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Synthesis and Morphological Characterization of Copper Oxide (CuO) Nanostructures

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Abstract:
Copper oxide (CuO) nanostructures were synthesized using a sol-gel route based on a copper salt precursor and citric acid as a chelating agent, followed by gel drying and calcination. The resulting black CuO powder was examined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) to evaluate its morphology across nanoscale and bulk scale. TEM micrographs revealed irregular, densely agglomerated nanostructures with scalloped, cauliflower-like edges and a fine-grained, porous internal texture, consistent with particle fusion occurring during thermal decomposition of the gel network. Complementary SEM revealed two distinct hierarchical surface architectures within the CuO powder: densely packed, near-spherical "cauliflower-like" agglomerates built from fine sub-particles, and larger flower-like (nanoflower) assemblies composed of thin, faceted nanoplates radiating from central nucleation points. Both SEM morphologies are consistent with the fused, porous nanostructure observed by TEM and indicate a hierarchically organized, high-surface-area powder. Together, the SEM and TEM results support the conclusion that the sol-gel method produces a highly agglomerated, hierarchically structured, porous CuO morphology well suited to surface-area-dependent applications such as catalysis and gas sensing, though XRD and BET analyses are still recommended for full crystallographic and surface-area confirmation.

1. Introduction

Copper oxide (CuO) is a p-type, monoclinic metal oxide semiconductor with a narrow band gap in the range of approximately 1.2–1.9 eV, consistent with structural and vibrational spectroscopic studies of CuO nanocrystals [1]. Owing to its low cost, natural abundance, chemical stability, and favorable electrical, optical, and catalytic properties, CuO has attracted considerable attention for applications in heterogeneous catalysis, gas sensing [6], antibacterial coatings, supercapacitor electrodes, biosensing [10], and solar energy conversion devices. The performance of CuO in these applications is strongly governed by its nanoscale morphology, since surface area, porosity, and particle connectivity directly influence charge transport, active site availability, and adsorption behavior.

Among the various synthesis routes available for CuO nanostructures (co-precipitation [5], sonochemical synthesis [2], hydrothermal/solution growth [4,7], green/biosynthesis, and sol-gel), the sol-gel method is widely used because it offers good compositional homogeneity, relatively low processing temperatures, and reasonable control over the final oxide morphology through variation of precursor concentration, chelating agent, pH, and calcination conditions.

The objective of the present short study was to synthesize CuO via a sol-gel route and to examine the resulting nanostructure morphology using transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

2. Materials and Methods

Copper (II) nitrate trihydrate (or copper acetate) was used as the copper precursor, with citric acid as the chelating/gelling agent. Deionized water and ethanol served as solvents, and dilute ammonia solution was used for pH adjustment.

The copper precursor was dissolved in deionized water under continuous magnetic stirring at room temperature to obtain a clear blue solution. Citric acid was then added dropwise to the precursor solution in a molar ratio suitable for complete metal-ion chelation, and the mixture was heated to 60–80 °C under continuous stirring. The pH of the solution was adjusted to approximately 7–8 using dilute ammonia, promoting complexation and initiating polymerization of the metal-citrate network. Continued heating and evaporation of the solvent produced a viscous, dark blue-green gel. The wet gel was dried in a hot-air oven at 100–120 °C overnight to obtain a dry xerogel. The xerogel was subsequently ground into a fine powder and calcined in a muffle furnace at 400–500 °C for 2–3 hours in an air atmosphere, during which decomposition of the organic citrate matrix and crystallization of the oxide phase occurred, consistent with the thermally driven dehydration pathway by which copper hydroxide intermediates convert into crystalline CuO [3], yielding a black CuO powder.

The morphology of the as-synthesized CuO powder was examined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). For TEM sample preparation, a small quantity of powder was dispersed in ethanol by ultrasonication and a drop of the resulting suspension was cast onto a carbon-coated copper grid and allowed to dry prior to imaging. For SEM analysis, the dry CuO powder was mounted directly onto a conductive carbon-taped stub and imaged without additional coating, allowing direct visualization of the powder's bulk surface morphology and agglomerate architecture. TEM and SEM are both established techniques for probing the size, shape, and agglomeration behavior of CuO nanostructures prepared by solution-based routes [4,6,7,8,9].

