

Supporting Information

Organic molecule-assisted intermediate adsorption for conversion of CO₂ to CO by electrocatalysis

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1. Experimental section

1.1 Chemical Reagents

Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, analytically pure), 5-mercapto-1-methylimidazole ($\text{C}_2\text{H}_4\text{N}_4\text{S}$, 98%), dimethyl sulfoxide ($\text{C}_2\text{H}_6\text{SO}$, analytically pure) and potassium bicarbonate (KHCO_3 , analytically pure) were obtained from Aladdin. Nafion solution (D-521, 5 wt%) was acquired from Alfa Aesar. D_2O (analytically pure) was procured from Macklin. Isopropanol ($\text{C}_3\text{H}_8\text{O}$, analytically pure), acetone ($\text{C}_3\text{H}_6\text{O}$, analytically pure), hydrochloric acid (HCl, 36.0~38.0%, analytically pure) and anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$, analytically pure) were purchased from Sinopharm. All reagents were used without further processing.

1.2 Characterization

The sample's phase composition was analyzed using a Shimadzu LabX XRD-6000 X-ray diffractometer (Japan), with $\text{Cu K}\alpha$ radiation and a transmission wavelength of 1.54 Å. The test range (2θ) was set to $20^\circ \sim 80^\circ$, with a scanning speed of 5° min^{-1} . The sample's microscopic morphology was observed using a Hitachi scanning electron microscope (SU8100, Japan) at 5 kV and a test current of 10 μA . The lattice fringe of the sample was characterized by transmission electron microscopy (FE TF20, United States) at a voltage of 200 kV, along with high-angle annular dark field imaging and element distribution. The sample's element information was obtained from a Thermo ESCALAB 250XI using $\text{Al K}\alpha$ radiation (1486.7 eV). To characterize MMTZ, the ATR accessory of a Thermo Nicolet iS10 FTIR (United States) was used.

1.3 Material and working electrode preparation

The conductive carbon paper (HCP020N, Shanghai Hesen) was cleaned by subjecting it to ultrasonic exposure with 5 M hydrochloric acid, acetone, ethanol, and 18.25 MΩ ultra-pure water for 30 minutes to remove any metal and organic impurities from the surface. The cleaned carbon paper was then dried in a vacuum drying oven at 60 °C for 12 hours.

To grow Zn NSs on the conductive carbon paper, a 0.5 M zinc sulfate solution was prepared using ultra-pure water as the electrolyte. The electrodeposition was carried out using a Pt sheet electrode (2 × 2 cm) as the counter electrode and a 3 M KCl saturated Ag/AgCl electrode as the reference electrode. The electrodeposition parameters were 150 mA cm⁻² for 1 minute. After electrodeposition, the surface of the electrode was rinsed with ultra-pure water to remove residual ZnSO₄ and then dried with an infrared baking lamp to yield Zn NSs.

To prepare MMTZ solutions of different concentrations (10, 20, 40, and 80 mg mL⁻¹), isopropanol was used as a solvent. Then, using a pipette gun, 40 μL of the MMTZ solution was dropped onto the surface of the Zn NSs and dried under an infrared baking lamp.

In addition, freshly prepared samples were used for each test and the samples were vacuum-sealed to protect against oxidation before testing.

1.4 Electrochemical test and product analysis

The electrochemical test was performed using a CHI760 workstation (Shanghai Chenhua). The reactor was a sealed double-chamber electrolytic cell made by Goldstar, and the Nafion produced by DuPont[®] 117 was used as the proton exchange membrane between the cathode chamber and the anode chamber, with 30 mL 0.5 M KHCO₃ electrolyte in each chamber. The reference electrode was a 3 M KCl saturated Ag/AgCl electrode and the counter electrode was a Pt plate electrode (2 × 2 cm). The effective area of the working electrode is 1 cm². To begin, the electrolyte in the cathode chamber

was filled with high-purity CO₂ for 30 minutes to saturate the CO₂ in the electrolyte and exhaust the air in the upper part of the chamber before evaluating the performance of the electro-catalytic CO₂ reduction. The flow rate of CO₂ was 30 sccm (standard cubic centimeter per minute) and was controlled by a mass flow meter (Beijing Sevenstar, D07 7K). The linear sweep voltammetric curve (LSV) test voltage range was -0.6 ~- 1.1 V vs. RHE, and the scanning speed was 10 mV s⁻¹. The test voltage of electrochemical impedance spectroscopy was -0.9 V vs. RHE, the disturbance voltage was 10 mV, and the frequency was 100000 Hz ~ 0.1 Hz. The double-layer capacitance (C_{dl}) was measured and calculated by the cyclic voltammetric curve method, with the scanning speed being set at 40, 60, 80, 100, 120 mV s⁻¹. The slope obtained by fitting the scanning speed and the current density difference at -0.45 V vs. RHE was the double-layer capacitance. The formula for calculating the voltage (E (V vs. RHE)) relative to the reversible hydrogen electrode¹ is as follows:

$$E \text{ (V vs. RHE)} = E \text{ (V vs. Ag/AgCl)} + 0.197 \text{ V} + 0.05916 \times \text{pH} \quad (1)$$

