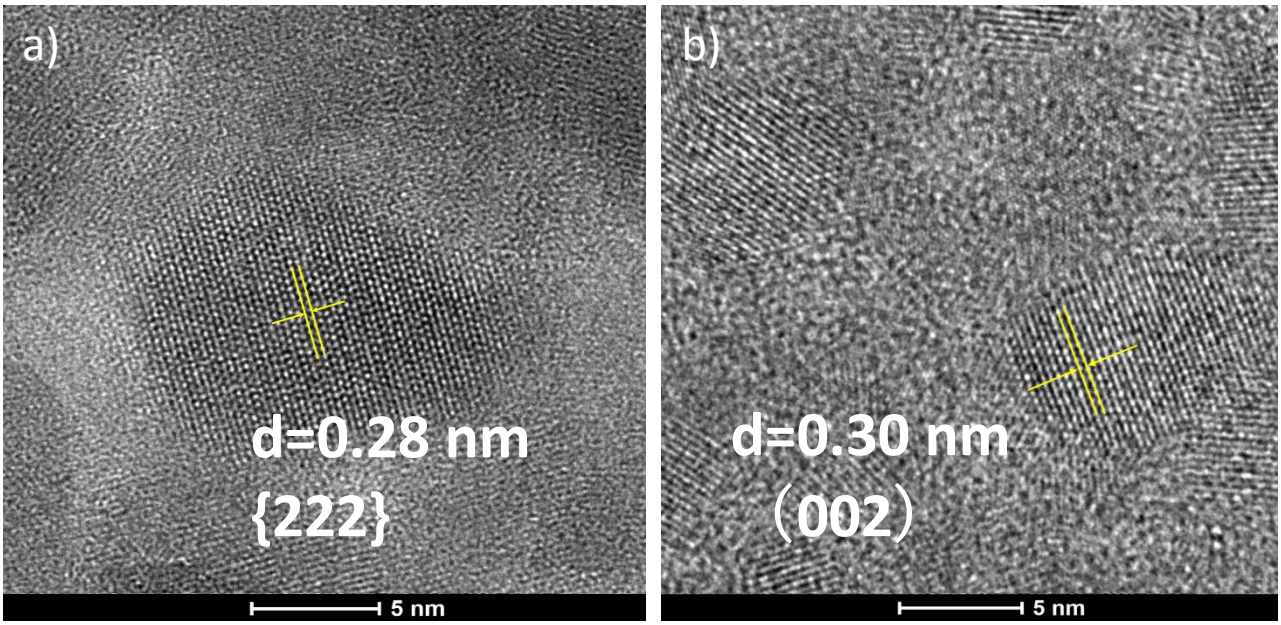
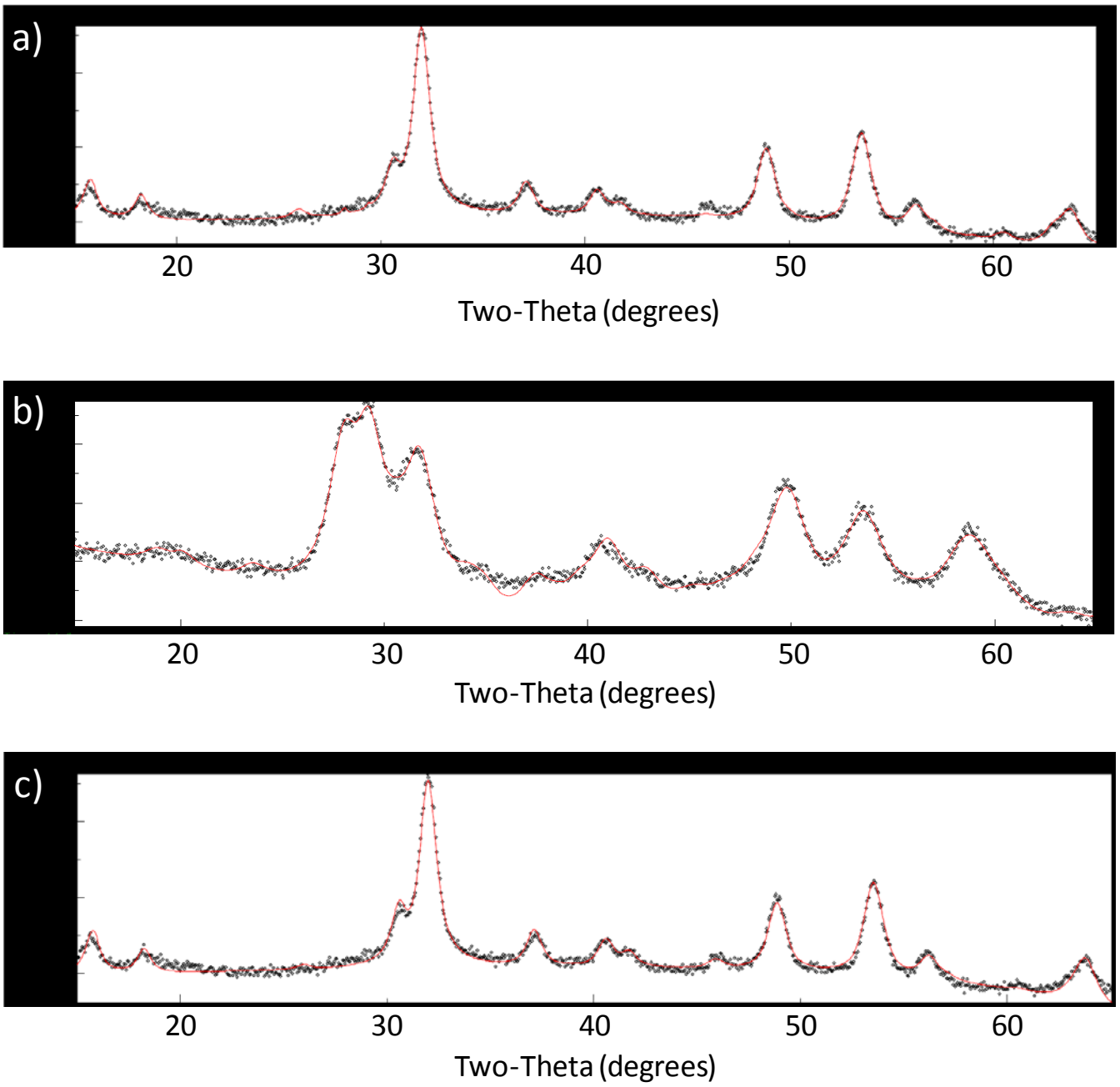
