

Three-dimensionally ordered macroporous Cu₂O/Ni inverse opal

electrodes for electrochemical supercapacitors

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Materials Synthesis and characterization

All chemicals were of reagent quality and used without further purification. The multilayer polystyrene (PS) opal template was prepared on slow gravimetric sedimentation of colloidal particles onto a substrate as detailed elsewhere.¹ The PS spheres of diameter ~500 nm were synthesized according to a published procedure.¹ Briefly, an aqueous emulsion composed of ethanol (60 mass %; J. T. Baker, 99.9 %), deionized water (34.9 mass %), styrene (5 mass %; Showa, 99.5 %), and potassium persulfate (0.1 mass %; Showa, 98.0 %) was stirred at 70 °C for 24 h under a nitrogen atmosphere. After the polymerization was accomplished, the PS spheres were collected with a centrifuge. These spheres were supersonically washed in ethanol and water, and then collected with a centrifuge. To remove the unreacted reagents, the

cleaning procedures were repeated at least three times.

An electrode, gold-sputtered on a glass substrate coated with indium tin oxide (Au/ITO), was immersed vertically in an aqueous dispersion of PS spheres (0.2 mass %) at 70 °C. The PS spheres self-assembled on the electrode surface progressively as the water evaporated, yielding a 3DOM PS template. These PS spheres were used to prepare the templates on an ITO/Au electrode. Electrodeposition was performed with a potentiostat (AUTOLAB) in a three-electrode cell with the PS coated substrate as the working electrode, a platinum counter electrode, and an SCE reference electrode. To obtain 3DOM Cu₂O/Ni inverse opals, Ni metal was first electrodeposited within the pore space of the PS films in a bath prepared by dissolving a mixture of NiSO₄ (1 M), NiCl₂ (0.1 M) and H₃BO₃ (0.5 M) in distilled water at a constant potential -1.0 V (vs. SCE); the total cathodic passed charge was controlled to be 0.5 C (area ~1.0 cm²). The obtained samples were soaked in mixtures of tetrahydrofuran (Echo, 100 %) and ethanol to remove the PS templates, leaving the 3DOM Ni inverse-opal structures. To prepare the thin Cu₂O films on the 3DOM Ni inverse opals, we used anodic electrodeposition of Cu oxide grown from a solution containing Cu(CH₃COO)₂ (0.3 M) and Na(CH₃COO) (0.1 M), adjusted to pH 6 with acetic acid (1 M). A potential -0.5 V (vs. SCE) was applied to yield a total passed charge density 0.15 C cm⁻² on the surface of the 3DOM Ni inverse opals. The typical mass of the deposited samples

(3DOM Cu₂O/Ni or Cu₂O films), measured using a microbalance with an accuracy of 0.01 mg, was approximately 0.2-0.22 mg cm⁻². The nano-structured samples were examined with a scanning electron microscope (SEM, JEOL 6500F) and a transmission electron microscope (TEM, JEOL 2000FX) for analysis. The crystallinity was determined with an X-ray diffractometer (XRD, Rigaku MiniFlex II) with a Cu target.

The same amount of Cu oxide was deposited on flat Ni substrates to make a counterpart electrode used in this work. The flat Ni (area ~1.0 cm²), pretreated by degreasing in acetone, etching in hydrochloric acid and rinsing thoroughly with water, after drying, then served as the working electrode. The electrochemical performance of the three electrodes was evaluated with cyclic voltammetry (CV) in KOH solution (6 M) at 30 °C; the potential was scanned in a range from -0.2 V to 0.4 V (vs. SCE) at varied sweep rates (10 – 500 mV s⁻¹). Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage with 5 mV s⁻¹ amplitude in a frequency range from 0.01 Hz to 100 kHz at the open circuit potential. The applied potential and current were regulated with a potentiostat (AUTOLAB). The variation of the oxidation state of Cu in the 3DOM Cu₂O/Ni electrode was investigated at various applied potentials in KOH solution (6 M) with a Cu K-edge XAS spectrum recorded in situ in the fluorescence-yield mode. A sealed spectro-electrochemical cell

with a fluorescence- transparent window (Kapton tape) was used. Before measuring the absorption spectra at a given potential, we kept the electrode at a set potential for 15 min to allow the 3DOM Cu₂O/Ni electrode to attain a steady state. Cu K-edge XANES measurements were conducted in situ at beamlines 01C1 and 17C1 of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. A Si(111) double-crystal monochromator served to tune the X-ray photon energy with a resolution $\Delta E/E \sim 2 \times 10^{-4}$. The X-ray absorption energy was calibrated with the known Cu K-edge absorption inflection point at 8978.9 eV of a Cu foil, which was measured before each XAS scan. X-ray photoemission spectra (XPS) served to probe the variation of the Cu oxidation state during the charge and discharge cycling at beamline 20A of NSRRC.

