Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of monodisperse copper nanoparticles using a modified digestive ripening technique and formation of superlattices

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1. Experiments

1.1. Materials required

Copper chloride dihydrate ($CuCl_2.\ 2H_2O$), Dodecanethiol (DDT) were purchased from SD Fine Chemicals, India. Ethanol (AR 99.9%) was received from Jiangsu Huaxi International, China. Sodium borohydride, toluene, 1-butanol and Tween 80 were obtained from Merck, India. Tetraoctylammonium bromide (TOAB) was purchased from Sigma Aldrich, USA. All the chemicals were used as received without any purification step.

1.2. Deoxygenation of solvents

All the solvents used in the experiment were deoxygenated with inert gas (N_2/Ar) for 30 min prior to synthesis to reduce the dissolved oxygen present in the solvents.

1.3. Synthesis of copper nanoparticles in organic phase

Copper nanoparticles in toluene phase was synthesized by modifying the Brust's method. Initially, 30 ml 25 mM $CuCl_2.2H_2O$ aqueous solution was mixed together with 30 ml of 25 mM tetraoctylammonium bromide (TOAB) in toluene and 0.1 ml of dodecanethiol (DDT) followed by stitirring for 20 min. After stirring, 10 ml of 80 mM sodium borohydride ($NaBH_4$) solution was added dropwise to the above two phase mixture and stirred for 2 hours under inert gas environment. After 2 hours, the stirring stopped and the reddish brown organic phase was separated which contains the polydisperse copper nanoparticles.

1.4. Synthesis of monodispersed copper nanoparticles by digestive ripening process

3 ml of polydisperse colloid was taken into 50 ml conical flask and 0.1 ml of fresh dodecanethiol was added to it. Next, this colloid was refluxed at 110 ^oC for 24 h after which uniform monodisperse copper nanoparticles are formed.

2.7. Characterization

The absorption spectra of copper nanoparticles was measured using UV-Vis spectrophotometer (Shimadzu UV-1800). The size and shape of copper nanoparticles was investigated by Transmission Electron Microscope (Tecnai G2 20S Twin) with an accelerating voltage of 200 KV and Scanning Electron Microscope (MERLIN). The phase purity of copper nanostructures was studied using X-ray Diffraction (XPERT PRO). The d-spacing and electron diffraction patterns of copper nanostructures was investigated using High Resolution Transmission Electron Microscope (JEOL). Size distribution was generated using Image-J software. Although automated thresholding (~54%) and bandpass filters (filtered lage structures down to 20 pixels and small structures upto 3 pixels) have been used in most cases, manual intervension was necessary in many cases, specially when overlapping particles were observed.

