Supporting Information

Dual active sites fabricated through atomic layer deposition of TiO$_2$ on MoS$_2$ nanosheet arrays for highly efficient electroreduction of CO$_2$ to ethanol

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Experimental Section:

1.1 Materials and Chemicals

Ammonium tetrathiomolybdate (ATM, 99.95%), N, N-dimethylformamide (DMF, ≥99.9 %) and hydrazine monohydrate (N$_2$H$_4$·H$_2$O, >98.0%), analytical reagents of KHCO$_3$, acetone, and hydrochloric acid were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. Dimethylsulfoxide (DMSO) and ethanol (HPLC pure) were purchased from J&K chemicals. Mo mesh was purchased from Shengzhuo Stainless Steel Mesh Company. All chemicals were used without further purification. All the aqueous solutions were prepared with Milli Q water (18.2 MΩ cm). 1 × 4 cm$^2$ Mo mesh was washed with acetone, dilute hydrochloric acid, and high purity water before use.

1.2.1 Synthesis of ultrathin MoS$_2$ nanosheet arrays on Mo mesh

In a typical process, 10 mg of ATM was dissolved into 30 mL of DMF under ultrasonification. A piece of clean 1 × 4 cm$^2$ Mo mesh was put in the solution. Then 50 µl of N$_2$H$_4$·H$_2$O was added to
the solution and stirred for 15 minutes. After that, it was transferred to a Teflon-lined stainless-steel autoclave, kept at 200 °C for 15 h. After the temperature cooled to room temperature, the Mo mesh containing MoS\textsubscript{2} was washed with highly purified water and dried at 65 °C under vacuum.

1.2. 2 Preparation of TiO\textsubscript{2}/MoS\textsubscript{2}

Different thickness of TiO\textsubscript{2} thin film was deposited upon the pre-prepared MoS\textsubscript{2}/Mo with ALD system. The Titanium isopropoxide (TTIP) was used as Ti precursor, H\textsubscript{2}O was used as an oxygen source. High-purity N\textsubscript{2} (99.999%) was used as the carrier gas with a flow of 100 sccm along the reactor. High-purity O\textsubscript{2} (99.999%) was used as the plasma gas with a flow of 300 sccm along the reactor. Each cycle of ALD deposits 0.4 Å of TiO\textsubscript{2} 25, 50, and 75 cycles were applied to obtained TiO\textsubscript{2} with thicknesses of 1, 2, and 3 nm, respectively.

1.3 Characterizations.

Powder X-ray diffraction (XRD) was carried out with a Bruker D8 Advance X-ray diffractometer using Cu K\textalpha radiation (\(\lambda = 0.15418\) nm) at a scanning rate of 7°/min in the 2\(\theta\) range from 20° to 80°. Field emission scanning electron microscopy (FESEM) images were taken on a Nova NanoSEM 200 scanning electron microscope. Transmission electron microscopy (TEM) observations and high-resolution transmission electron microscope (HRTEM) images were performed with a JEOL JEM 2010 HRTEM, using an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were acquired on an ESCALAB 250 with Al K\textalpha (h\(\nu = 1253.6\) eV) as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.8 eV. The gaseous products from CO\textsubscript{2} electrochemical reduction were analyzed by gas chromatography (Agilent 7890A). The liquid products were analyzed by \textsuperscript{1}H NMR spectroscopy (Bruker, 500M), with water suppression using a presaturation method.

1.4 Electrochemical measurements.

The electrocatalytic experiments were carried out through electrochemical workstation CHI760E in an H-type three-electrode electrochemical cell with 0.5 M KHCO\textsubscript{3} electrolyte saturated with Ar, CO\textsubscript{2}, or CO. The working electrode and the anode compartment were separated by a cation exchange membrane (Nafion N115, DuPont). MoS\textsubscript{2}/Mo and TiO\textsubscript{2}/MoS\textsubscript{2} were used as working electrode.
Platinum plate and Ag/AgCl (in saturated KCl solution) electrode were used as the counter electrode and the reference electrode, respectively. The area of the cathode immersed in the electrolyte was confined to $1 \times 1 \text{cm}^2$. The voltage was applied from 0 to -1.2 V versus RHE. The scan rate was set as 5 mV s$^{-1}$. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed to analyze the electrocatalytic activities of the as-obtained materials for CO$_2$RR. The electrochemical impedance spectra (EIS) were carried out at open circuit potential with an amplitude of 10 mV in a frequency range from 1 MHz to $10^2$ Hz. The electrochemically active surface area (ECSA) was obtained through CV method. The specific capacitance was calculated by plotting the difference of the anodic and cathodic current densities at $-0.1$ V vs. RHE against the scan rate. Considering that flat sulfides electrode with $1 \text{cm}^2$ has a specific capacitance of about 40 mF cm$^{-2}$, this value was also used to calculate ECSA of MoS$_2$ and TiO$_2$/MoS$_2$ electrodes through the following equation:

$$A_{ECSA} = \frac{\text{Specific capacitance}}{40 \mu F \text{cm}^{-2} \text{cm}^{-2}}$$

