Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information for:

Metal Dication Cross-Linked Polymer Network Colloids as an Approach to Form and Stabilize Unusually Small Metal Nanoparticles

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Contents:

Experiments:

All materials were purchased from Sigma-Aldrich (Milwaukee, WI) and used as received. An example of hydrazine reduction of Cu^{+2} precursor was prepared as following: aqueous stock solutions of $Cu(BF_4)_2$ (0.05 M) and NaPA (0.002 M) were prepared before mixed. While being monitored in UV-vis spectroscopy, an aliquot amount of $Cu(BF_4)_2$ solution was slowly titrated into a vial in which contained the NaPA solution until the baseline shift of absorbance occurred. Then, $Cu(BF_4)_2$ solution was added into the vial at a rate 0.01 mL/s before desired concentrations of Cu^{+2} and NaPA were reached. The vial was then sealed and bubbled with N_2 gas for 15 minutes before a fresh-made hydrazine solution (1.0 M) was injected into the vial dropwisely. It is noted that the initial molar ratio between Cu^{+2} and N_2H_4 was at a fixed value of 1:5 for all reductions. The entire process of reduction was carried under ambient room temperature and monitored by UV-vis spectroscopy. After 90 minutes of mild stirring, the reactions was then quenched by ice-water bath before further dilution for depositing onto TEM grids.

Analytical techniques:

Shimadzu UV-1800 spectrometer was used to record the UV-vis spectra. Transmission Electron Microscopy (TEM) images were taken from a JEOL JEM-1400 TEM machine. Diameters and zeta-potential analysis of metal and colloidal Cu^{+2}/NaPA particles were accomplished by using a Malvern ZetaSizer Nano ZEN 5600.

