

Electronic supplementary information for the title

Synthesis and catalytic applications of amine interacted $\text{Cu}_2(\text{OH})\text{PO}_4$ nano plates (Copper NPs) and tubes (Copper NTs)

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Synthesis of copper NPs and copper NTs

In a typical synthesis of copper hydroxy phosphate nano plates (Copper NPs) 240 ml aqueous solution of ammonium dihydrogen phosphate (3.915 g) is dropwise added to the 20 ml ethanol solution containing 3.36 g copper chloride with continuous stirring at room temperature. To the resultant mixture, an ethanol solution containing the mixture of 7.8 g dibutyl amine (DBA) and 15 g of hexadecyl amine (HDA) is slowly added at 323 K with constant stirring. The final synthetic mixture thus obtained is transferred into a Teflon layered autoclave for hydrothermal treatment at 383 K for 4 to 16 h period followed by cooling, filtration and through washings of the product using anhydrous ethanol and its drying at 313 K for 24 h. Similar procedure is adopted for the synthesis of copper hydroxy phosphate nano tubes (Copper NTs) but the concentration of HDA is decreased from 15 g to 1.5 g in this case.

Characterization

Powder X-ray diffraction patterns of the samples were recorded on D8 advance, Bruker, Germany equipped with rotating anode and CuK α radiations. SEM images were recorded for obtaining particle morphology on Quanta 200f instrument, Netherland. The IR spectra of the both samples were recorded on Thermo Nicolet 8700 instrument, Thermo scientific Corporation, USA. The reaction products are analysed by using GC equipped with the DB wax column and FID detector. TEM images were recorded on Tecnai-12 model, FEI, Netherland.

Reaction

The oxidation reaction was carried out in round bottom flask at reflux condition with constant cold water flow and constant stirring. In a typical reaction study, 0.8 g cyclohexane, 2 ml acetonitrile, 50mg catalyst are taken in round bottom flask followed by the addition of 1.7 g 50% H_2O_2 in dropwise manner. The temperature then increased up to 343K and this temperature was maintained for 4h. The reaction mass then cooled out and product was collected by filtration and analysed by GC. Performance of the catalyst after three reaction cycles was also evaluated where the catalyst was separated by filtration and dried at 373 K, the reaction is conducted in above same manner.

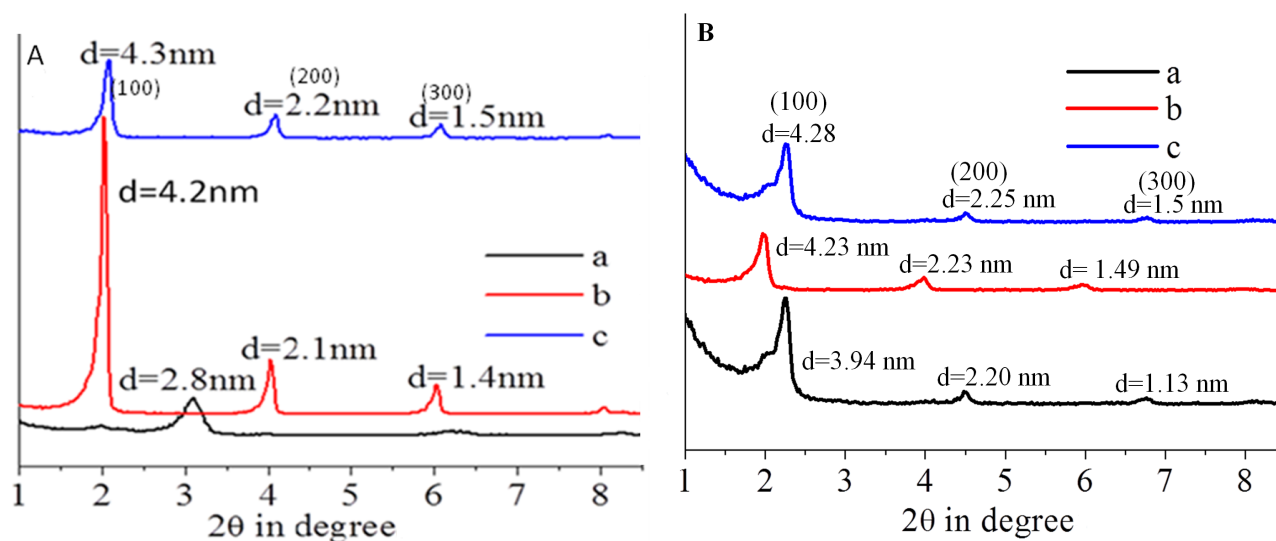


Fig. S1 Low angle XRD of A) Copper NPs and B) Copper NTs where a,b,c are the samples synthesized at crystallization time of 4h, 9h and 16h respectively.

