

## Role of Halide Ions for Morphology Controlled Synthesis of Cu<sub>7</sub>S<sub>4</sub> Nanoparticles

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Morphology controlled copper sulfide (Cu<sub>7</sub>S<sub>4</sub>) nanoparticles were synthesized by adding elemental sulfur ethanol solution into an aqueous solution containing Cu(II) precursor, branched polyethyleneimine (BPEI), and ascorbic acid. By varying the Cu(II) precursor, we could control the morphology of the nanoparticles from quasi-spherical nanoparticles (CuF<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, and CuSO<sub>4</sub>) to vine-like nanofibers (CuCl<sub>2</sub> and CuBr<sub>2</sub>). By comparison experiments and following calculations, we found that selective adsorption of Br<sup>-</sup> and Cl<sup>-</sup> on the specific facets of the crystal and slowing down the reaction rate by formation of Cu(I)-anion-BPEI complex would lead to the morphology change from spherical particles to vine-like nanofibers. In addition, we also exhibited that the morphology change of Cu<sub>7</sub>S<sub>4</sub> nanoparticles affected the electrochemical performance for Li-battery.