Self-supporting catalyst beat powder electrode for electrocatalytic oxygen evolution reaction: cobalt-based catalyst as an example

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Synthesis of Co_3O_4 on Ni foam

Before the preparation, the coarse Ni foam (3*5 cm) support should be pretreated for 10 min in 3 M HCl solution, acetone and water respectively using ultrasonication method. $Co(NO_3)_2 \cdot 6H_2O$ (15 mmol), NH_4F (15 mmol) and urea (15 mmol) was dissolved in 80 ml ultrapure water. The cleaned Ni foam was placed vertically into a 100 mL Teflon-lined autoclave which contained above uniform solution. The autoclave was sealed and heated at 100 °C for different time (11 h) to prepare Co_3O_4 NA precursors in an oven. After the reactor was cooled down to room temperature, the precursors were washed three times with the ultrapure water and ethanol and dried in air at 60 °C. Subsequently, the Ni foam with the as-prepared precursors was transfer into a meffle furnace and then annealed at 350 °C for 2 h to gain monolithic nanostructured Co_3O_4 nanoarray catalysts. The synthetic materials were denoted as Co_3O_4/NF.

2.3. Material characterization

The composition and purity of the resulting materials was researched by X-ray powder diffraction (XRD) using a X'Pert-Pro MPD diffractometer (Netherlands PANalytical) (Cu Kα radiation). The morphologies of the samples were studied by Hitachi S-4800 microscope Scanning electron microscopy (SEM) images. X-ray photoelectron spectroscopy spectra (XPS) were recorded on a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer.

2.4. Electrochemical measurement

Electrocatalytic activity testing were done with a CHI 660E (CH Instruments, Inc., Shanghai) electrochemistry work station in a typical three-electrode system. Co_3O_4/NF is used as the working electrode, Hg/HgO electrode as the reference electrode as the counter electrode. The electrolyte of 1 M KOH was used for the OER tests. The as-synthesized Co_3O_4 on Ni foam were directly applied as electrodes without using a binder. The electrode was fixed by an electrode clamps for the electrocatalytic test. Linear sweep voltammetry (LSV) measurements were done from 0.2 to 0.8 V at a scan rate of 5 mV s^{-1} for OER. TOF =JA/4Fn, where J is the current density, A is the geometrical electrode area, and 4 expresses the moles of electron consumption for one mole O_2 evolution, F is the Faraday constant (96485.3 C mol^{-1}).

To prepare the working electrode: (1) 5 mg of the catalyst was first dispersed in ethanol (10 mL) to form a homogeneous mixture; (2) 20 μL of this solution was then drop-cast onto a glassy carbon electrode (GCE, 3 mm in diameter), and left to dry in air; (3) 20 μL of 0.5% Nafion solution in ethanol was cast on the top of the sample film to coat the catalyst.

DFT calculation

The DFT calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP) with the plane-wave pseudo-potential method. The geometrical structures of the (111) plane of $CuCo_2O_4$/NF and Co_3O_4/NF were optimized by the generalized gradient approximation (GGA) methods. The Revised Perdew-Burke-Ernzerh of (RPBE) functional was used to treat the electron exchange correlation interactions. A Monkhorst Pack grid k-points of 6*6*1 of $CuCo_2O_4$/NF and Co_3O_4/NF, a plane-wave basis set cut-off energy of 500 eV were used for integration of the Brillouin zone. The structures were optimized for energy and force convergence set at 0.05 eV/A and 2.0×10^{-5} eV, respectively. The vacuum space was up to 0.002 A to eliminate periodic interactions.

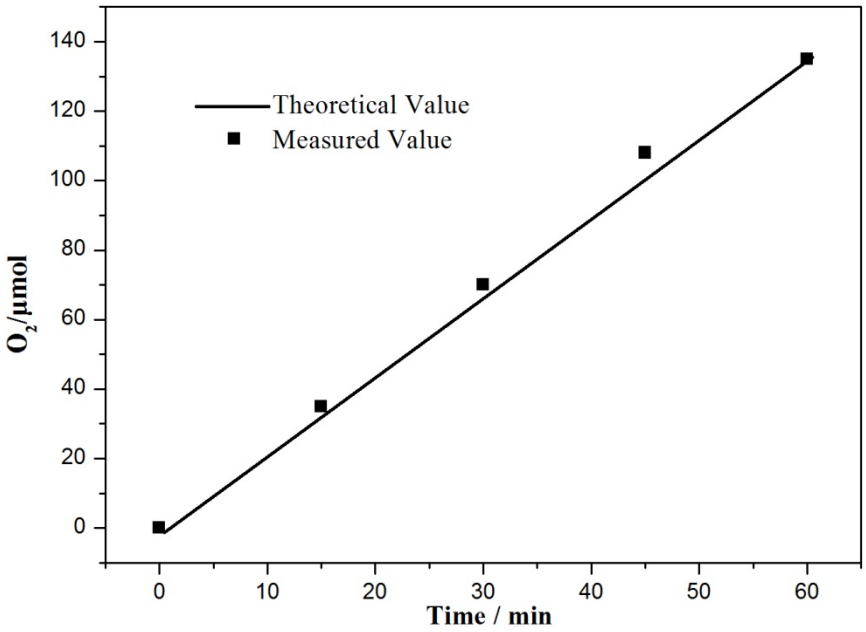

Fig. S1 Electrocatalytic efficiency of O_2 production over $CuCo_2O_4$/NF at a potential of ca. 1.50 V, measured for 60 min.

