4-NP concentration, (d) optimised reaction condition of 4-NP reduction.

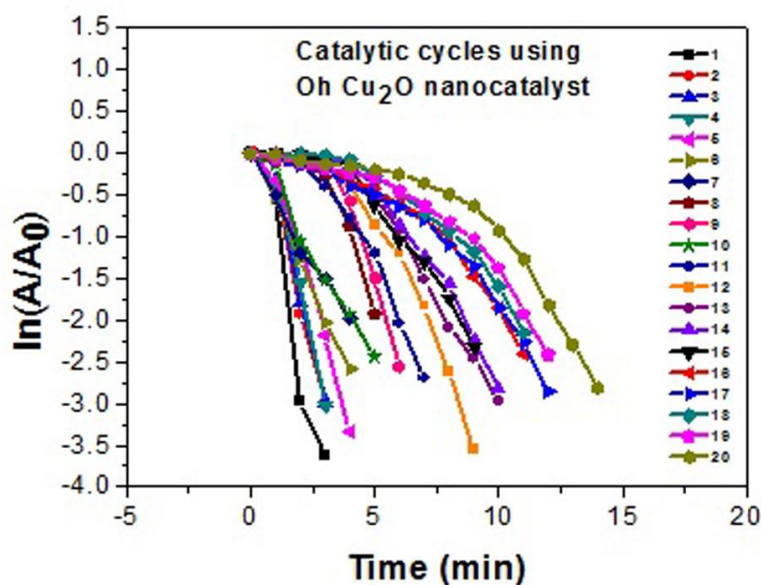


Figure S15. Ln(A/A<sub>0</sub>) vs time graph for 20 catalytic cycle of 4-nitrophenol reduction.

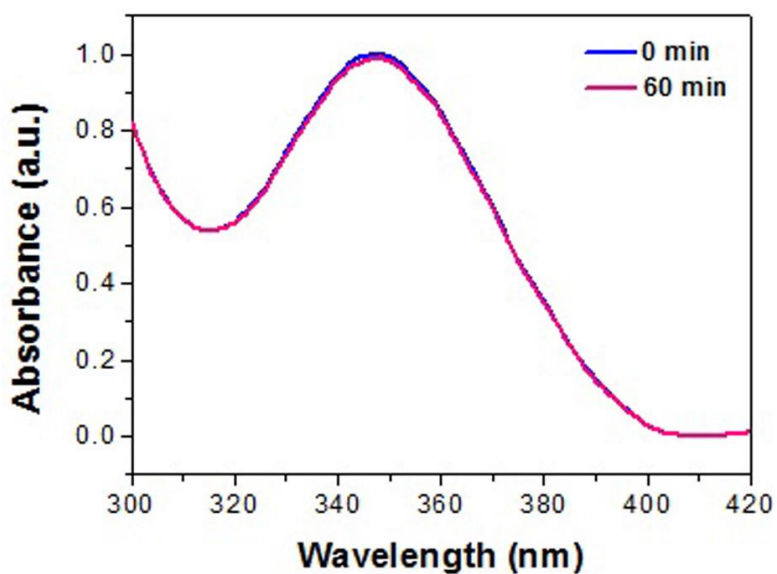


Figure S16. Absorption spectrum of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> reduction reaction in absence of catalyst.