

ABSTRACT - POSTER

Controlling Particle Size and Shell Morphology in Hollow CuO_x Nanostructures via Sequential Templating

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Hollow copper oxide (CuO_x) nanostructures are highly attractive for applications in catalysis, energy storage, and sensing due to their high specific surface area, low density, and tunable functional architectures.^[1] Compared with conventional hard-templating routes that require laborious shell deposition and sacrificial core removal, sequential templating starting from homogeneous poly[Cu(II)-tannic acid] (p[Cu-TA]) coordination polymer precursors offers an alternative, where thermal decomposition drives phase separation and shell formation to yield hollow particles during the calcination step.^[2] However, a limited understanding of how specific synthesis parameters dictate particle and shell characteristics hinders the precise tunability required for broad application.

In this work, we systematically elucidate the synthesis parameters governing the nucleation, structural evolution, and final morphology of hollow CuO_x particles. Dynamic light scattering (DLS) measurements showed that fine-tuning the initiation pH within a narrow window from 9.5 to 9.7 controls base-catalyzed nucleation kinetics, producing precursor particle sizes that systematically decrease from 474 to 145 nm due to rapid, simultaneous nucleation triggered at higher hydroxyl ion concentrations. Transmission electron microscopy (TEM) further revealed that varying the Cu²⁺ loading alters the precursor morphology, transitioning from rough, porous particles at lower loadings to smoother surfaces with localized voids at higher loadings without affecting overall precursor dimensions. Finally, energy-dispersive X-ray spectroscopy (EDX) mapping confirmed a homogeneous elemental composition throughout the initial p[Cu-TA] precursor particles.

Thermal conversion of precursors with an average diameter of approximately 300 nm yielded hollow CuO_x nanostructures, with X-ray diffraction (XRD) confirming the formation of different crystalline copper oxide phases. Increasing the Cu²⁺ loading produced progressively denser, more defined shells with inner cavity diameters expanding from 100 to 154 nm, while the shell thickness remained constant at around 16 nm. This structural evolution directly aligns with the sequential templating mechanism, in which higher metal concentrations enable phase separation at lower degrees of thermal degradation, resulting in larger inner cavity dimensions at a constant shell wall thickness.

Overall, these findings provide quantitative design rules for tailoring the cavity dimensions, shell density, and structural uniformity of hollow CuO_x architectures, offering a versatile methodology applicable to a wide range of other single- and mixed-metal oxide nanostructures.

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References:

[1] Wang, X., *et al.*, *Chemical Reviews*, (2016) 116, 10983.

[2] Wang, G., *et al.*, *ACS Applied Materials & Interfaces*, (2019) 11, 35060.