Supporting Information

Crystal Structure Optimization of Copper Oxides for Benzyl Alcohol Oxidation Reaction

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1. Experimental Section

1.1 Preparation of Electrodes

Typically, a piece of Cu foam $(3.0 \times 3.0 \text{ cm}^2)$ was cleaned with HCl solution (3.0 M), deionized water, and ethanol before use. Cu(OH)₂ nanowires *in situ* grow from the commercial Cu foam using a wet-chemical method. The cleaned Cu foam was immersed into an aqueous solution containing 0.15 M (NH₄)₂S₂O₈ and 2.5 M NaOH for 30 min at ambient temperature. The resultant sample was washed several times with deionized water and ethanol, and dried at 60 °C overnight, denoted as Cu(OH)₂/CF. The Cu(OH)₂/CF was calcined in a tube furnace at 180 °C for 1 h in an air atmosphere to form CuO/CF.

Briefly, $Cu(OH)_2$ nanowire arrays were *in situ* grown on the surface of CF by a chemical oxidation reaction in alkaline solutions (labeled as $Cu(OH)_2/CF$). Afterward, the as-prepared $Cu(OH)_2/CF$ was calcined at 180 °C for 1 h, yielding dark brown CuO/CF. For comparison, $Cu(OH)_2/CF$ was heated in an Ar atmosphere at 400 °C for 1 h to obtain Cu_2O/CF . Additionally, the phase transformation from CuO to Cu was realized by an electroreduction process in Ar-purged 1 M KHCO₃ solution (labeled as Cu/CF).

The Ni(OH)₂/CF and Co(OH)₂/CF were fabricated by the hydrothermal method. Afterward, the conversion of Ni(OH)₂ into NiO (NiO/CF) was conducted by the heat treatment of the hydrothermal product at 350 °C for 1 h in the air. Co(OH)₂/CF and CoO/CF were prepared using similar procedures.

1.2 Characterizations

X-ray diffraction (XRD) patterns were collected on a Rigaku D8 diffractiometer. The morphologies of the electrodes were investigated using scanning electron microscope (SEM: Zeiss Supra 55). The microstructures were studied by transmission electron microscope (TEM: FEI TECNAI G at 200 kV) and high-resolution TEM (HRTEM). X-ray photoelectron spectroscope (XPS) was performed using a scanning X-ray microprobe (K-Alpha Thermo VG Scientific). High-performance liquid chromatography (HPLC) was measured on a Shimadzu ultraviolet-visible detector of 254 nm using a 4.6 mm \times 150 mm Shim-pack GWS 5 μ m C18 column. ¹H nuclear magnetic resonance (NMR) spectra were collected using Bruker AM 300 (300 MHz). Single-crystal data was collected using a single-crystal X-ray diffractometer (Bruker Smart Apex II).

1.3 Electrochemical Analyses

The electrochemical performance was evaluated on an electrochemical workstation (Bio-logic VMP-300) 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 BAOR was 1 M KOH solution in the presence of 0.2 M BA. Linear sweep voltammetry (LSV) curves were recorded at a scan rate of 5 mV s⁻¹. *In situ* electrochemical impedance spectroscopy (EIS) was conducted in 1 M KOH with and without 0.2 M BA at frequencies ranging from 100 kHz to 0.01 Hz, with an amplitude voltage of 5 mV and applied potentials ranging from 1.1 V to 1.7 V (versus RHE). Chronopotentiometry was performed at a constant current density of 200 mA cm⁻². All the potentials were referenced to the RHE by the Nernst equation (E(versus RHE) = E(versus Ag/AgCl) + 0.197 + 0.059 × pH). All the curves were calculated by iR compensation.