Fig. S2 A photograph showing electrocatalytic test on the $CuCo_2O_4$/NF electrodes.

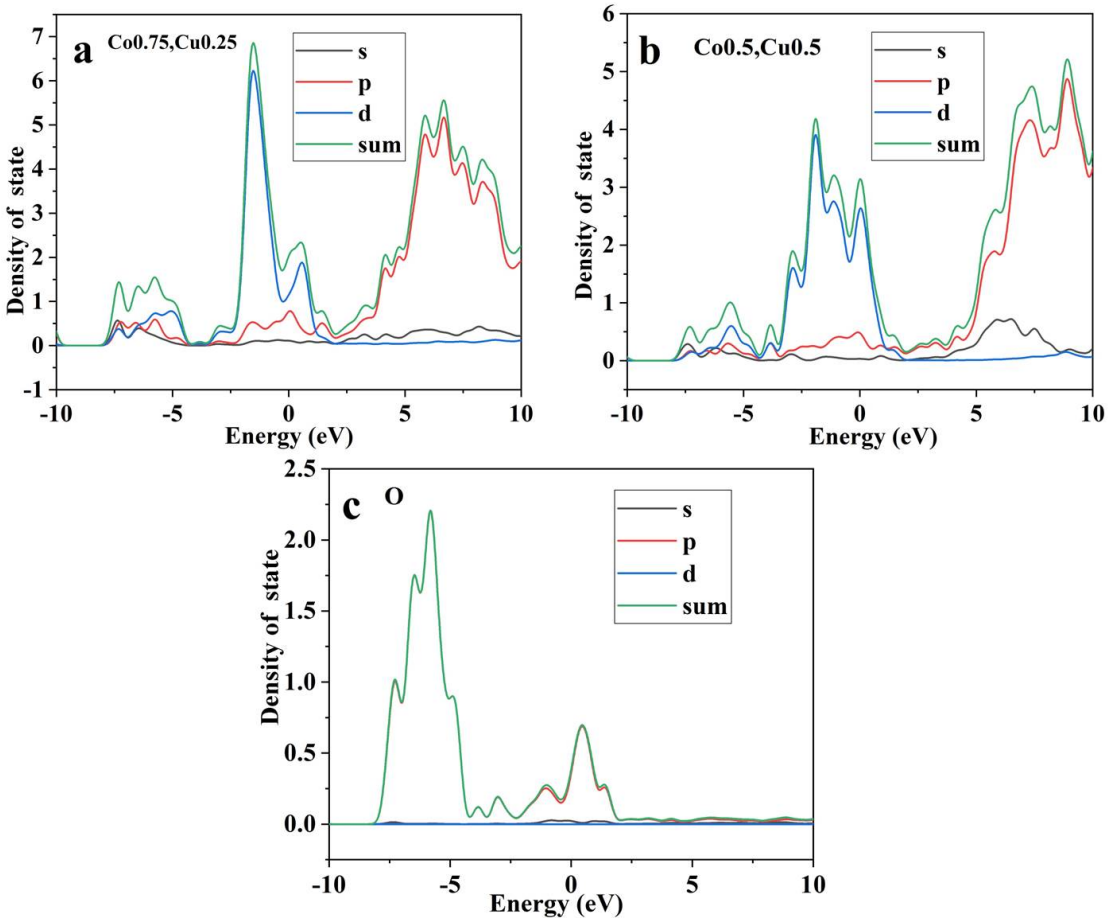

Fig. S3 Density of states for $CuCo_2O_4$, (a) Co 0.75, Cu 0.25 , (b) Co 0.5, Cu 0.5 and (c) O.

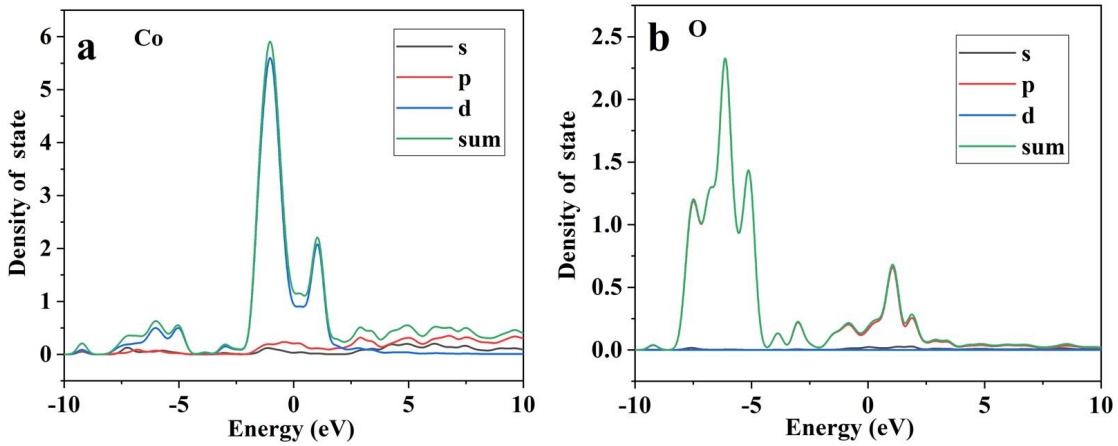

Fig. S4 Density of states for Co_3O_4, (a) Co and (b) O.