

Hierarchical Shape Evolution of Cuprous Oxide Nano and Micro-crystals by Surfactant Assisted Electrochemical Deposition

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The shape evolution of semiconducting nano-crystals (NCs) or micro-crystals (MCs) is one of the interesting issues in nanotechnology, biology, chemistry and materials engineering, because the surface morphology of semiconducting NCs or MCs is related to the surface energy, electronic structure, bonding and chemical reactivity.¹⁻³ As one of the best candidates for shape evolutionary single crystal materials, cuprous oxide (Cu_2O), which have typically p-type semiconductor with a direct band gap of 2.1eV, is an attractive material for catalysis, fuel cells, solar cells, gas sensing, lithium batteries and water splitting.

In recent years, various synthesis methods such as chemical vapor deposition, laser ablation, sol-gel, spray, hydrothermal method, and electrochemical deposition (ED) of Cu_2O NCs have been developed. Among these, solution-based process is suitable for practical use in the commercial industry, because it is low temperature and high volume production technology of NCs. Especially ED is a fast, flexible, low-cost process for synthesis of NCs.

In the present study, we investigate the nucleation and growth mechanism of Cu_2O NCs to MCs on 300nm Ti coated Si wafer by using different capping effect of surfactants during ED process. When the Cu_2O crystals were deposited in the solution without surfactant at pH 12, the shapes of Cu_2O crystals had cubic structure. This shape of Cu_2O crystals was maintained regardless of deposition time (fig. 1). When the surfactants were added to the solution, the shapes of Cu_2O changed with the type and the concentration of surfactants. The shapes of Cu_2O MCs could be altered by the difference of adsorption behavior of surfactants. Hexamethylene-tetramine (HMT) can hydrolyze in the aqueous solution, and forms the $(\text{CH}_2)_6\text{N}_4\text{-4H}^+$ complex cationic, which has four positive charges.⁴ However, poly(vinyl pyrrolidone) (PVP) forms the polarized functional group '-C=O' with a negative charge in the aqueous solution.⁵ In case of Cu_2O , while HMT can be adsorbed on the 'O'-terminated {100}, 'Cu'-coordination saturated {100} and the coordination unsaturated {111} surfaces, PVP can only be adsorbed on {111} surfaces. At the nanoscale, the shape of Cu_2O NCs was the octahedrons regardless of surfactants. However, the different growth behavior of Cu_2O crystals with HMT and PVP could be observed at the microscale. As shown in fig. 2, the HMT assisted Cu_2O MCs were the pyramid

like shape and the PVP assisted Cu_2O MCs had the branched octahedral structure.

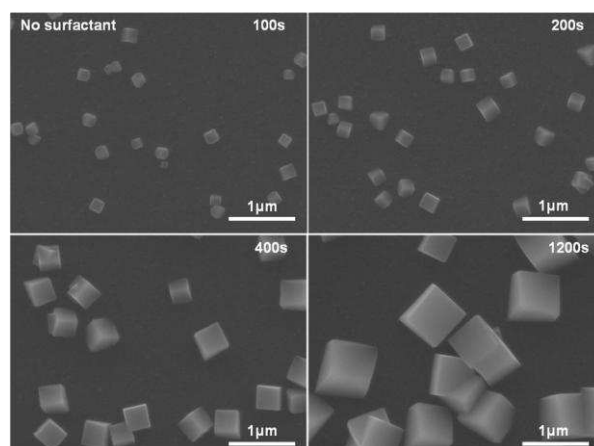


Fig. 1. SEM images of morphological variations of Cu_2O crystals at different deposition times (without surfactant)

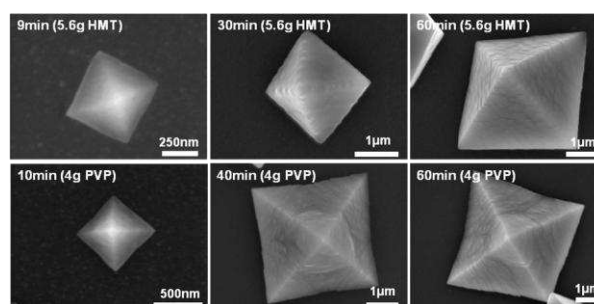


Fig. 2. The shape evolutions of Cu_2O crystals with different surfactants (HMT and PVP)

Reference

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