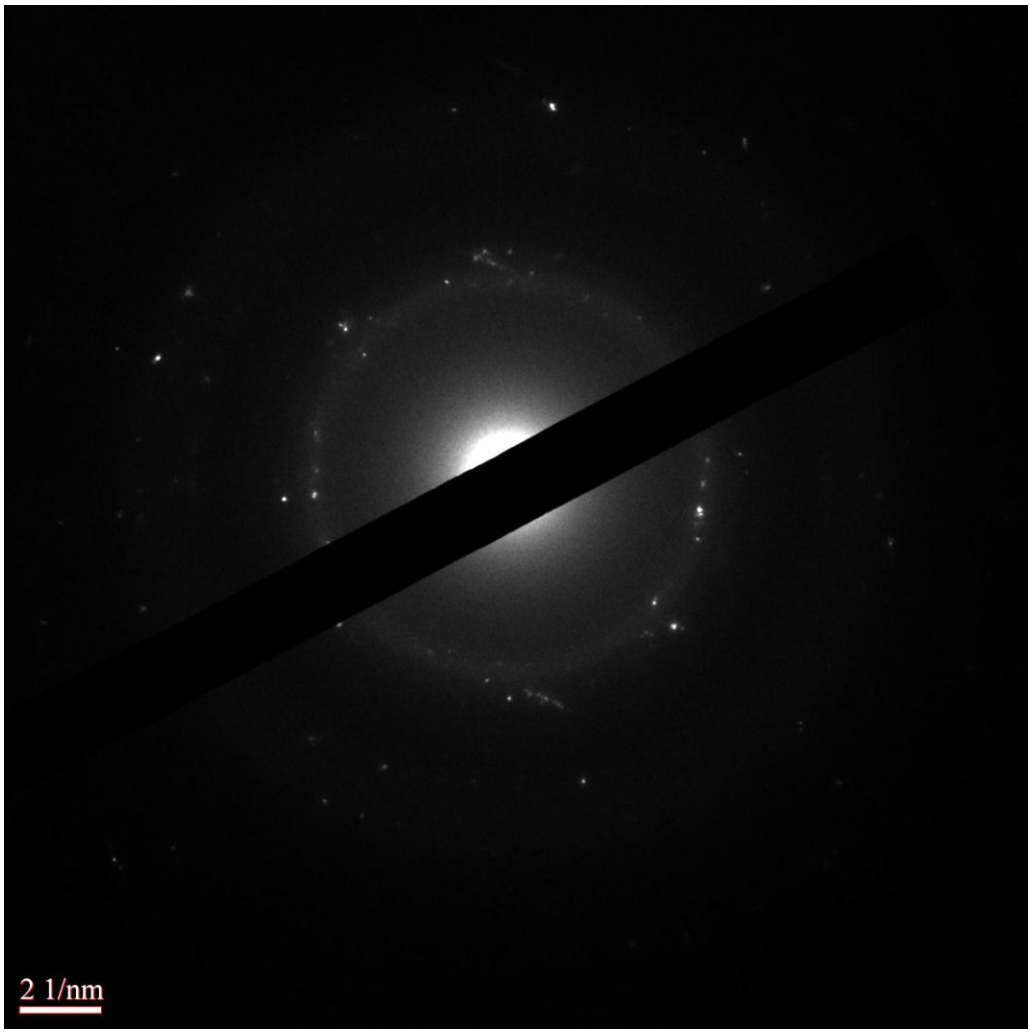

Figure S1. Electron diffraction image of the sample copper nanoparticles made in Figure S1. A featured ring for Cu lattice (1, 1, 1) with a diameter of 9.6 nm^{-1} was shown along with noise signals possibly attributed to residual polymer and $NaBF_4$ salts.

