

Formation of Hierarchical CuO Nanostructures on Copper Foil by Chemical Bath Deposition for Applications in Superhydrophobic Surfaces

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Abstract. Hierarchical CuO nanostructures (urchin-like and grassy island structure) were successfully synthesized by a simple chemical bath deposition method at low temperature of 70°C in a short reaction time of 1h. XRD analysis revealed the presence of pure crystalline monoclinic CuO. Morphological analysis revealed the formation of spherical structures composed of numerous hair-like structures. The pH of the solution was also investigated to have a great effect on the morphology of the CuO nanostructures. At lower pH, the structures tend to form urchin-like structures; while at higher pH, the structures tend to form grass-like islands. A growth mechanism was also proposed in this paper. Lastly, wettability test proved the stable superhydrophobic property of the CuO nanostructured thin film surface.

1 Introduction

Cupric oxide (CuO) is a p-type transitional metal oxide semiconductor with a narrow bandgap of 1.2-2.1 eV. It is naturally black in color, and observes a monoclinic crystal structure. Nanostructured CuO, which is defined as having at least one dimension in the nanometer scale, differs in properties as with the bulk material due to quantum-size effects [1-2]. In any case, CuO nanostructures remain to exhibit superior optical, electrical, magnetic, thermal and electrochemical properties which render them usable for a wide variety of potential applications. These include solar cells [3], gas and chemical sensors [4-7], nanofluidics [8], photocatalysis [9-10], superhydrophobic surfaces [11], antimicrobial and antifungal agents [12-13] and electrochemical energy storage applications [14-19]. In particular, CuO superhydrophobic surfaces have been gaining interest because they have superior hydrophobicity but are very economical.

Several synthesis techniques for CuO nanostructures have been developed, such as thermal oxidation, wet chemical method, solution-phase synthesis, microwave-assisted synthesis, and chemical bath deposition. Among these, chemical bath deposition is least explored, but is one of the most promising methods because it is simple, inexpensive and potentially scalable. Also, chemical bath deposition on Cu foil allows direct formation onto a conductive substrate, which is ideal for use in energy storage devices such as lithium ion batteries and supercapacitors [14-19].

In this study, hierarchical CuO nanostructures were successfully synthesized by chemical bath deposition at a

low temperature of 70°C in a short reaction time of 1h. The effect of pH on the morphology of the nanostructures was also investigated. A plausible growth mechanism is also proposed. Lastly, the superior hydrophobic properties of the unique CuO nanostructures were observed.

2 Experimental

High purity Cu foils (99.99%, 1x1 cm) were manually ground using silicon carbide sheets and sonicated in 4M HCl solution for 15 mins to remove surface impurities and native oxide layers. In three beakers, 60 ml of 0.1 M Cu(NO₃)₂ solution was mixed with 20 ml NH₃ solution of varying concentrations to achieve increasing pH values (pH 10.2, 11.3 and 11.9). The clean Cu foils were then submerged in the solutions after thorough mixing. The chemical bath was then heated to 70°C for 1h. The foils turned pitch black after the given reaction time. Finally, the foils were dried in an oven at 60°C for 3h.

2.1 Characterization techniques

The surface morphology of the CuO nanostructures was examined using scanning electron microscope (JEOL 5300) operating at 25 kV. The composition and crystal structure of the as-grown CuO nanostructures were determined by Shimadzu X-ray diffractometer (XRD-7000) operated at 40 kV and 30 mA with Cu K α radiation in the range of 30–80°. Wettability tests against water were performed using a simple contact angle set up.

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3 Results and discussion

3.1 Structural analysis

Figure 1 shows the XRD pattern of the CuO nanostructures formed. Highest peaks located at 43.4°, 50.1° and 73.9° represent pure metallic Cu, which is the substrate used. The other characteristics peaks located at 32.5°, 36.3° and 39.4° can be attributed to (110), (11-1) and (111) peaks of pure monoclinic CuO (JCPDS 05-661). This signifies that no contaminations were detected in the sample.

