# Supporting Information

## Nanocube-aggregated cauliflower-like copper hierarchical architectures: synthesis, growth mechanism and electrocatalytic activity

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**Preparation of the copper hierarchical 3D nanostructures:** The zinc foil was first treated with hydrochloric acid (HCl) to remove surface contamination, and rinsed with absolute alcohol and deionized water, respectively. In a typical synthesis, 0.50 g $Cu(NO_3)_2$ powder was dissolved in deionized water (2 mL) to obtained $Cu(NO_3)_2$ solution. Zinc foil was immersed into the container with $Cu(NO_3)_2$ solution. The whole reaction was performed at room temperature and ambient pressure and lasted for 60 s, and the cauliflower-like products can be synthesized on the surface of zinc foil. Then, the product was washed with distilled water and absolute alcohol in sequence.

**Characterizations:** The crystal phase of as-prepared products was characterized by an X-ray diffraction (Bruker-AXS D8 ADVANCE) using Cu Kα radiation (λ = 1.54 Å) in the range (20 ~ 80 °). The morphology of the products was investigated by field-emission scanning electron microscopy (FE-SEM) using JEOL (JSM-7000F) at an accelerating voltage of 20 kV. The chemical composition and purity of the products were examined by electron energy dispersive X-ray (EDX) analysis.

**Electrochemical Measurements:** A three-electrode cell was used to carry out the electrochemical measurements. A 1cmx1cm Pt coil was used as the counter electrode, and the Ag/AgCl (in 3 M NaCl) was used as the reference. To prepare the working electrode, a GC disk electrode (5.0 mm diameter) was first polished with alumina slurries (50 nm) and then cleaned by sonication in $H_2SO_4$, ethanol and ultrapure water for some minutes. 10 μL of copper 3D nanostructures dispersed in ethanol (1.0 mg/mL) was then deposited onto the clean GC electrode surface by a microliter syringe (the resulting electrode was denoted as Cu/GC). The Cu/GC electrode was then dried in a vacuum drying oven. Voltammetric measurements were performed on an Electrochemical Analyzer Instrument (Pine AFCBP1). The electrolyte was 0.1M KOH and the potential scan rate was 100 mV/s. Cyclic voltammograms were firstly carried out in $N_2$- saturated 0.1M KOH solution which was purged with nitrogen for 20 min prior to, and during the measurement .Oxygen reductions were examined when the electrolyte solution aerated with purity oxygen for at least 20 min and then keeping the solution with an oxygen atmosphere during the entire experimental procedure. All eclectrochemical experiments were carried out at room temperature (298 k).