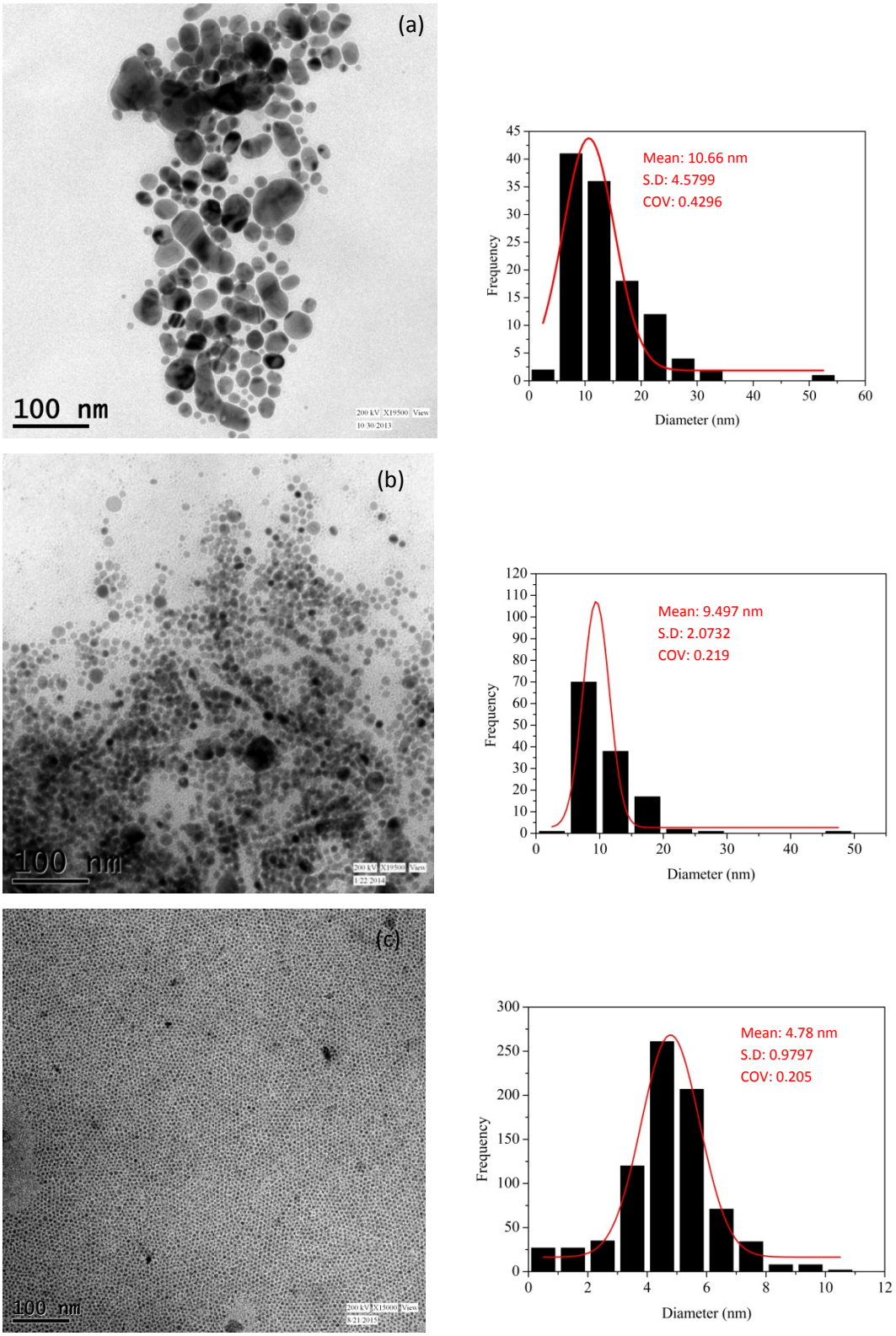

Fig. S1 Representative TEM images and particle size distribution histograms of copper nanoparticles digestive ripened for (a) 3 h (b) 6 h and (c) 15 h.

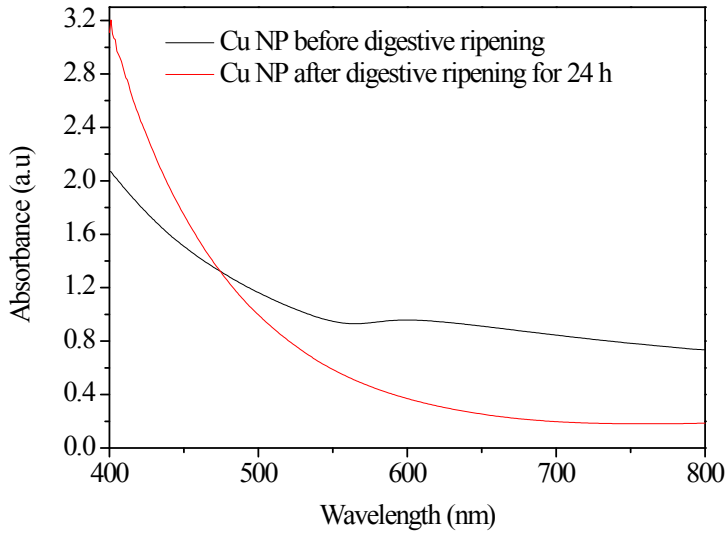

Fig. S2 UV-Vis of copper nanoparticles before and after digestive ripening process.