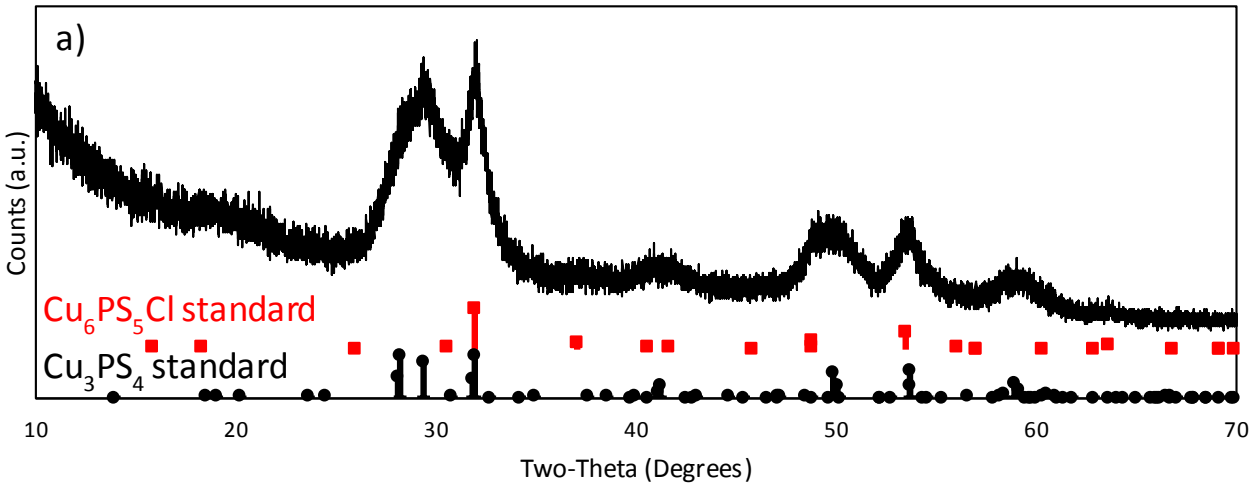
Electronic Supplementary Material (ESI) for RSC Advances.