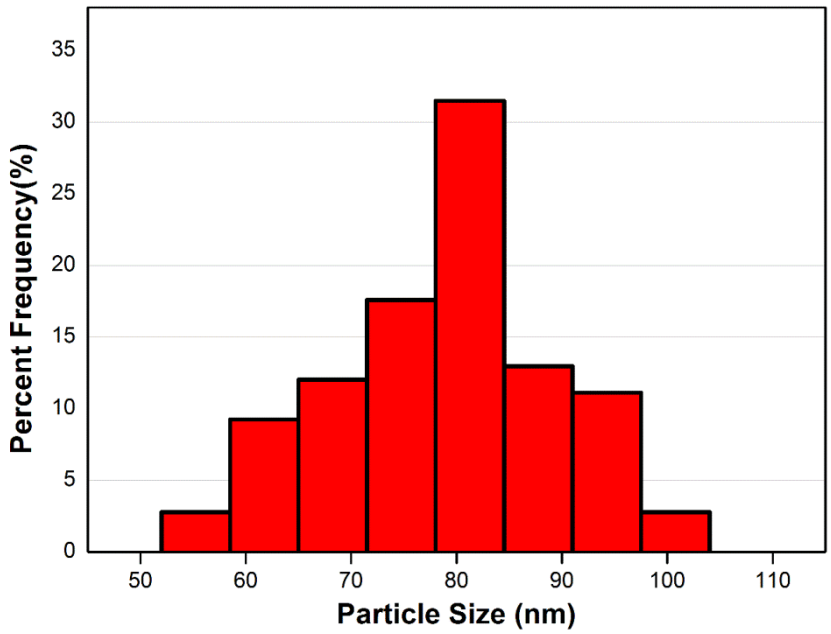


**Fig. S1** The size-distribution diagram of cubic nanoparticles prepared at 60s

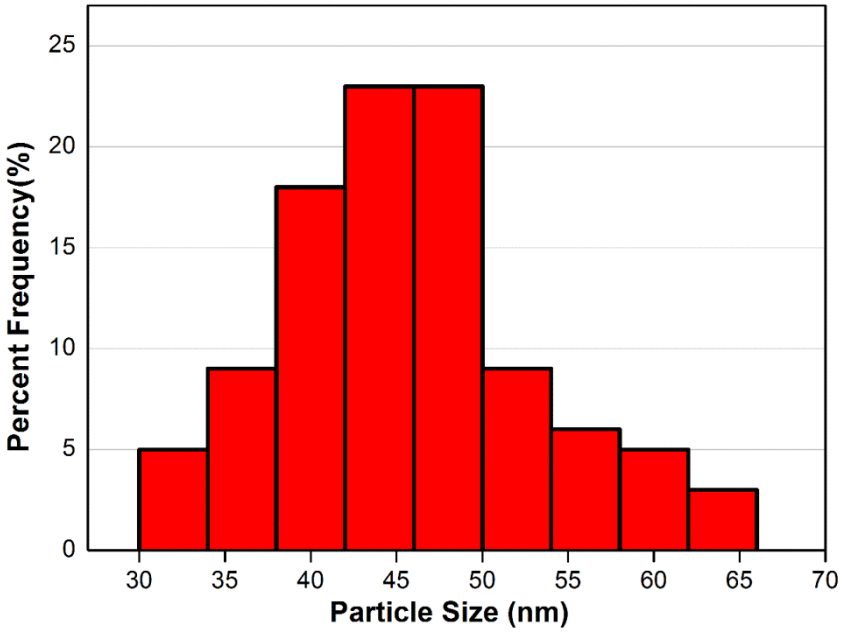


**Fig. S2** The size-distribution diagram of nanoparticles prepared at 45s

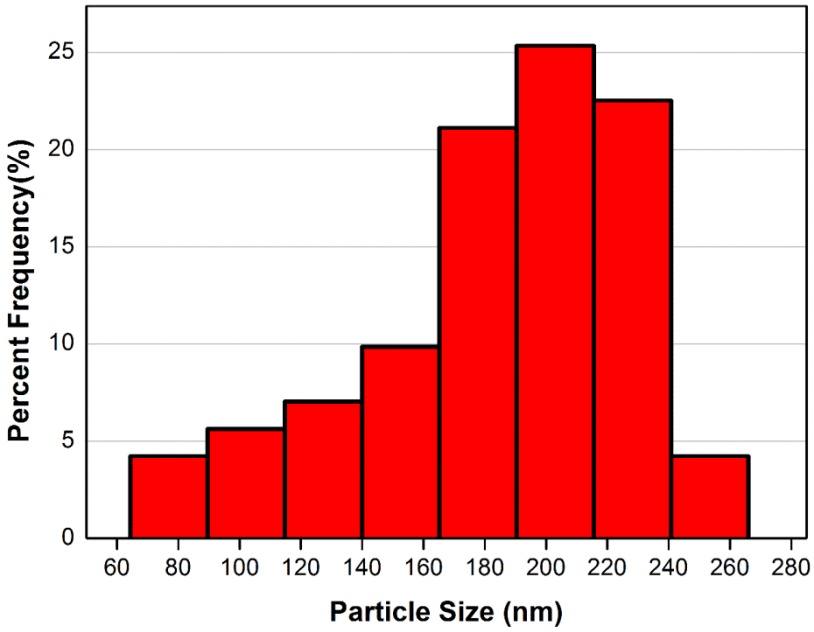


**Fig. S3** The size-distribution diagram of cubic nanoparticles prepared at 120s

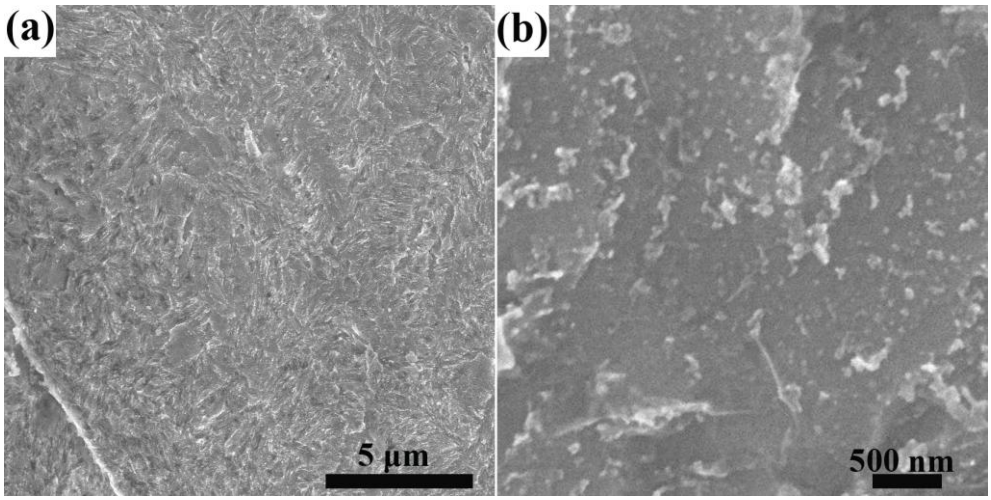