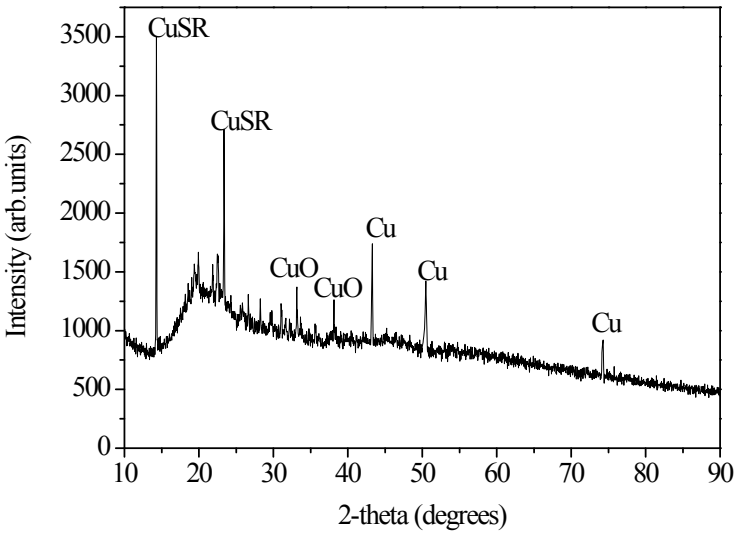

Fig. S3 XRD of digestive ripened sample.

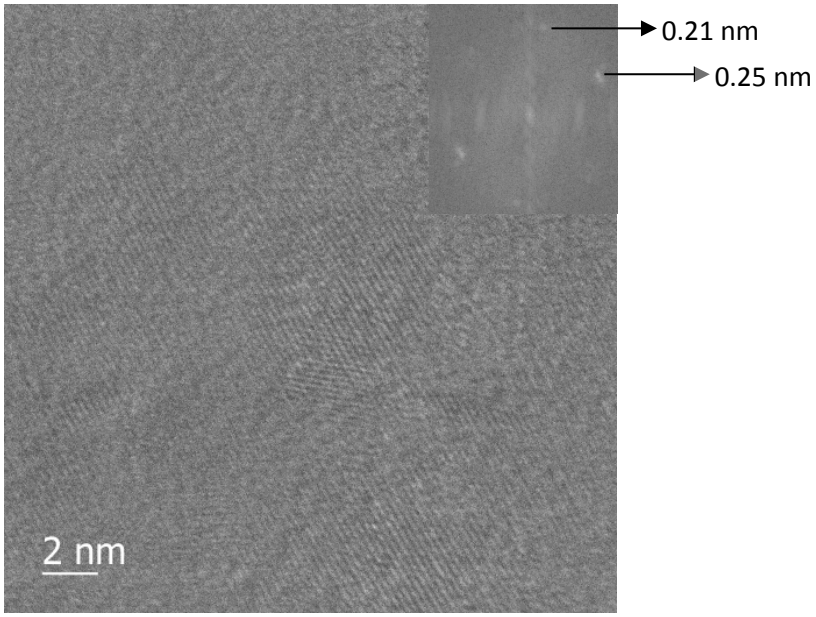

Fig. S4 HRTEM image of digestive ripened copper nanoparticles.