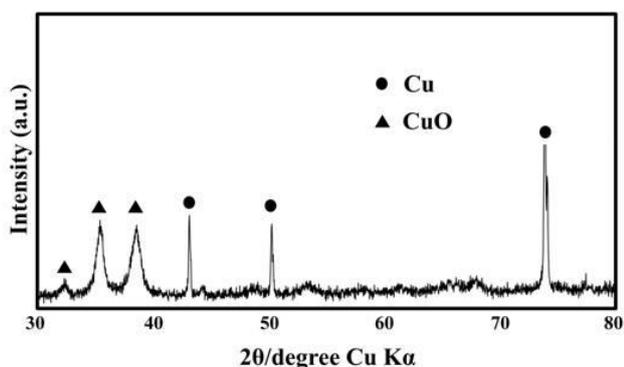


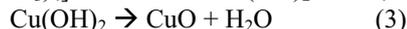
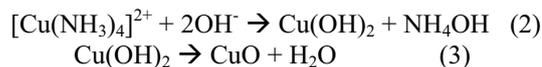
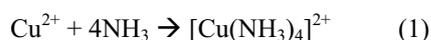
Figure 1. XRD pattern of urchin-like CuO nanostructure.

3.2 Morphological analysis

Figure 2 shows the SEM images of the hierarchical CuO nanostructures formed at pH 10.2, 11.3 and 11.9. The nanostructures were synthesized between pH 10 to 12 because the high alkalinity favors the oxidation of the Cu foils. At pH 10.2, spherical structures comprised of numerous nanowires were produced, resembling an urchin structure. The diameters of these urchin-like nanostructures were 2-5 μm. When the pH was increased to 11.3, similar urchin-like structures were formed, but are aggregated to form large clumps. At a very high pH of 11.9, nanowires are grouped together in the form of islands. This shows that pH greatly affects the morphology of the CuO nanostructures.

3.3 Proposed Formation Mechanism

Shown below are the reactions involved in the formation of CuO nanostructures:



Cu^{2+} ions coming both from the substrate and from the chemical bath react with NH_3 to form a copper-ammonium complex. OH^- ions which come from the dissociation of ammonia to ammonium hydroxide then reacts with this complex to form $\text{Cu}(\text{OH})_2$. Then, upon dehydration caused by exposure to high temperature (70°C), oxidation to CuO occurred.

Figure 3 shows a plausible growth mechanism of the hierarchical CuO nanostructures. It starts with the formation of $\text{Cu}(\text{OH})_2$ nuclei. These nuclei then grow into nanowires, followed by oriented attachment. At lower pH, preferentially oriented attachment is favored. This is because at low pH, less OH^- ions are present, which drives the oxidation to CuO at a slow pace. This means that the nanowires are given more time to preferentially attach in an orderly manner, which in this case is urchin-like formation. When pH is increased to 11.3, a less orderly structure composed of aggregated urchin-like structures was formed. The possible reason for this is the presence of more OH^- ions that drives the reaction faster, resulting to the disruption of the orderly formation of urchin-like structures because oxidation was achieved at a faster pace. The incomplete urchin-like structures have high surface energy, which led to aggregation to form clumps. Finally, at a very high pH of 11.9, the nanowires tend to be much easily attracted to each other as dictated by the ultrafast-paced reaction. They then tend to be attracted in a parallel fashion into small groups (islands). These islands then tend to aggregate because of their high surface energy.

3.4 Superhydrophobic properties

Figure 4 shows the water contact angle measurements of the CuO nanostructures. The grassy island structures displayed the most superior hydrophobic property, having a contact angle of 152.1°. This is due to the very high surface area of the nanowires grouped into islands. The urchin-like nanostructures also showed good hydrophobic properties having a water contact angle of 125.4°. This is caused by the high surface area of the spherical structures, which is further improved by the presence of nanowires. The clumped urchin-like nanostructures showed the lowest hydrophobicity, with a water contact angle of 74.5°. The clumping caused the surface area of the urchin-like surface to greatly decrease.