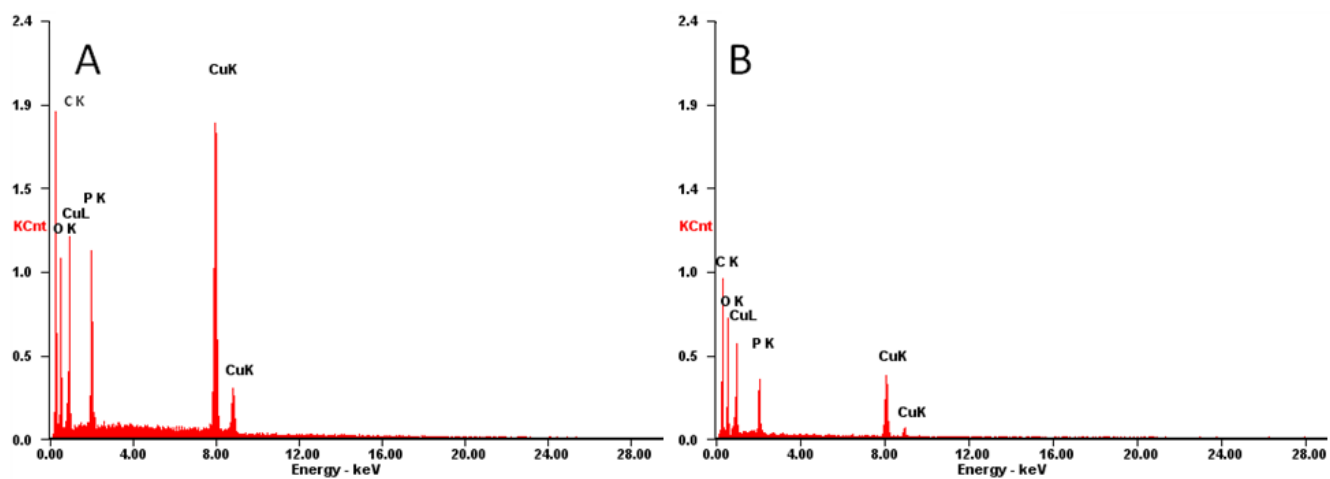


Fig. S2 EDX spectra of A) Copper NPs and B) Copper NTs synthesized at 16 h crystallization time.