The pH value of the 0.5 M KHCO₃ electrolyte saturated with CO₂ was measured to be 7.2. The single oxidative linear sweep voltammetry curve was measured in 0.1 M KOH electrolyte saturated with N₂, using a Pt plate electrode as the counter electrode and a 3 M KCl saturated Ag/AgCl electrode as the reference electrode. The Pt plate electrode had a size of 2 × 2 cm.

The gaseous products were quantitatively analyzed online by gas chromatography (GC9860). The liquid products in the electrolyte were analyzed using the one-dimensional hydrogen spectrum of a Brooke's 400 MHz nuclear magnetic resonance spectrometer, with DMSO as the internal standard. For the test solution group, 200 μL of electrolyte, 200 μL of D₂O, and 100 μL of DMSO (1/1000, V/V) were used, with 64 scanning times.

$$\text{FE} = (\text{ppm} \times \text{flow rate} \times nF) / ((RTI_{\text{total}}) \times 100\%) \quad (2)$$

where ppm refers to the concentration of CO obtained from chromatography, the flow rate is the flow rate of CO₂, n is the electron-transfer number, F is the Faraday constant with a value of 96485 C mol⁻¹, P is atmospheric pressure with a value of 101325 Pa, R is the gas constant with a value of 8.314 J mol⁻¹ K⁻¹, T is ambient temperature, and I_{total}

represents the current density.

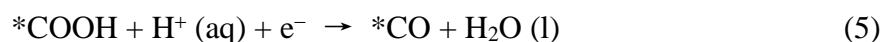
1.5 Density functional calculation

To begin, the model was constructed using Materials Studio (version 2019) software developed by Accelrys in the United States, followed by performing relevant density functional calculations using the DMol3 module. The exchange interaction between electrons was optimized using the generalized gradient approximation (GGA) with the PBE function. The supercell size of metal Zn on the (101) crystal surface was set to 2×4 , with a vacuum layer thickness of 15 Å along the Z-axis and a k-point value of $5 \times 5 \times 1$. The convergence criteria for geometric structure optimization were set to energy less than 10^{-5} Ha, maximum force of $0.002 \text{ Ha } \text{Å}^{-1}$, and maximum distance of 0.005 Å . The convergence standard for the electron self-consistent field was set to less than 10^{-6} .

The formula for calculating Gibbs free energy (G)² is as follows:

$$G = E + \text{ZPE} - TS \quad (3)$$

Where E is the single-point energy, ZPE is the zero-point energy, T is the temperature (298.15 K), and S is the entropy. E is obtained from the energy obtained after geometric structure optimization, while ZPE and S are obtained by calculating the frequency properties of the adsorbates. The electrocatalytic reduction of CO₂ to produce CO undergoes three reaction steps³, as shown below:



Where * represents the catalyst substrate. The Gibbs free energy change (ΔG) of the three reaction steps⁴ is expressed as follows:

$$\Delta G[4] = G[*\text{COOH}] - G[\text{CO}_2] - G[*] - G[\text{H}^+ + \text{e}^-] \quad (7)$$

$$\Delta G[5] = G[*\text{CO}] + G[\text{H}_2\text{O}] - G[*\text{COOH}] - G[\text{H}^+ + \text{e}^-] \quad (8)$$

$$\Delta G[6] = G[\text{CO}] + G[*] - G[*\text{CO}] \quad (9)$$

The adsorption energy (BE)⁵ can be calculated using the following formula:

$$BE = E[\text{surface+intermediate}] - E[\text{surface}] - E[\text{intermediate}] \quad (10)$$