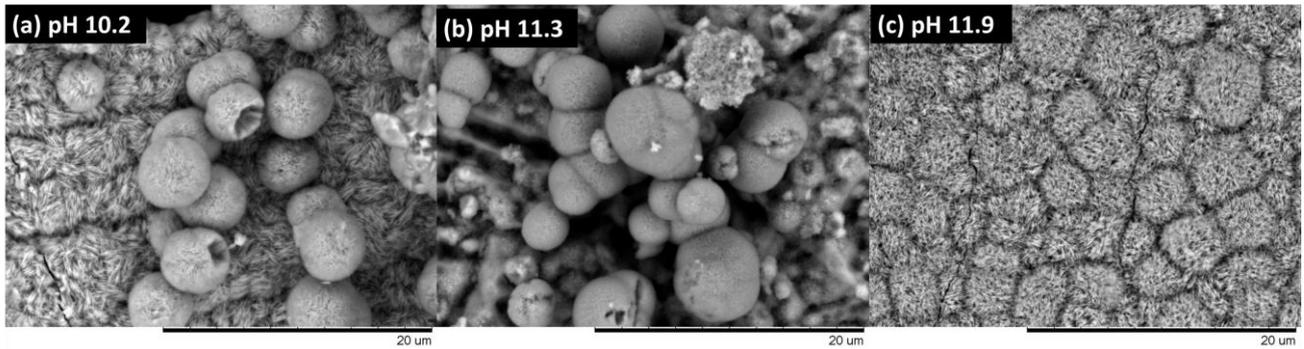


Figure 2. SEM images of hierarchical CuO nanostructures synthesized at different pH: (a) pH 10.2, (b) pH 11.3, and (c) pH 11.9.

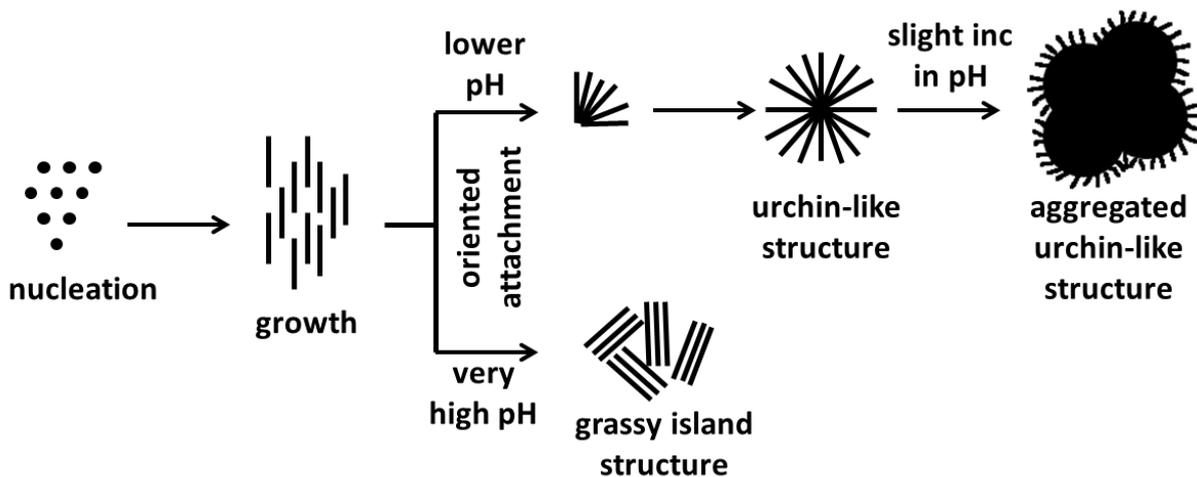


Figure 3. Schematic diagram of the proposed growth mechanism of hierarchical CuO nanostructures.

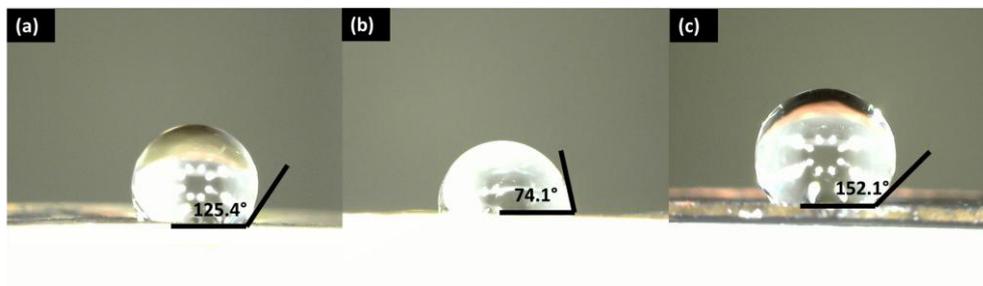


Figure 4. Schematic diagram of the proposed growth mechanism of hierarchical CuO nanostructures.

4 Summary

A simple chemical bath deposition method at low temperature (70°C) in a short reaction time (1h) to synthesize hierarchical CuO nanostructures was demonstrated in this study. XRD results confirmed the presence of pure crystalline monoclinic CuO. SEM analysis showed the formation of urchin-like and grassy island structures. At a relatively low pH of 10.2, urchin-like structures were formed. When pH was increased to 11.3, these urchins aggregated. But at a very high pH value of 11.9, grassy island structures were formed. All of the structures showed superior superhydrophobic properties, which finds their role in producing potentially

scalable, cheap but high quality superhydrophobic surfaces.

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