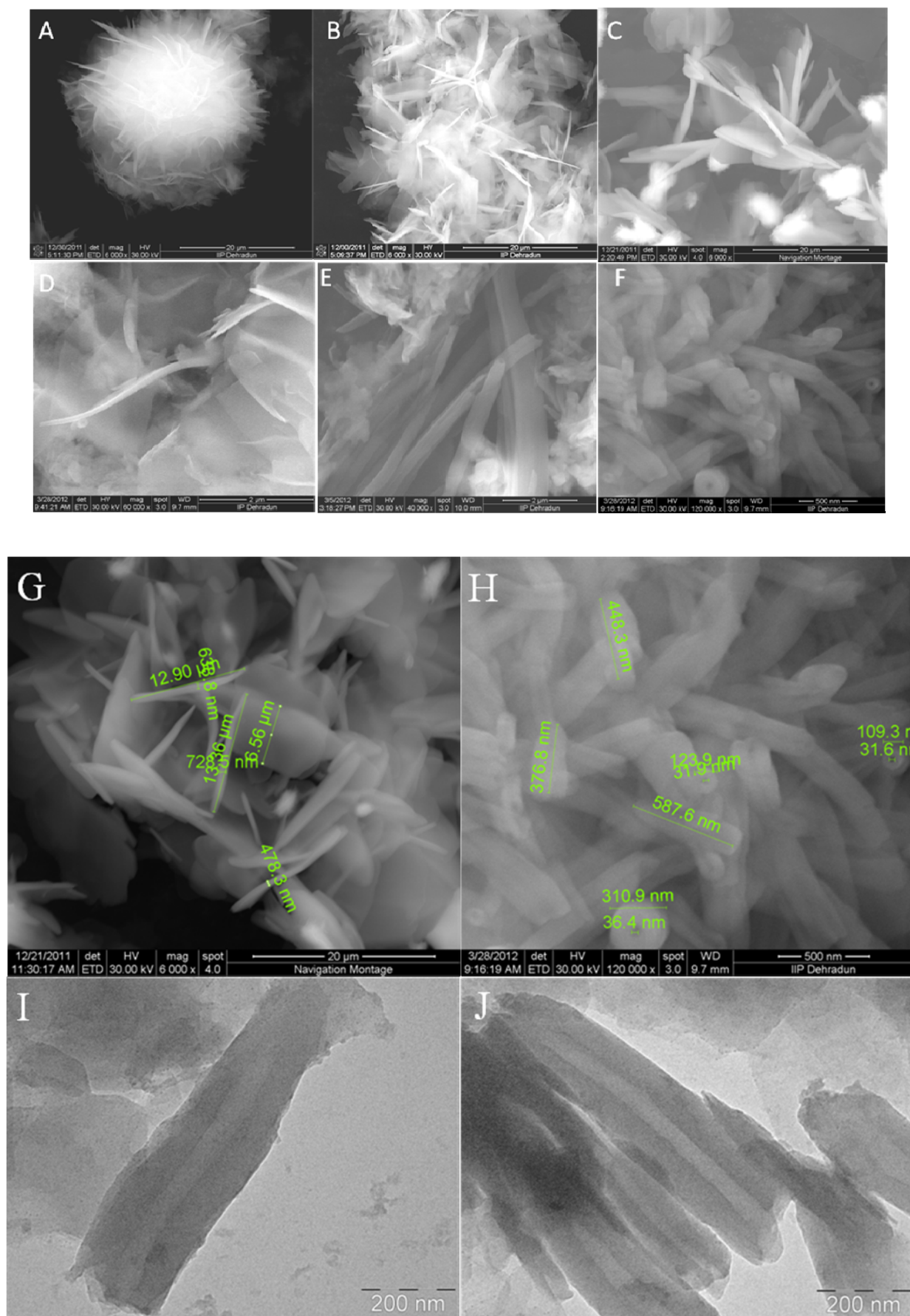


Fig. S3 SEM images of Copper NPs (A, B, C) and Copper NTs (D, E, F) obtained at different crystallization times of 4h, 9h and 16 h respectively. G and H are the SEM images of copper NPs and copper NTs at 16 h, I and J are the TEM images of copper NTs at 16 h