Here, $E[\text{surface+intermediate}]$ represents the energy of the adsorbed state, $E[\text{surface}]$ represents the energy of the catalyst substrate without the adsorbed intermediate, and $E[\text{intermediate}]$ represents the energy of the intermediate. The energy of the intermediate COOH^6 can be calculated indirectly using the following formula:

$$E[\text{COOH}] = E(\text{HCOOH}) - 1/2E[\text{H}_2] \quad (11)$$

2. Supporting Figures

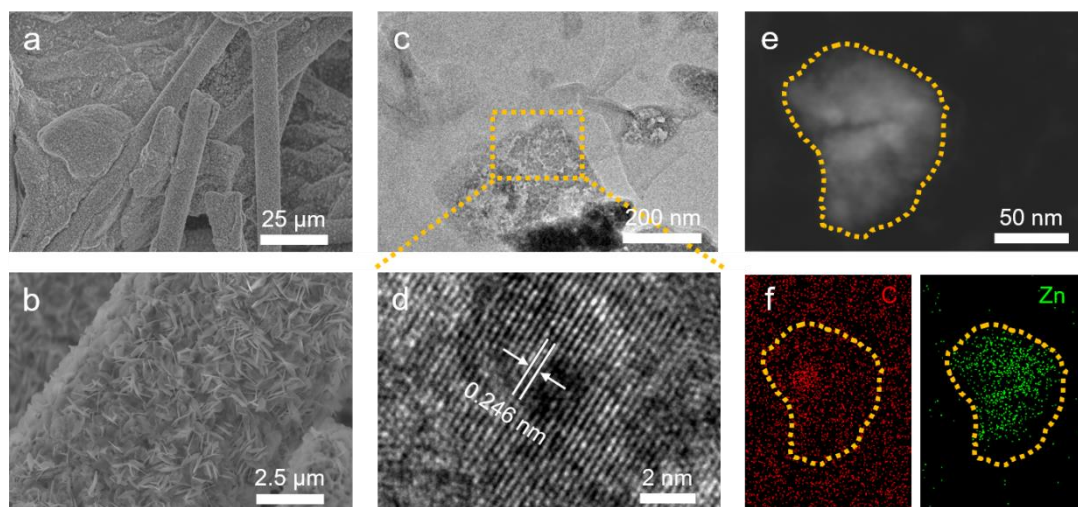


Figure S1. SEM images (a-b), TEM images (c-d), HADDF-STEM and EDX element mapping images (e-f) of the ZnNSs deposited on carbon paper.

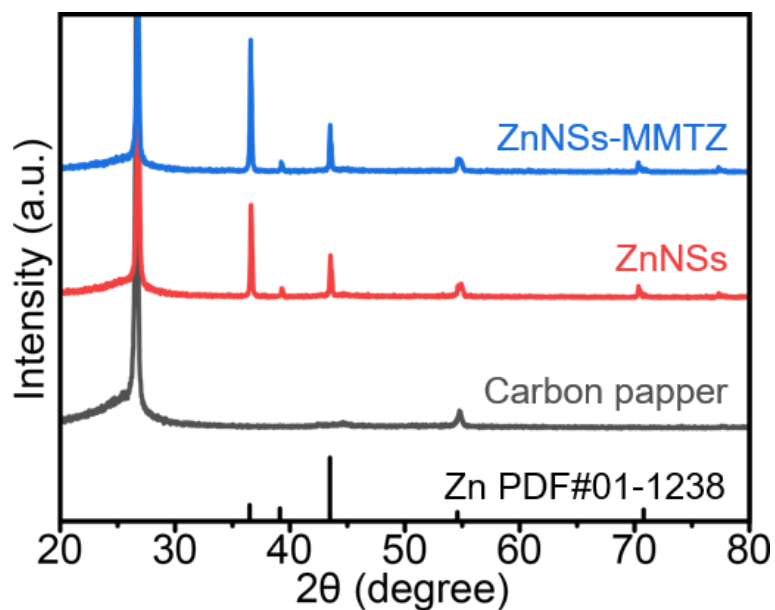


Figure S2. XRD patterns of MMTZ modified ZnNSs, ZnNSs and pristine carbon paper.

The XRD pattern of carbon paper shows only the characteristic peak of carbon, whereas, after ZnNS electrodeposition and MMTZ modification, the diffraction peaks of Zn NSs and Zn NSs-MMTZ match those of conductive carbon paper and metal Zn (PDF # 01-1238), indicating that the MMTZ modification does not influence the phase composition of electrodeposited Zn.