2.4 Theoretical Calculations

The present calculations were performed by the Vienna Ab initio Simulation Package implementation of density functional theory (DFT).^{40, 41} Consequently, the H $1s^1$, C $2s^22p^2$, O $2s^22p^4$, and Cu $4s^{13}d^{10}$ states were treated as the valence electrons. Geometry optimizations and adsorption energies (E_{ads}) were calculated using the generalized gradient approximation (GGA)-Perdew-BurkeErnzerhof (PBE) functional. In these calculations, the energy cut-off was set to 500 eV. The force and energy convergence criteria were set as 0.01 eV/Å and 10⁻⁴ eV, respectively. To describe the strong electron correlations of transition metals, the Hubbard parameter U is introduced for Cu-3d with the U = 7.5 eV and J = 0.98 eV. The vacuum layers on the Cu (111), Cu₂O (111), CuO (111), and Cu(OH)₂ (111) surfaces were set to be 20 Å.

For the above surface, the adsorption energy of BA on the surface was calculated using Equation (1)

$$E_{ad} = E_{(surface-BA)} - E_{(surface)} - E_{(BA)}$$
 Equation (1)

where $E_{(surface)}$ is the energy of the optimized Cu (111), Cu₂O (111), CuO (111), and Cu(OH)₂ (111) surfaces: $E_{(BA)}$ is the energy of BA; and $E_{(surface-BA)}$ is the total energy of the optimized adsorption structure of BA on the surface. A negative adsorption energy indicates an effective adsorbate binding.



Fig. S1. SEM patterns of bare CF.



Fig. S2. SEM patterns of Cu(OH)₂/CF.



Fig. S3. SEM patterns of CuO/CF.



Fig. S4. SEM patterns of Cu₂O/CF.



Fig. S5. SEM patterns of Cu/CF.



Fig. S6. Nyquist plots of Cu/CF, Cu₂O/CF, CuO/CF, and Cu(OH)₂/CF electrodes in 1



Fig. S7. Bode plots of CuO/CF for (a) OER (1 M KOH) and (b) BAOR (1 M KOH with 0.2 M BA).

In terms of the BAOR process, the LSV curve shows significantly increased current density before 1.60 V, suggesting that the BAOR process occurs in a low potential range.



Fig. S8. High-resolution Cu 2p XPS spectra of CuO/CF electrode before and after the BAOR.



Fig. S9. (a) TEM, (b) HRTEM images and (c) corresponding elemental mapping of CuO/CF after the BAOR.



Fig. S10. SEM patterns of CuO/CF after the BAOR.



Fig. S11. XRD patterns of Co(OH)₂/CF, Ni(OH)₂/CF, CoO/CF, and NiO/CF.



Fig. S12. SEM patterns of (a) $Ni(OH)_2/CF$ and (b) $Co(OH)_2/CF$.



Fig. S13. SEM patterns of (a) NiO/CF and (b) CoO/CF.



Fig. S14. The potentials to attain the current density of 200 mA cm⁻².



Fig. S15. Electrochemical CV scans recorded for (a) CuO/CF, (b) CoO/CF, and (c) NiO/CF at different potential scanning rates. Scan rates are 20, 40, 60, 80, 100, and 120 mV s^{-1} .



Fig. S16. XRD pattern of CF calcined at 350 °C for 1 h in an air atmosphere.



Fig. S17. SEM patterns of CF after a heat treatment in the air.



Fig. S18. LSV curves of bare CF and CF-AC toward BAOR.



Fig. S19. Standard curves of (a) benzoic acid, (b) benzyl alcohol, and (c) benzaldehyde.

High Performance Liquid Chromatography (HPLC) was used to identify and quantify the yield and faradaic efficiency of BA oxidation.¹

The yield (%) of benzoic acid formation were calculated following Equation:

Yield (%) = (mol of benzoic acid)/(mol of theoretical production) $\times 100\%$

The FE for the formation of benzoic acid on catalyst was calculated using the following equation:

FE (%) = (mol of benzoic acid)/(total passed charge/4F))×100% (3)

Faraday constant (F) = 96,485 $C \cdot mol^{-1}$



Fig. S20. The structural models of (a) parallel and (b) vertical adsorption of benzoic acid on Cu (111) surface.

