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Rational design and insights into the synergistic activity of CeO_x and Zn on Cu_2Se for the highly- selective electrocatalytic methanol oxidation to formic acid

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Materials Characterizations

X-ray diffraction (XRD) signals were characterized by Bruker D8 Venture with Cu Ka radiation (λ =1.54178Å) at a scan rate of 5° min⁻¹ in the range from 10° to 80°. Field emission scanning electron microscopy (SEM, ZEISS Supra 55) was used to detect the morphology of the samples. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) was performed using the Tecnai G2 F30 S-TWIN. Raman spectra were recorded using a Raman spectrometer of a Renishaw confocal microscope operated at room temperature with a laser excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi) was done to identify the chemical state of the sample surface with carbon (C 1s) as a reference at the binding energy of 284.8 eV. To explore the content of metallic elements, optical emission spectroscopy (EDS) were carried out. Ultraviolet photoelectron spectroscopy (UPS) was performed by a PHI 5000 Versa Probe III with a He I source (21.22 eV) at a negative bias of 5.0 V.

2. Electrochemical measurements

The electrocatalytic performances were evaluated in an electrochemical workstation (CHI 760E, China) with a standard three-electrode system. The catalytic activity of samples was tested in 1.0 M KOH+4 M CH₃OH. The as-prepared samples were directly utilized as the working electrodes. The saturated calomel electrode (SCE) acted as the reference electrode, Pt wire or graphite rod acted as the counter electrode. All the linear sweep voltammetry (LSV) curves were obtained with a scan rate of 5 mV s⁻¹ with 90% iR compensation. All the measured potentials were converted into a reversible hydrogen electrode (RHE) by the following formula: $E_{RHE} = E_{SCE} + 0.059 \text{ pH} + 0.241$ V. Electrochemical impedance spectroscopy (EIS) was performed within the frequency range from 0.01 to 10⁵ Hz at an AC amplitude of 5 mV. The in situ electrochemical impedance spectroscopy (EIS) test was measured with the frequency range from 10⁵ to 10⁻² Hz at different potentials. The electrical double-layer capacitance (C_{dl}) of the electrodes was calculated using cyclic voltammograms (CV) with various scan rates of

40, 60, 80, 100, and 120 mV s⁻¹ in a potential range free from non-faradaic region. The stability tests in different media were performed at approximately 50 mA cm⁻² using chronopotentiometry measurements without iR compensation.



Fig. S1. SEM images (a-b) of Cu(OH)₂.



Fig. S2. SEM images (a-b) of Cu(OH)₂/(Zn)Ce-ZIF.



Fig. S3. SEM images of (a-b) Cu₂Se and (c-d) Cu₂Se/CeO_x.



Fig. S4. Raman spectra of the Cu₂Se, Cu₂Se/CeO_x, and Cu₂Se/(Zn)CeO_x.

Samples	area of Ce ⁴⁺			sum	area o	f Ce ³⁺	sum	
$Cu_2Se/(Zn)CeO_x$	3770	3737	3997	3980	15484	6948	4287	11235
Ce ⁴⁺ /Ce ³⁺	1.378193146							
Cu ₂ Se/CeO _x	3361	1753	2146	1208	8468	2480	1805	4285
Ce ⁴⁺ /Ce ³⁺	1.976196032							

Table S1. The ratio of Ce^{4+}/Ce^{3+} in the Ce 3d of $Cu_2Se/(Zn)CeO_x$ and Cu_2Se/CeO_x .







Fig. S6. LSV plots of (a) Cu_2Se , (b) Cu_2Se/CeO_x , and (c) $Cu_2Se/(Zn)CeO_x$ with different concentrations.



Fig. S7. CV curves of (a) Cu_2Se , (b) Cu_2Se/CeO_x , and (c) $Cu_2Se/(Zn)CeO_x$ at different scan rates.



Fig. S8. the Tafel plots in OER



Fig. S9. ¹H-NMR spectra of the electrolyte before and after the MOR test.