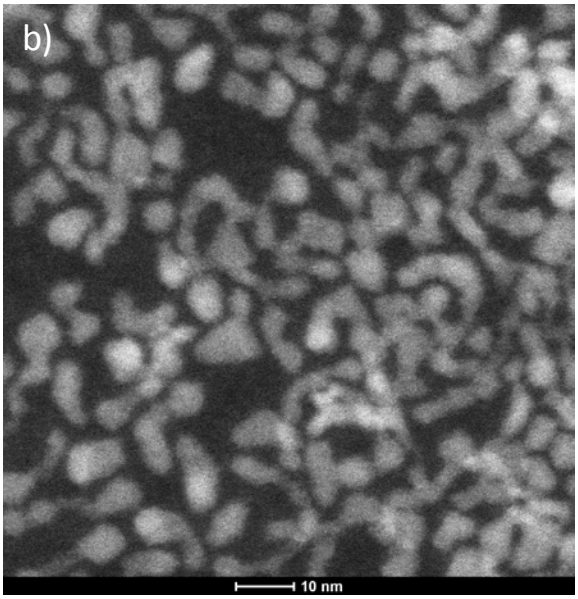


S1) HR TEM images and d-spacing measurements for a) Cu_6PS_5Cl and b) Cu_3PS_4. These measurements agree with standard crystallography data



S2) Rietveld fits for PXRD spectra a) Cu_6PS_5Cl nanoparticles using both Cu_3PS_4 and Cu_6PS_5Cl standards b) Cu_3PS_4 nanoparticles using both Cu_3PS_4 and Cu_6PS_5Cl standards c) and Cu_6PS_5Cl nanoparticles using Cu_6PS_5Cl standard. Due to the lack of any visible Cu_3PS_4 peak in the Raman spectra of the Cu_6PS_5Cl nanoparticles and that the Rietveld fitting for the Cu_6PS_5Cl nanoparticles using only the Cu_6PS_5Cl standard is able to account for all visible peaks, means that we believe the <1% Cu_3PS_4 reported in the quantitative analysis is likely due to experimental error and not the presence of any actual Cu_3PS_4. For the Cu_3PS_4 spectra, the refinement calculated 0% Cu_6PS_5Cl. (Cu_3PS_4 standard JCPDS: 01-071-3306, Cu_6PS_5Cl standard JCPDS: 01-073-5736)





S3) Data taken from an aliquot of the Cu_3PS_4 synthesis just after it reached 250 °C. From the Raman spectra shown in figure 4b) 250 °C, we expect both Cu_6PS_5Cl and Cu_3PS_4 to be present in the sample. a) Shows the PXRD spectra for this sample along with standards for both Cu_3PS_4 and Cu_6PS_5Cl (Cu_3PS_4 standard JCPDS: 01-071-3306, Cu_6PS_5Cl standard JCPDS: 01-073-5736) b) HAADF TEM image of the particles.