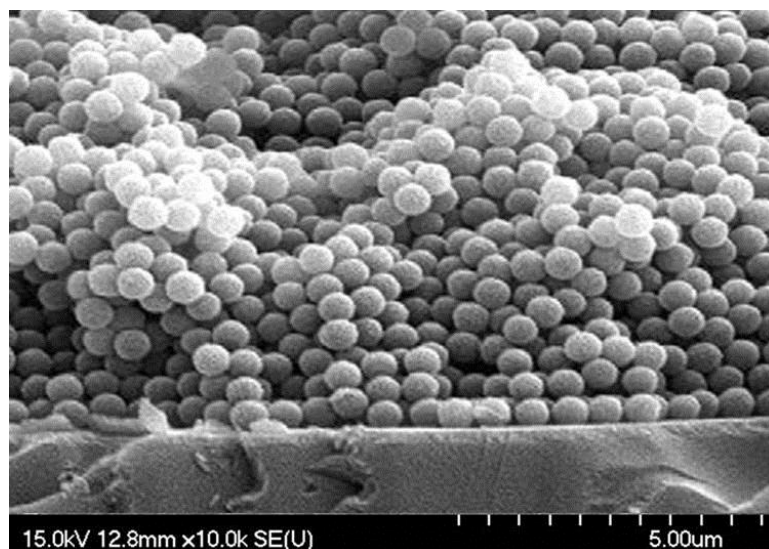


Figure S1 SEM micrographs of the cross-sectional PS template on a Au/ITO

electrode.

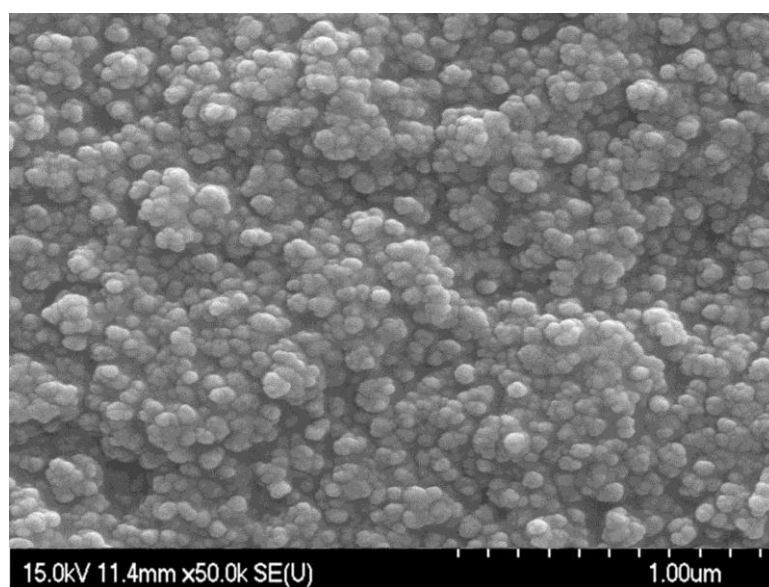


Figure S2 SEM micrographs of the prepared Cu₂O electrodes with flat Ni substrates.

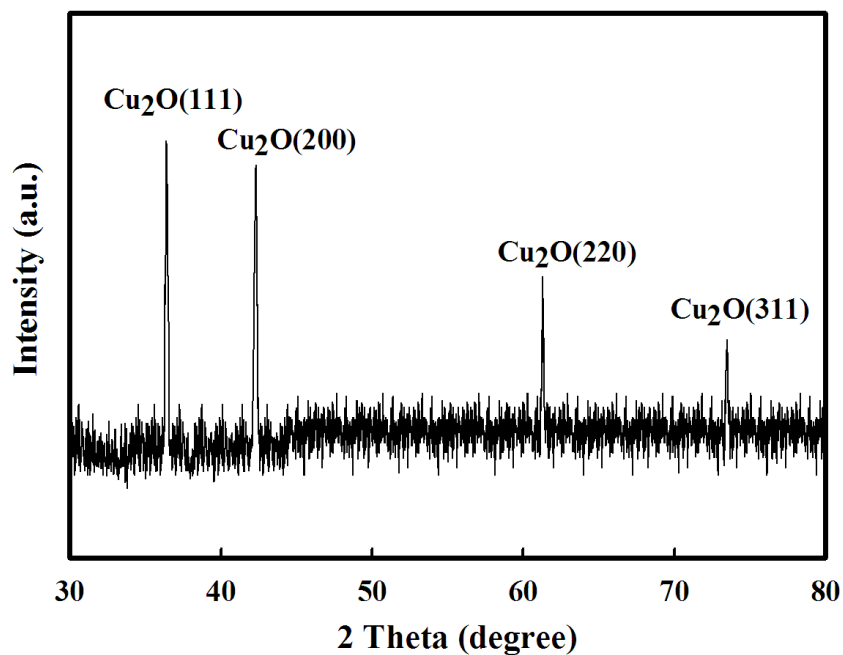


Figure S3 XRD patterns for Cu_2O powders from the 3DOM $\text{Cu}_2\text{O}/\text{Ni}$ electrode.