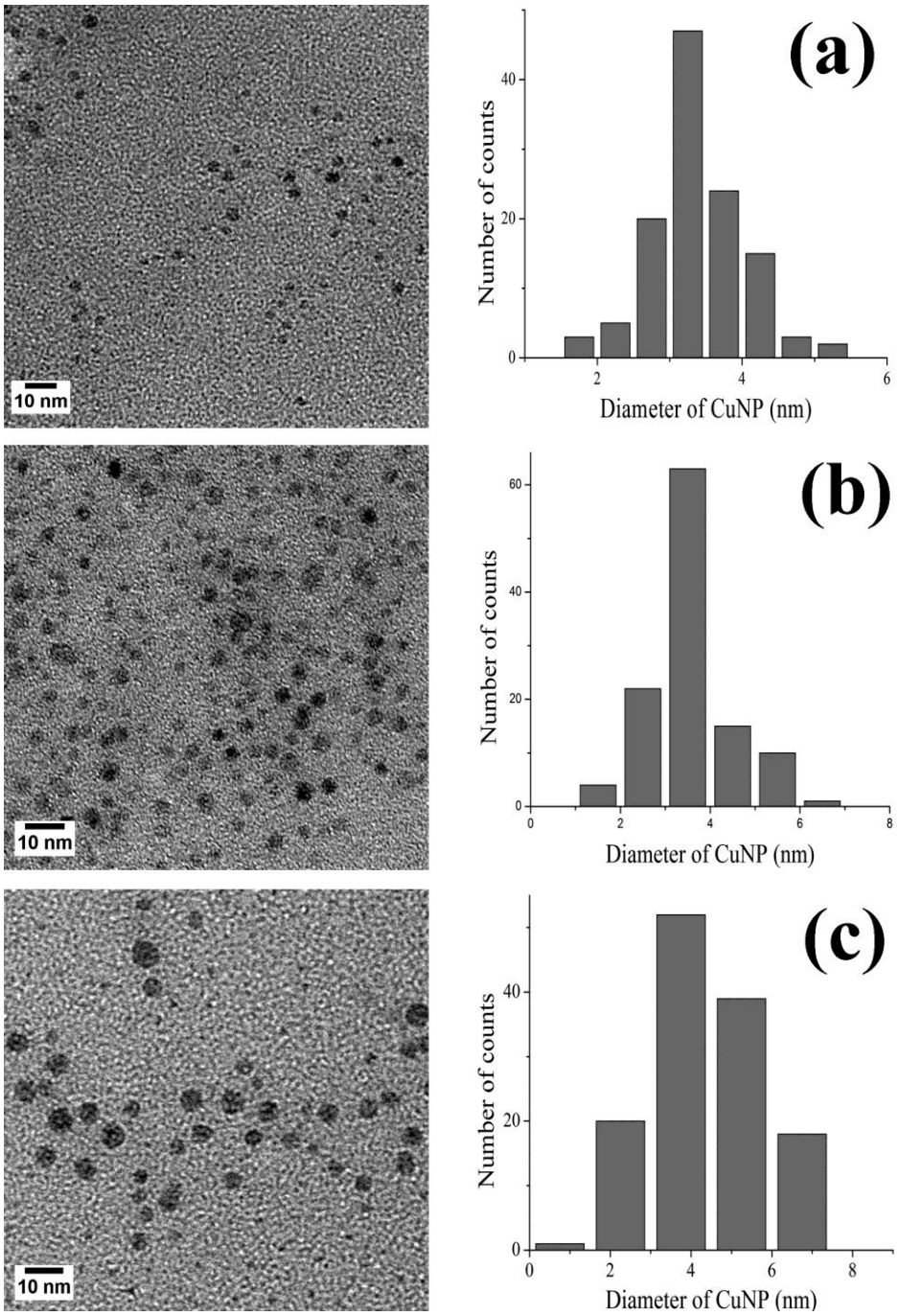

Figure S2. Reduction of $Cu(BF_4)_2$ in the presence of sodium poly acrylate (M_w = 15,000) at the initial pH = 4.8 and (a) $[Cu(BF_4)_2]_i = 2.2 \times 10^{-2}$ M, $[Na\text{-}Pa]_i = 1.2 \times 10^{-3}$ M; (b) $[Cu(BF_4)_2]_i = 2.2 \times 10^{-2}$ M, $[Na\text{-}Pa]_i = 1.0 \times 10^{-3}$ M; (c) $[Cu(BF_4)_2]_i = 2.2 \times 10^{-2}$ M, $[Na\text{-}Pa]_i = 7.3 \times 10^{-4}$ M, before 0.3mL hydrazine solution (1.0 M) was added. The diameters of CuNP were (a)3.4±0.6 nm, (b)3.8±1.0 nm and (c)4.3±1.4nm.