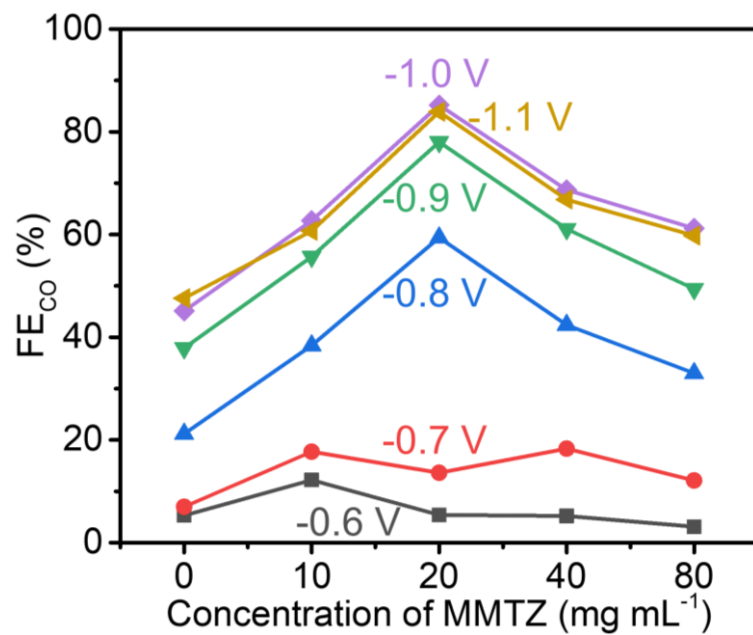


Figure S3. CO Faraday efficiency of ZnNSs modified with 0 to 80 mg mL⁻¹ of MMTZ measured at a voltage range of -0.6 to -1.1 V vs. RHE.

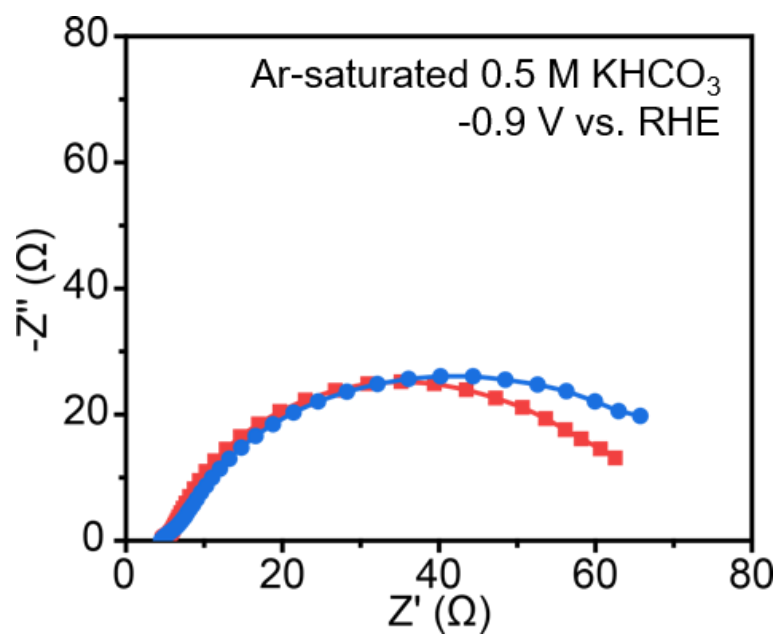


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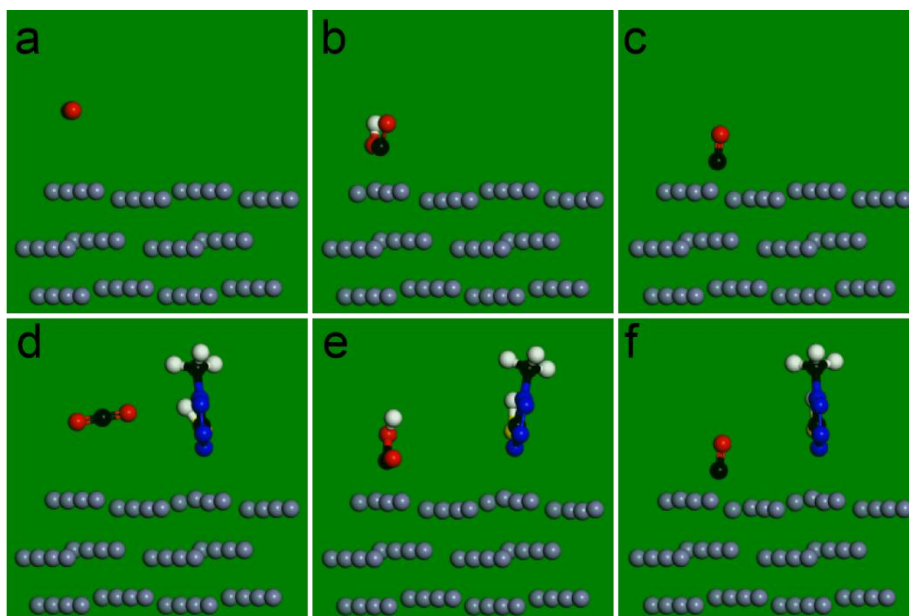


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