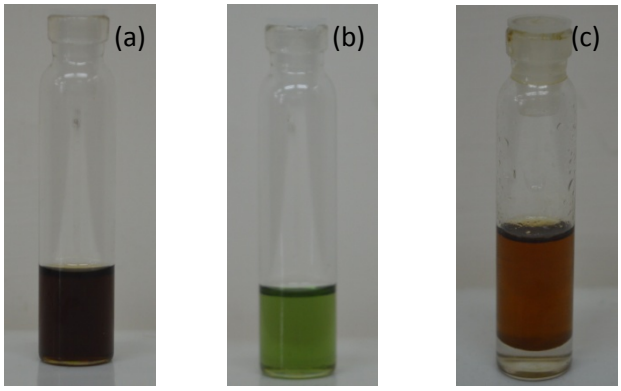

Fig. S5 Digital photo images of (a) as prepared digestive ripened sample and (b) digestive ripened sample after storing for more than a month and (c) after adding sodium borohydride to the green colloid and shaking for 2 minutes.

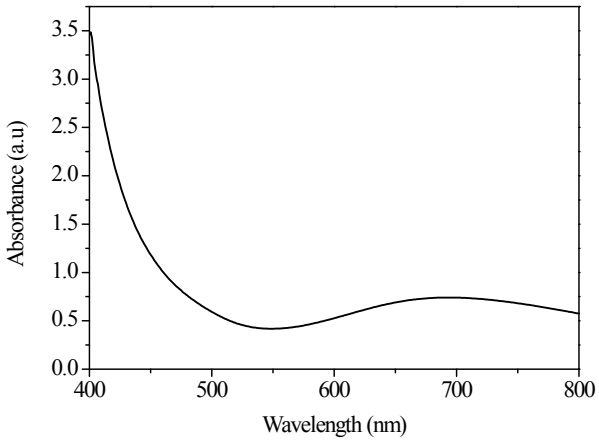

Fig. S6 UV-Vis of digestive ripened copper nanoparticles after storing without proper sealing for more than a month.

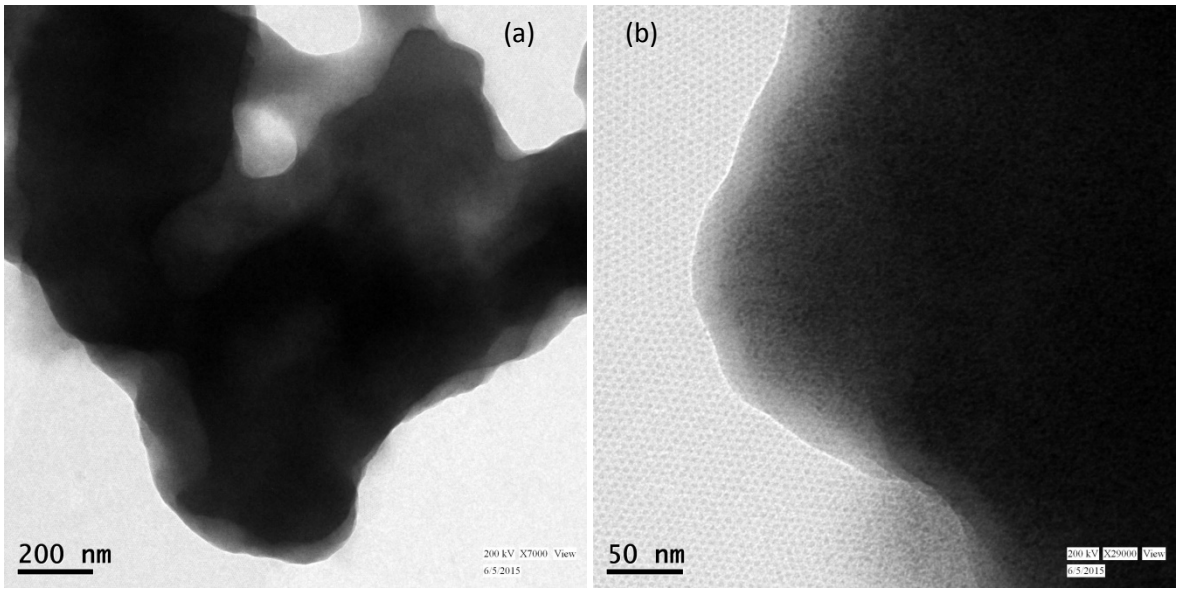

Fig. S7 TEM images of copper nanoparticles stored in emulsion at 5 ^{o}C for 10 days (a and b) at different magnifications.