3. Surface Characterization

3.1 TEM Analysis

The TEM micrographs (Figure 1a and 1b, scale bar 100 nm) show the CuO sample as an irregular, densely agglomerated mass rather than a collection of discrete, isolated particles. The particle boundaries are scalloped and cauliflower-like, formed by the coalescence of numerous smaller sub-units into a continuous network. The interior of the aggregates displays a fine, mottled, grainy contrast, suggestive of a nanocrystalline internal structure composed of many small domains fused together, consistent with the grain-size-dependent contrast reported for nanocrystalline CuO [1], while the outer edges appear thinner and more electron-transparent than the darker, thicker core regions. In Figure 1a, elongated dark features near the particle edge may correspond to thicker folded regions or overlapping fragments of the material, similar to the rod-like features whose aspect ratio and number density have been shown to depend strongly on growth conditions in solution-grown CuO nanostructures [4]. The overall aggregate morphology observed in both images extends well beyond the 100 nm scale bar, indicating that while the primary building blocks are nanoscale, they are strongly fused into larger secondary structures — a common outcome of the calcination step in sol-gel processing, where the organic gel network collapses and sinters

the oxide phase. No lattice fringes are resolved at this magnification, so direct measurement of individual crystallite size or confirmation of the CuO monoclinic phase would require higher-resolution TEM (HRTEM) or selected-area electron diffraction (SAED).

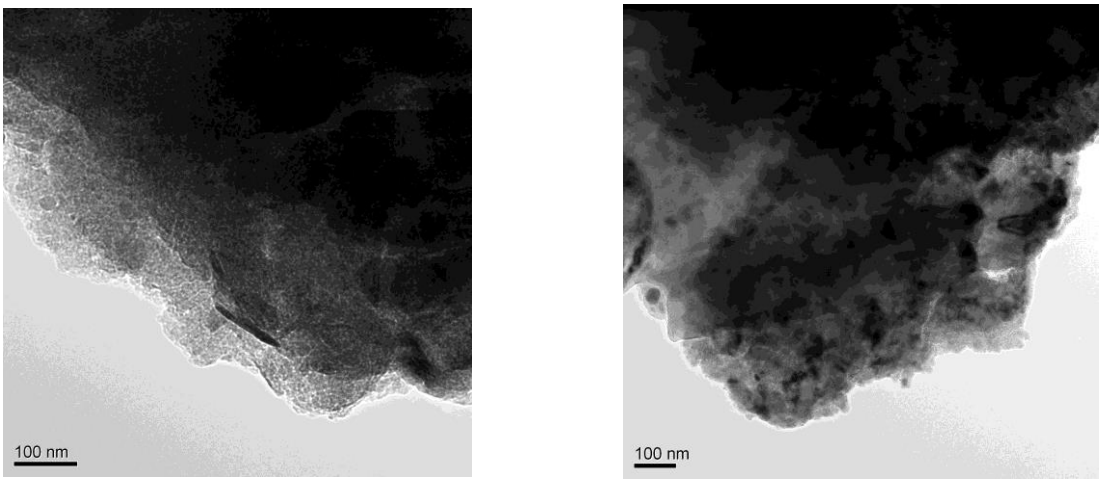

Figure 1. TEM micrographs of the sol-gel synthesized CuO sample: (a) and (b) show irregular, agglomerated nanostructures with scalloped edges and a fine, porous internal texture

3.2 SEM Analysis

Two SEM micrographs were obtained to examine the bulk surface morphology of the CuO powder (Figure 2a and 2b).

Figure 2a ("CuO Nanoparticles") shows the powder surface densely and uniformly covered by near-spherical, cauliflower- or raspberry-like agglomerates. Each individual sphere is itself built up from numerous much finer sub-particles, giving the cluster surfaces a rough, granular texture rather than a smooth spherical shell. The clusters are closely and continuously packed across the entire field of view, with little exposed flat substrate, indicating a high degree of secondary agglomeration and a hierarchically porous network between adjacent clusters, a self-assembly behavior also reported for hollow and hierarchical CuO microspheres synthesized by solution routes [6]. Cluster sizes appear reasonably uniform, consistent with a nucleation-and-growth process in which many primary nanoparticles aggregate around common centers during gelation and calcination.