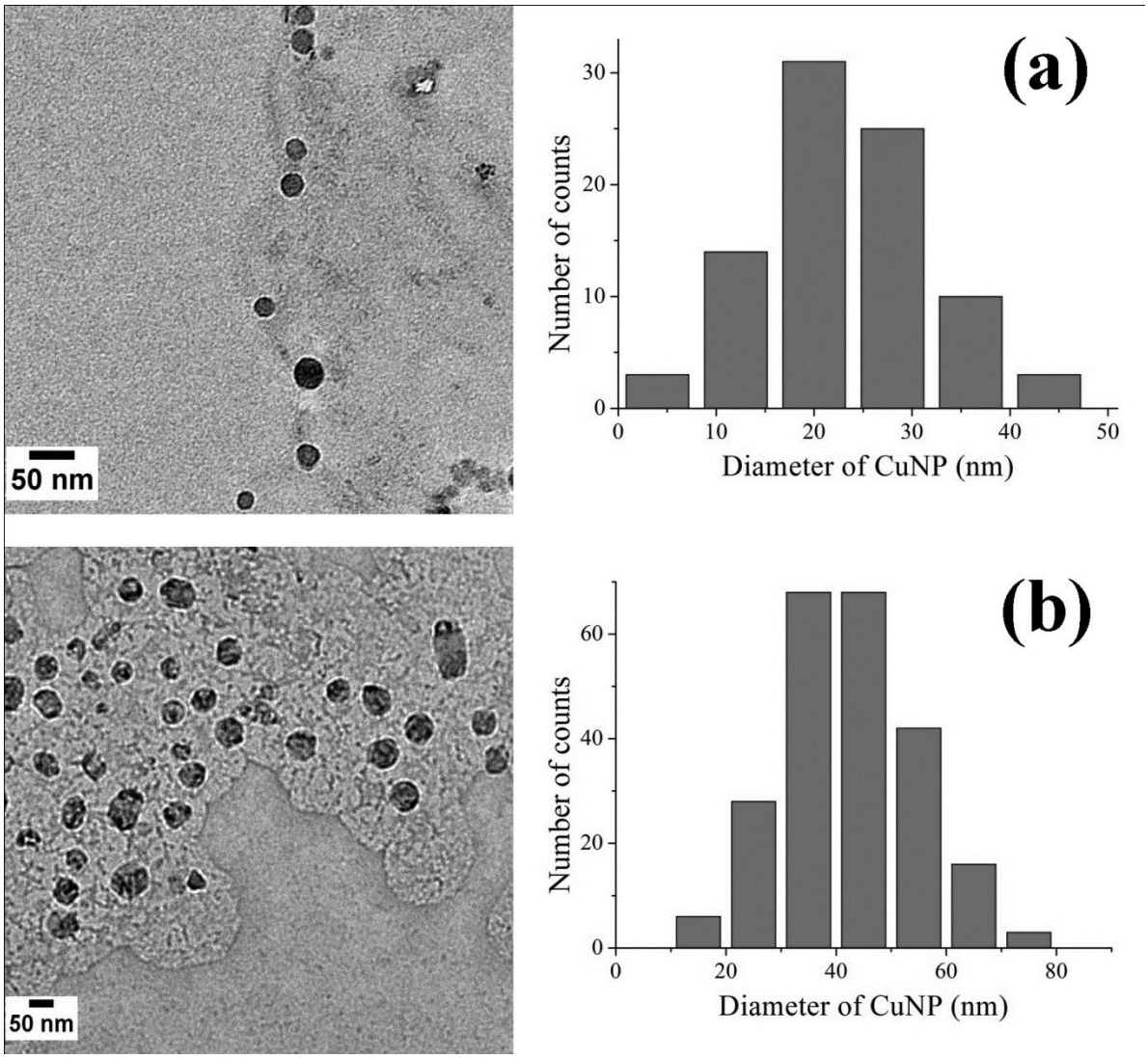

Figure S3: Reduction of $Cu(BF_4)_2$ in the presence of sodium polyacrylate (M_w = 15,000) at the initial pH = 4.8 and (a) $[Cu(BF_4)_2]_i = 2.2 \times 10^{-2}$ M, $[Na\text{-}Pa]_i = 2.5 \times 10^{-3}$ M; (b) $[Cu(BF_4)_2]_i = 2.2 \times 10^{-2}$ M, $[Na\text{-}Pa]_i = 6.1 \times 10^{-3}$ M. The diameters of CuNP were (a) 23±8.0nm and (b) 42±12nm.

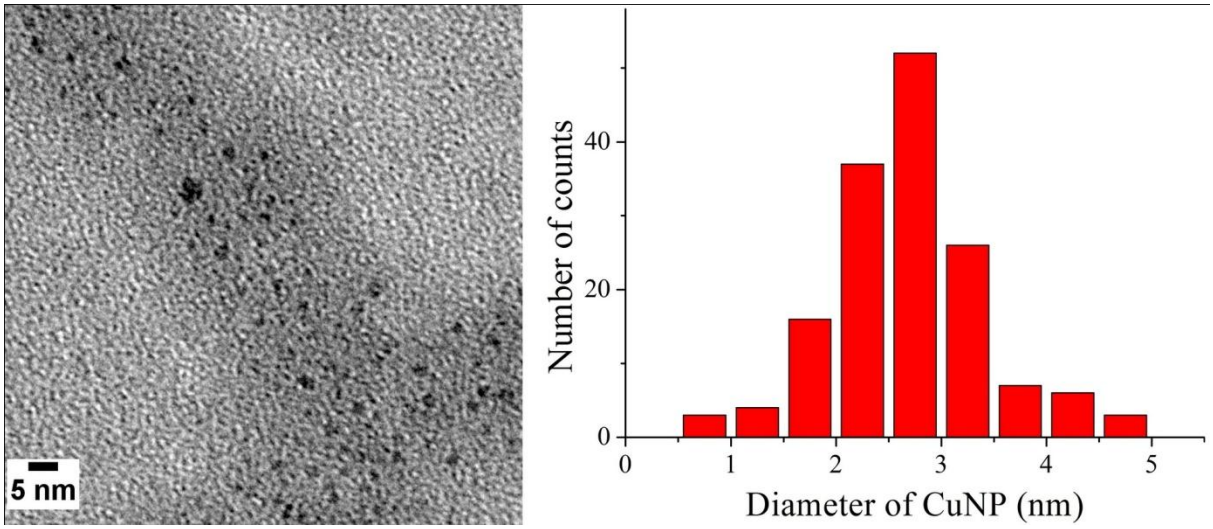

Figure S4. Reduction of $Cu(BF_4)_2$ in colloidal Cu+2/NaPA cross-linked networks in the presence of $CaCl_2$ as co-crosslinker after 90 minutes reaction with 0.3 mL hydrazine solution (1.0 M). Initial concentrations are as following: (**a**) $[Cu(BF_4)_2]_i = 1.7 \times 10^{-2}$ mol/L, $[CaCl_2]_i = 5.5 \times 10^{-3}$ mol/L , $[NaPA]_i = 1.1 \times 10^{-3}$ mol/L. The diameter of CuNP was 2.7 ± 0.7nm.