

Balancing Electronic Structure and Surface Reconstruction of Cu-based Nanostructure for Iodide Oxidation Reaction

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1. Experimental Section

1.1 Preparation of Electrodes

A commercial copper foam ($2.0 \times 3.0 \text{ cm}^2$) was sequentially cleaned with 3.0 M hydrochloric acid, deionized water, and ethanol to remove surface impurities. Subsequently, $\text{Cu}(\text{OH})_2$ nanowires were grown in situ on the foam via a wet-chemical oxidation process. Specifically, the cleaned foam was immersed in an aqueous solution containing 0.15 M ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and 2.5 M sodium hydroxide (NaOH) for 30 minutes at room temperature. The resulting $\text{Cu}(\text{OH})_2$ -coated foam (denoted $\text{Cu}(\text{OH})_2/\text{CF}$) was thoroughly rinsed with deionized water and ethanol, then dried at 60°C overnight. To prepare CuO-coated foam (CuO/CF), the $\text{Cu}(\text{OH})_2/\text{CF}$ sample was calcined at 180°C for 1 hour in air. Alternatively, thermal treatment of $\text{Cu}(\text{OH})_2/\text{CF}$ at 400°C for 1 hour in an argon atmosphere yielded $\text{Cu}_2\text{O}/\text{CF}$. Finally, metallic copper foam (Cu/CF) was obtained via electrochemical reduction of CuO/CF in an Ar-saturated 1 M KHCO_3 solution.

1.2 Characterizations

X-ray diffraction patterns were collected on a Rigaku D8 diffractometer. The morphologies of the electrodes were investigated using scanning electron microscope. Raman spectroscopy was conducted using an HR Evolution Raman spectrometer (Horiba) with a laser excitation wavelength of 532 nm. The in situ electrochemical three-electrode cell comprised Cu-based electrocatalysts as the working electrode, Ag/AgCl as the reference electrode, and a Pt wire as the counter electrode. The electrolyte used was 1 M KOH with the addition of a 0.33 M KI solution.

1.3 Electrochemical Analyses

The electrochemical performance was evaluated on an electrochemical workstation (CS350H, Wuhan CorrTest Instrument Corp.) using a standard three-electrode system. The as-obtained, self-supported electrodes were used directly as working electrodes. A carbon rod was used as the counter electrode, and Ag/AgCl was used as the reference electrode. The electrolyte for the OER was 1 M KOH solution and the electrolyte for IOR was 1 M KOH solution in the presence of 0.33 M KI. Linear

sweep voltammetry (LSV) curves were recorded at a scan rate of 5 mV s⁻¹. Chronopotentiometry was performed at a constant current density of 50, 100, and 200 mA cm⁻². All the potentials were referenced to the RHE by the Nernst equation ($E(\text{versus RHE}) = E(\text{versus Ag/AgCl}) + 0.197 + 0.059 \times \text{pH}$). All the curves were calculated by iR compensation.

2. Simulation methods

All spin-polarized DFT calculations were performed using the ABINIT code^{1,2} with the projector-augmented wave (PAW) method.³ The PAW pseudopotentials were employed. The kinetic energy cutoff was set at 14.7 Ha. The Perdew-Burk-Ernzerhof (PBE) functional⁴ under the generalized gradient approximation (GGA) scheme was used for electron exchange correlations. The CuO substrate was modeled by the p(2×2) unit cell of CuO (111) containing three layers of O-Cu-O configuration. As a result, there are three copper atomic layers and six oxygen atomic layers, in which the bottom three layers were fixed to simulate the bulk properties and the uppermost six layers were fully relaxed. The CuO (111) surface was chosen because this surface has previously been reported to be thermodynamically stable with lower free energy^{5, 6} and it has also been observed in the experiment. A vacuum space of 12 Å along the c direction was added for all substrates to avoid strong interactions between neighboring substrates. The Brillouin zone was sampled using a Gamma centered k-mesh with spacing smaller than $2\pi \times 0.04/\text{\AA}$ until the energy and force converged within 1×10^{-5} eV and 0.02 eV/Å, respectively. The adsorption energy was calculated as

$$\Delta E_{\text{ads}} = E_{\text{ads-A}} - E_{\text{slab}} - E_{\text{A}} \quad (1)$$

where $E_{\text{ads-A}}$ is the total energy of the adsorbate–substrate system; E_{slab} is the energy of the naked surface slab; and E_{A} is the energy of the isolated atom I. Under such definition, a negative E_{ads} implies an exothermic process for the adsorption of this molecule. The free energy was calculated as

$$\Delta G = \Delta E_{\text{ads}} + \Delta E_{\text{ZPE}} - T\Delta S \quad (2)$$

where ΔE_{ads} is the adsorption energy, ΔE_{ZPE} corresponds to the zero-point energy,

and ΔS denotes the entropy difference, T is the standard temperature (298 K). The zero-point energy and vibrational entropy contributions were estimated from vibrational frequency calculations of the adsorbed species and gas-phase molecules using the harmonic approximation, as implemented in the vaspkit⁷. The entropy ΔS and ΔE_{ZPE} values for the three slabs with adsorbed I^* are summarized in **Tab. S2** for reference.