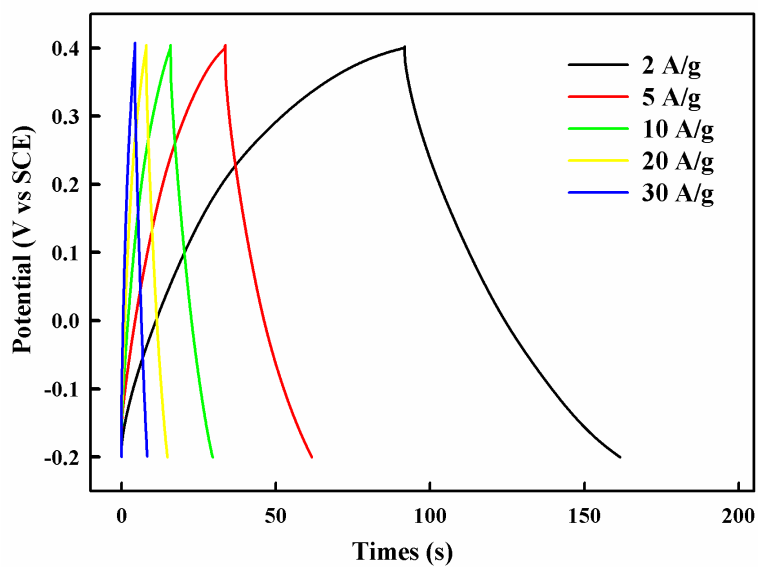


Figure S4 CV for charge-discharge cycles of the 3DOM $\text{Cu}_2\text{O}/\text{Ni}$ electrode measured in the potential range from -0.2 V to 0.4 V at different current density from 2 to 30 A

g^{-1} .

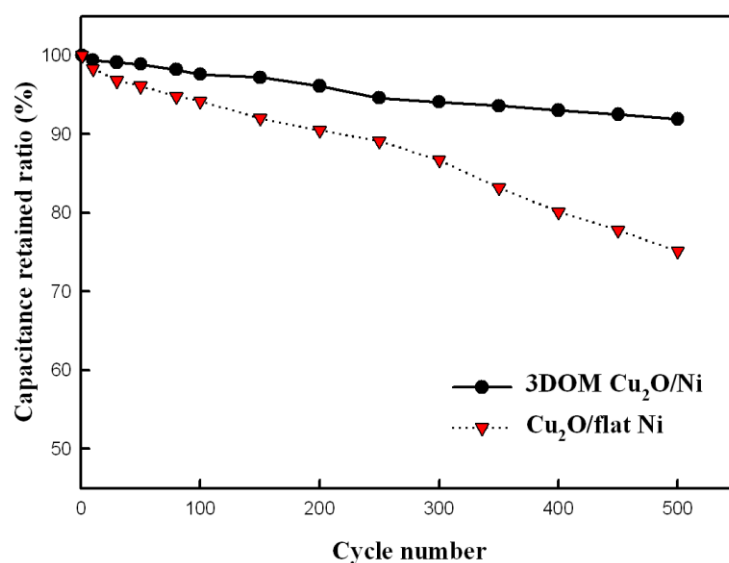


Figure S5 Cycle performance of the 3DOM Cu₂O/Ni and Cu₂O/flat Ni electrodes.

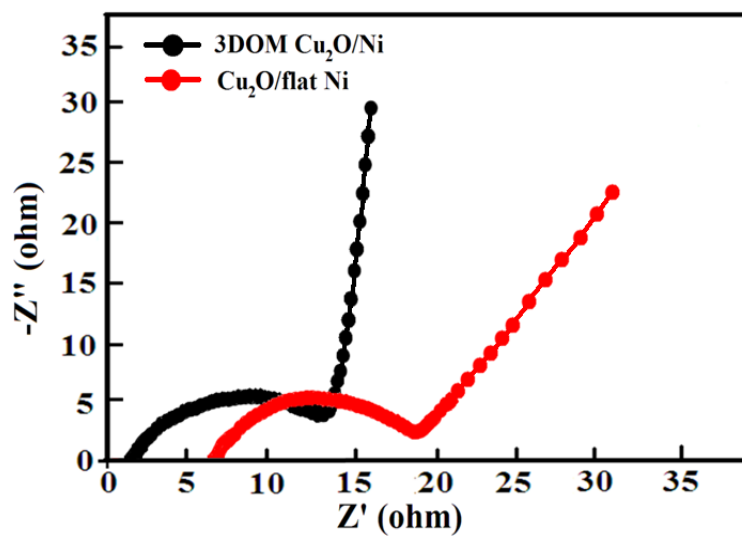


Figure S6 EIS comparison curves of the 3DOM Cu₂O/Ni and Cu₂O/flat Ni electrodes.

The specific capacitance (C_{sp}), energy density (E), and power density (P) were calculated from the chronopotentiometric curves according to Eqs (1~3):²⁻⁴

$$C_{sp} = I \Delta t / w \Delta V \quad (1)$$

$$E = (C(\Delta V)^2)/2 \quad (2)$$

$$P = E / \Delta t \quad (3)$$

where I is the charge/discharge current, Δt is the time for a full charge or discharge, w is the mass of the active electrode material (3DOM Cu₂O/Ni or Cu₂O), and ΔV is the voltage change after a full charge or discharge.

Reference

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