Fig. S10. The SEM images of Cu₂Se after MOR



Fig. S11. The SEM images of Cu_2Se/CeO_x after MOR



Fig. S12. The SEM images of $Cu_2Se/(Zn)CeO_x$ after MOR

Electrocatalyst	Potential at 100 mA cm ⁻²	electrolyte	Tafel slope (mV dec ⁻¹)	Ref.	
	(V)				
Cu ₂ Se/(Zn)CeO _x	1.36	1 M KOH+4	95.2	This work	
		M MeOH			
Co _x P@NiCo-	1.34	1 M KOH+0.5	58	J. Energy Chem.	
LDH/NF		M MeOH		2020, 50, 314–323	
NiCoxP@NiCo-	1 35	1 M KOH+0.5	UN	J. Alloys Compd.	
LDH/CC	1.55	M MeOH	UN	2022, 906, 164305	
FeRu-MOF	1.05	1 M KOH+4 M	40.0	J. Mater. Chem. A,	
(100:3)/NF	1.37	МеОН	48.0	2023, 11, 2876–2888	
	1 401	1 M KOH+1 M	2 0.1	Green Chem., 2024,	
Fe ^{EP} -NiCo-LDH	1.401	МеОН	29.1	26, 2638-2644	
Os-Ni _x P/N-		1 M KOH+1 M	•	J. Mater. Chem. A,	
C/NF)	1.41	МеОН	20	2022, 10, 18126	
N'M I DH	1 41	1 M KOH+3 M	20.4	Nature Comm. 2023,	
N1Mn LDH	1.41	МеОН	39.4	14, 1686	
	1 42	1 M KOH+1 M	24	J. Mater. Chem. A,	
CINFS(WINISE/CC	1.45	MeOH	24	2019, 7, 25878	
D4 NI; C	1 45	1 M KOH+1 M	69	Nano-Micro Lett.	
Pt-IN1352	1.45	MeOH	08	2024, 16, 80	
				ACS Appl. Mater.	
Nb ₂ O ₅ -HD@NF	1.47	I M KOH+3 M	31.8	Interfaces 2024, 16,	
		МеОН		44938-44946	
	1 40	1 M KOH+0.5	122.0	Small 2024, 20,	
N1-IVION/NF-6	1.48	M MeOH	122.9	2303300	
CUONS/OF	1 47	1 M KOH+1 M	127	Angew. Chem. Int.	
CuONS/CF	1.4/	МеОН	13/	Ed. 2021, 60, 3148	

Table S2. Comparison of recently reported electrocatalysts for selective MOR to formate.



Fig. S13. Nyquist plots of Cu₂Se/(Zn)CeO_x in (a) 1.0 M KOH, (b) 1.0 M KOH+1.0 M MeOH and (c) 1.0 M KOH+4.0 M MeOH at different potentials.

	R (Ω)						
Potential (V)	1.0 M KOH	1.0 M KOH+1.0 M MeOH	1.0 M KOH+4.0 M MeOH				
1.14	673	1414	1413				
1.24	504	520.9	307				
1.34	272	61.33	26.92				
1.44	167	8.15	4.9				
1.54	78	2.34	1.87				
1.64	13	1.1	1.1				
1.74	6.5	0.76	0.8				

Table S3. Optimum fit R values of the in-situ EIS data for $Cu_2Se/(Zn)CeO_x$.



Fig. S14. Nyquist plots of Cu₂Se in (a) 1.0 M KOH, (b) 1.0 M KOH+1.0 M MeOH and (c) 1.0 M KOH+4.0 M MeOH at different potentials.

	R (Ω)						
Potential (V vs. RHE)	1.0 M KOH	1.0 M KOH+1.0 M MeOH	1.0 M KOH+4.0 M MeOH				
1.17	865.3	172.8	494.6				
1.27	449.5	149.1	56.31				
1.37	248.5	93.02	8.09				
1.47	181.8	10.49	2.93				
1.57	63.27	4.485	1.64				
1.67	12.83	4.089	1.23				
1.77	5.82	4.49	0.85				

Table S4. Optimum fit R of the in-situ EIS data for Cu_2Se .



Fig. S15. XPS spectra of (a) Ce 3d, (b) O 2p, (c) Cu 2p, and (d) Se 3d in the asprepared Cu₂Se/(Zn)CeO_x and the after MOR ones.



Fig. S16. Raman spectra of the as-prepared catalysts after the OER.



Fig. S17. Raman spectra of the as-prepared catalysts after the MOR.



Fig. S18. XPS spectra of (a) Cu 2p and (b) Se 3d in the as-prepared and the activated Cu₂Se/(Zn)CeO_x.

Samples	Zn/Ce (%)
as-prepared	40.48583
CVs-actived	17.60563
after MOR	8.92857

Table S5. ICP-OES elemental analysis results of Zn and Ce contents in $Cu_2Se/(Zn)CeO_x$.

Samples	area of Ce ⁴⁺			sum	area of Ce ³⁺		sum	
as-prepared	3770	3737	3997	3980	15484	6948	4287	11235
Ce ⁴⁺ /Ce ³⁺	1.378193146							
CVs-actived	13018	9911	1116 8	9391	43488	11817	9296	21113
Ce ⁴⁺ /Ce ³⁺	2.059773599							
After MOR	6383	4065	4391	4263	19102	4003	2666	6669
Ce ⁴⁺ /Ce ³⁺	2.864297496							

Table S6. The ratio of Ce^{4+}/Ce^{3+} in the Ce 3d of $Cu_2Se/(Zn)CeO_x$.

Samples	area of	Cu ⁺	sum	area of Cu ²⁺		sum			
as-prepared	18945	8636	27581	15585	8312	23897			
Cu ⁺ /Cu ²⁺	1.15416161								
CVs-actived	31618	17600	49218	12388	30307	42695			
Cu ⁺ /Cu ²⁺	1.152781356								
After MOR	17687	9210	26897	15680	6466	22146			
Cu ⁺ /Cu ²⁺	1.214530841								

Table S7. The ratio of Cu^+/Cu^{2+} in the Cu 2p of $Cu_2Se/(Zn)CeO_x$.