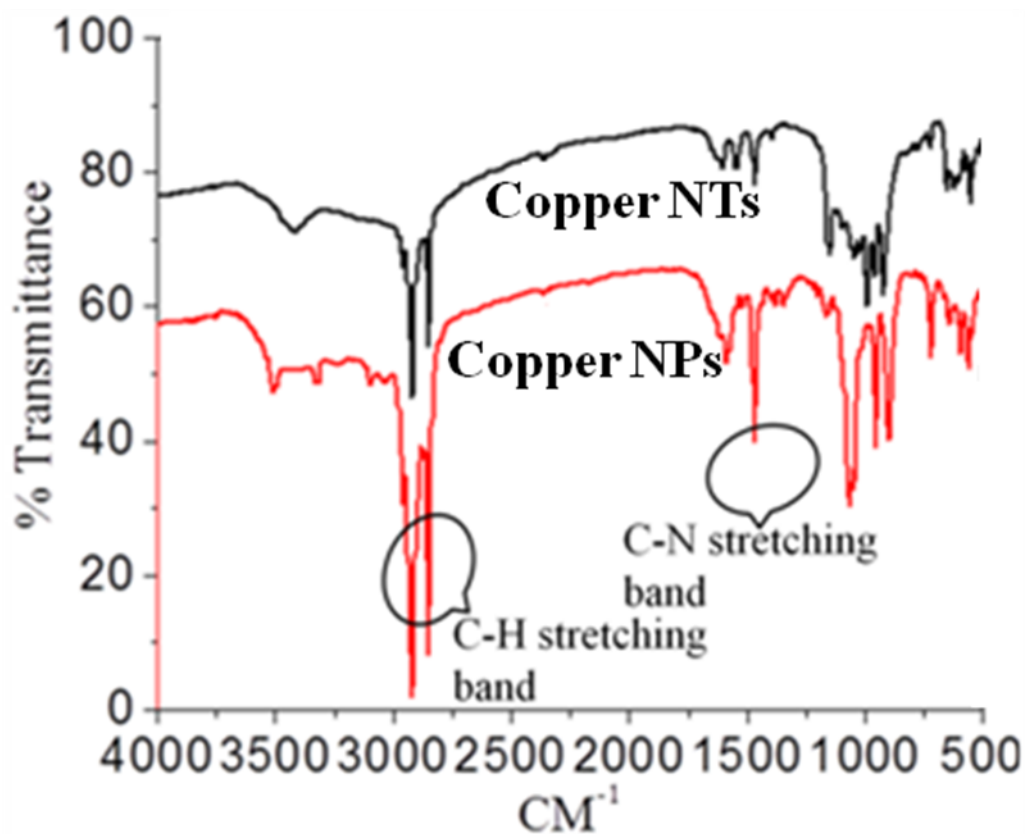


Fig. S4 IR spectra of Copper NPs and Copper NTs.

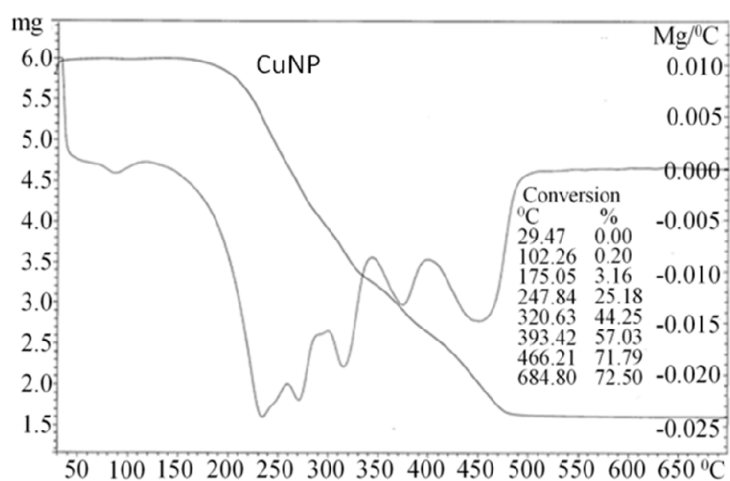


Fig. S5 DT/TGA spectra of Copper NPs.

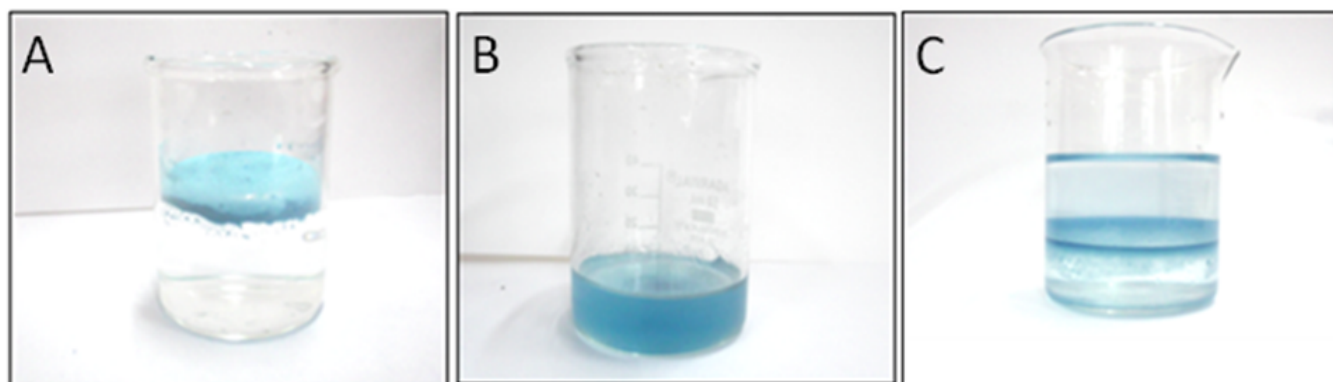


Fig. S6 Surfactant properties of Copper NPs; A) Copper NPs floating on water, B) Copper NPs dispersed in toluene, C) Copper NPs forming intermediate layer between water and toluene layers of the water-toluene mixture.