**Fig. S4** The SEM images of zinc foil with different magnification

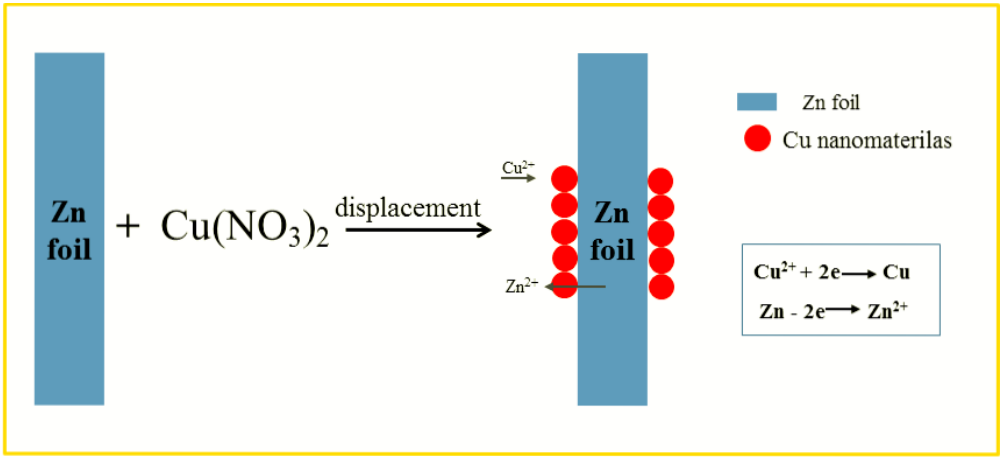


**Fig. S5** A schematic of galvanic displacement on Zn foil in the presence of $Cu(NO_3)_2$ solution.

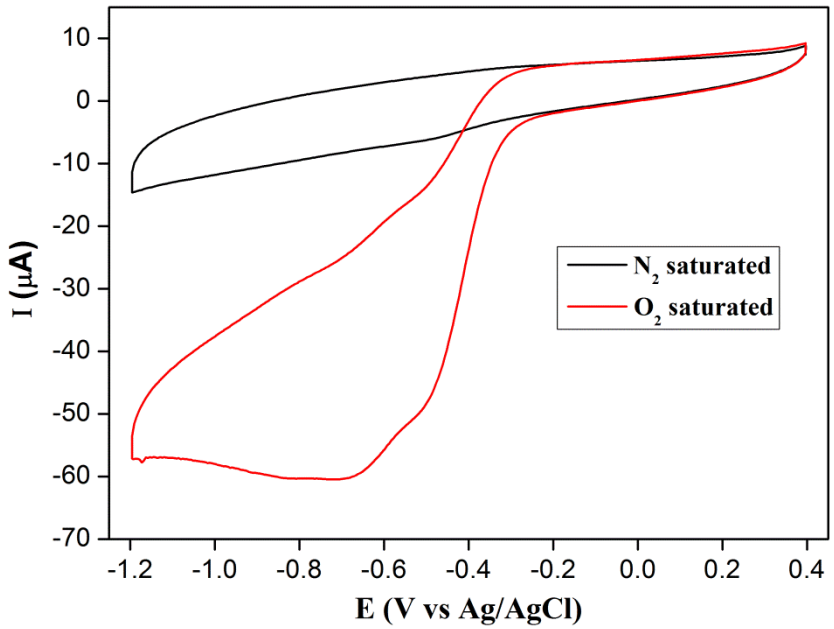


**Fig. S6** Cyclic voltammograms of Cu/GC electrode in $N_2$- or $O_2$- saturated solution with the products obtained at 120s