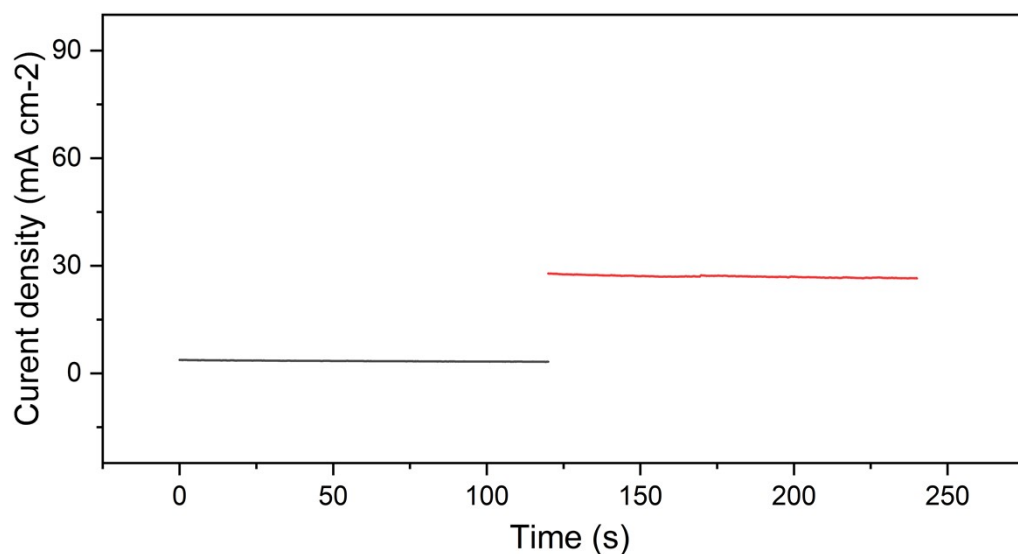


Fig. S1 Current densities response of CuO NA/CF before and after injecting KI.

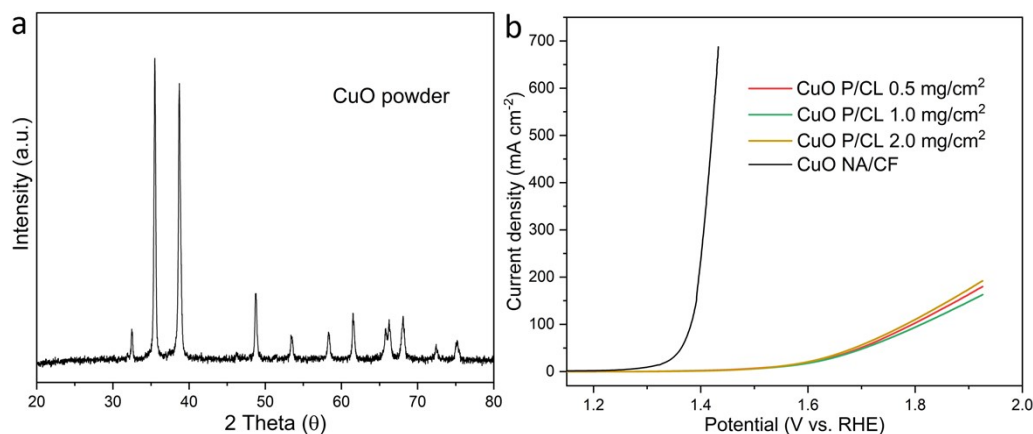


Fig. S2 Polarization curves of CuO NA/CF and CuO powder loaded on the carbon cloth (CuO P/CL) in 1 M KOH + 0.33 M KI.

To emphasize the significance of nanoscale structural engineering in enhancing electrocatalytic performance, we employed commercially available CuO powder as a

model catalyst and uniformly deposited it onto carbon paper substrates via a simple drop-casting method. By varying the loading amount, we systematically evaluated the relationship between catalyst mass and electrochemical activity. The results revealed that CuO NA/CF exhibited markedly improved performance, characterized by lower overpotentials and higher current densities. These enhancements are attributed to the nanostructured nature of the CuO integrated with CF, which provide a higher electrochemically active surface area, improved exposure of active sites, and more efficient electron/ion transport pathways.

Tab. S1 Comparisons of the IOR activity of CuO NA/CF electrode with other reported transition-metal-based electrocatalysts.

Catalysts	Current density (mA cm ⁻²)@ Potential (V)	Reference
CuO NA/CF	500@1.42	This work
CuO NA/CF	200@1.39	This work
Se ₂₅ -NiTe/NF	100@1.376	8
Pt/C	200@1.6	9
Co1Fe1-N-C	50@1.35	10
FeCo-DACs	120@1.35	11
Ni-Co(OH) ₂ NSAs	20@1.3	12

Tab. S2 Entropy and zero-point energy for I*

Substrate	Entropy (eV/K)	Zeron-point energy (eV)
CuO(111)	5.43×10 ⁻⁴	0.0138
Cu(111)	5.28×10 ⁻⁴	0.0123
Cu ₂ O(111)	5.39×10 ⁻⁴	0.0124

Tab. S3 Adsorption energies for I*

Substrate	Energy (eV)
CuO (111)	−0.752
Cu (111)	−1.584
Cu ₂ O (111)	−1.183

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