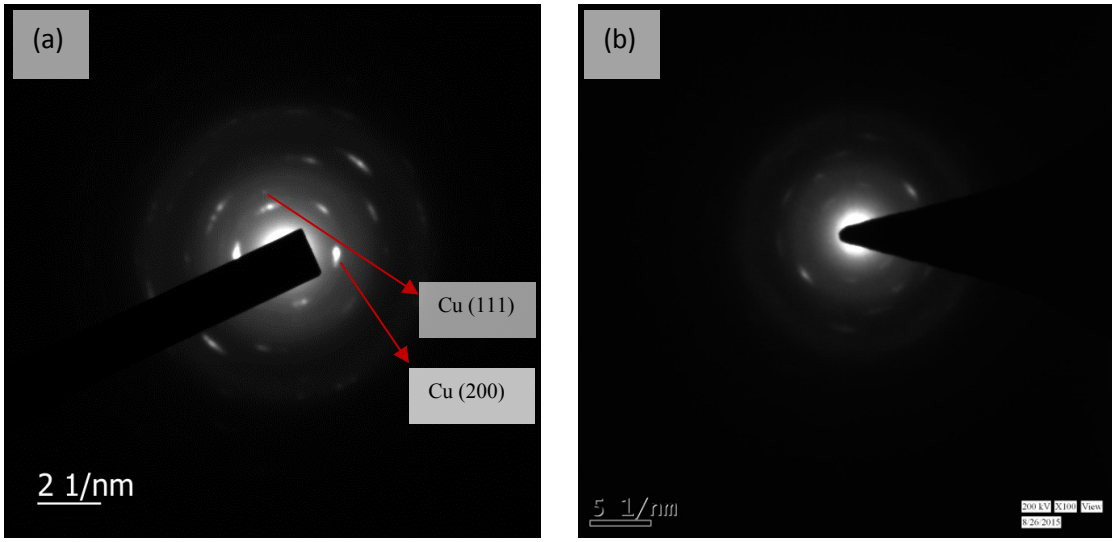

Fig. S8 Electron diffraction pattern of (a) 2D and (b) 3D superlattices of copper nanoparticles.

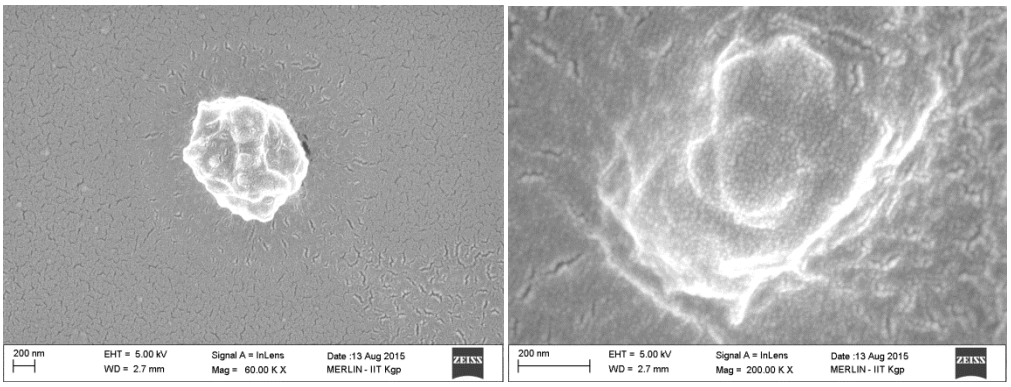

Fig. S9 SEM images of copper nanoparticles stored in emulsion at -4 ^{o}C for 10 days.