Considering that the CuO (111) surface is thermodynamically stable with lower free energy, we chose (111) surfaces for different Cu-based phase structures.

Additionally, for the Cu_2O and CuO substrates, the electronic transfer between the substrates and BA further promotes the stability of the adsorption structure. In particular, in the CuO phase structure, the charge can be transferred from the Cu atoms to the entire BA molecule, which verifies the strong coupling effect between BA and the phase substrate. Therefore, the adsorption capacity of BA can be increased by regulating the interaction between BA and the phase structure substrate, which enhances BAOR activity.

Catalysts	Potential at J# ^a	Electrolyte	Ref.
CuO/CF	1.39 V @ J ₂₀₀	1 M KOH + 0.2 M BA	This work
A-Ni-Co-H/NF	1.35 V @ J ₁₀₀	1 M KOH + 0.1 M BA	2
CC@NiO/Ni ₃ S ₂	1.39 V @ J ₅₀	1 M KOH + 0.2 M BA	3
Ni@NC-280	1.39 V @ J ₂₅	1 M KOH + 0.5 mM BA	1
NiCo-61-MOF/NF	1.52 V @ J ₃₃₈	1 M KOH + 0.1 M BA	4
Co ₃ O ₄ /NF	1.5 V @ J ₈₆	1 M KOH + 20 mM BA	5
Ni(OH) ₂	1.33 V @ J ₁₀₀	1 M NaOH + 0.1 M BA	6
Co _{0.83} Ni _{0.17} /AC	1.54 V @ J ₁₀	1 M KOH + 10 mM BA	7
NC@CuCo ₂ N _x /CF	1.44 V @ J ₂₀₀	1 M KOH + 15 mM BA	8

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

 a J_{\#} means at a current density of a given value (#, mA cm^-2)

Crystal	Benzoic acid		
CCDC number	2204390		
Empirical formula	$C_7H_6O_2$		
Formula weight	122.12		
<i>T</i> (K)	296.15		
Crystal system	monoclinic		
Space group	$P2_{1}/n$		
<i>a</i> (Å)	5.502(3)		
<i>b</i> (Å)	5.137(3)		
<i>c</i> (Å)	21.927(15)		
α (deg)	90		
β (deg)	97.045(16)		
γ (deg)	90		
$V(Å^3)$	615.0(7)		
Ζ	4		
$D_{c} (g \cdot m^{-3})$	1.319		
μ (mm ⁻¹)	0.097		
F (000)	256.0		
Crystal size (mm ³)	$0.14 \times 0.13 \times 0.01$		
2θ range (deg)	3.744 to 50.08		
Reflens collected	2498		
Independent reflens	1074		
Data/restraints/parameters	1074/0/72		
$R_{ m int}$	0.0872		
Goodness-of-fit on F^2	0.910		
$R_1/\omega R_2 \left[I > 2\sigma(I)\right]$	0.0834/0.1830		
$R_1/\omega R_2$ (all data)	0.2130/0.2237		
Max./Min. $\Delta \rho$ (e'Å ⁻³)	0.22/-0.21		

Tab. S2. The X-ray single crystals data summary of compound benzoic acid.

Tab. S3. The adsorption energy (E_{ad}) corresponding to vertical and parallel modes of benzoic acid on Cu (111), Cu₂O (111), CuO (111), and Cu(OH)₂ (111) surface. The unit is eV.

	Cu (111)	Cu ₂ O (111)		$C_{2}O(111)$	$C_{\rm W}(\rm OH)$ (111)
		Surface1	Surface2	CuO (III)	$Cu(OH)_2(111)$
Eab (parallel)	0.16	-0.34	-1.25	-0.78	0.89
Eab (vertical)	0.12	-0.99	-1.29	-1.49	0.08

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