Figure 2b ("CuO Nanomaterials") shows a markedly different, more strongly faceted morphology: flower-like ("nanoflower") assemblies composed of thin, plate-shaped nanosheets that radiate outward from central nucleation sites, resembling stacked petals, in agreement with previously reported flower- and sheet-shaped CuO nanostructures grown by low-temperature solution processes [7,8,9]. The plate edges are sharp and well-defined, and several elongated, blade- or rod-like fragments are visible projecting from or lying across individual flower assemblies. As in Figure 2a, these flower-shaped units are packed closely together over the whole imaged area, forming a continuous, highly textured, hierarchically porous surface; nanosheet-based flower architectures of this type have also been exploited as high-surface-area platforms for enzymatic glucose biosensing [10].

Taken together, the two SEM images indicate that the CuO powder is not composed of simple, isolated primary particles but instead self-organizes into hierarchical secondary architectures — spherical agglomerates in one region/preparation and plate-based nanoflowers in another — both of which expose a large amount of internal and external surface area through their open, porous packing. This bulk-scale hierarchical organization is consistent with, and helps explain, the fused, porous, nanocrystalline texture

observed at higher magnification by TEM (Section 3.1): the TEM images likely capture cross-sections or edge regions of these same spherical or plate-based secondary structures at the nanoscale, consistent with particle fusion effects reported for CuO nanopowders prepared by rapid precipitation and sonochemical routes [2,5].

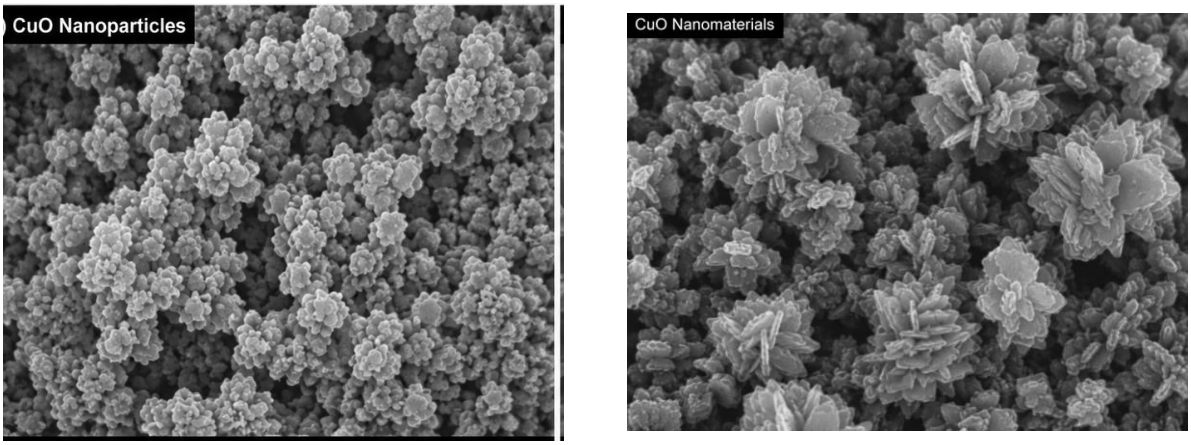

Figure 2. SEM images of the CuO powder: (a) spherical, cauliflower-like nanoparticle agglomerates and (b) flower-like (nanoflower) nanoplate assemblies.

4. Conclusion

CuO nanostructures were successfully prepared via a sol-gel route involving citric acid-assisted gelation followed by calcination. Combined SEM and TEM analysis revealed a hierarchically organized, highly porous material rather than a collection of discrete, isolated particles. At the bulk scale, SEM showed two characteristic secondary architectures — near-spherical cauliflower-like agglomerates and plate-based nanoflower assemblies — both densely and continuously packed to form an open, porous network. At the nanoscale, TEM showed that these secondary structures are themselves built from smaller fused domains with irregular, scalloped edges, consistent with sintering effects typical of calcined sol-gel oxides. This multi-scale porous, high-surface-area architecture is generally favorable for applications such as catalysis, gas sensing [6], biosensing [10], and electrode materials [4], where surface accessibility is important. Further characterization by XRD (to confirm crystallographic phase purity) and BET (to quantify specific surface area) is recommended to complete the structural picture established here.

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