**Computation method**

Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP).[1] Electron-ion interactions were described using standard projector-augmented wave (PAW) potentials.[2] The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional were used to describe the electron-electron exchange and correlation functional.[3] A plane wave cutoff energy of 400 eV was applied in our calculations. The spin polarization was considered in all calculation. The vacuum layer is 15 Å. The Brillouin-zone integrations were performed using the only Gama point during the optimization. The iterative process considered was convergences, when the force on the atom was less than 0.02 eV Å$^{-1}$ and the energy change was less than $10^{-5}$ eV per atom. van der Waals (VDW) interactions were corrected using the D2 method of Grimme.[4]

The computational hydrogen electrode (CHE) approach was used to calculate the free energy of all intermediate species. The formula is defined as

$$\Delta G = \Delta E + \Delta ZPE - T \times \Delta S$$
Where $\Delta E$ is the reaction energy calculated by the DFT method. $\Delta ZPE$ and $\Delta S$ are the changes in zero-point energies and entropy during the reaction, respectively.\textsuperscript{[5]}

Reference


Fig. S1 FESEM images of the used Mo mesh at different magnification.
Fig. S2 XRD patterns of the as-synthesized MoS$_2$ nanosheet arrays and TiO$_2$/MoS$_2$.

Fig. S3 Raman spectra of MoS$_2$ (a) and TiO$_2$/MoS$_2$ (b).
**Fig. S4** LSV curves obtained over TiO$_2$ with different thicknesses/MoS$_2$ in CO$_2$-saturated 0.5 M KHCO$_3$ aqueous solution (a). LSV curves of 2 nm TiO$_2$/MoS$_2$ in Ar- and CO$_2$-saturated 0.5 M KHCO$_3$ aqueous solution (b).

**Fig. S5** $^1$H NMR spectra of liquid products obtained through CO$_2$ electrolysis over TiO$_2$/MoS$_2$ nanosheet arrays.
Fig. S6 CV curves of MoS$_2$ (a) and TiO$_2$/MoS$_2$ (b) performed at different scan rates. Charging current density differences plotted against scan rates (c).
Fig. S7 EIS spectra of MoS$_2$ and TiO$_2$/MoS$_2$.

Fig. S8 Stable interfacial structure model of TiO$_2$/MoS$_2$. 
Fig. S9 Charge density difference and net Bader charge transfer of TiO$_2$/MoS$_2$.

Fig. S10 LSV curve of TiO$_2$/MoS$_2$ in CO-saturated 0.5 M KHCO$_3$ aqueous solution (a). Corresponding $^1$H NMR spectrum of liquid products (b).
Fig. S11 FESEM image (a) and XRD pattern (b) of MoS$_2$ nanosheet arrays grown on Mo mesh after annealing in air at 300 °C for 4 h. * and # denote MoO$_3$ and MoO$_2$, respectively.

Fig. S12 Free energy diagrams for the coupling reaction of CO over MoS$_2$. 
Fig. 13 Free energy diagrams for CO$_2$RR over TiO$_2$/MoS$_2$ toward ethylene (a). The optimized geometries for the reaction intermediates during the CO$_2$RR process to C$_2$H$_4$ over the interface of TiO$_2$/MoS$_2$ (b).
**Fig. S14** $^1$H NMR spectrum of liquid products obtained through CO$_2$ electrolysis over MoS$_2$ nanosheet arrays loaded by excess TiO$_2$.

**Fig. S15** $^1$H NMR spectrum of liquid products obtained through CO electrolysis over TiO$_2$/MoS$_2$ nanosheet arrays in the presence of formate ions.
Fig. S16 Free energy diagrams for CO$_2$RR over TiO$_2$/MoS$_2$ toward acetate (a). The optimized geometries for the reaction intermediates during the CO$_2$RR process to CH$_3$COOH over the interface of TiO$_2$/MoS$_2$ (b).
### Table S1. Comparison of electrocatalytic activity of different electrocatalysts for CO₂RR toward ethanol.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction condition</th>
<th>FE (%)</th>
<th>Partial current density [mA cm⁻²]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu nanoparticle ensembles</td>
<td>0.1 M KHCO₃, −0.86 V vs RHE</td>
<td>16.6</td>
<td>3.4</td>
<td>1</td>
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<tr>
<td>B doped Cu</td>
<td>0.1 M KCl −1.1 V vs RHE</td>
<td>27</td>
<td>18.9</td>
<td>2</td>
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<tr>
<td>Cu₄Zn</td>
<td>0.1 M KHCO₃ −1.05 V vs RHE</td>
<td>29.1</td>
<td>8.2</td>
<td>3</td>
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<tr>
<td>Cu-Au alloy</td>
<td>0.5 M KHCO₃ −1.1 V vs SCE</td>
<td>12</td>
<td>0.24</td>
<td>4</td>
</tr>
<tr>
<td>Phase-blended Ag-Cu₂O</td>
<td>0.2 M KCl −1.2V vs RHE</td>
<td>34.2</td>
<td>0.9</td>
<td>5</td>
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<tr>
<td>Cu/TiO₂</td>
<td>0.2 M KI −1.45 V vs RHE</td>
<td>27.4</td>
<td>8.7</td>
<td>6</td>
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<tr>
<td>Cu₂S–Cu-V</td>
<td>0.1 M KHCO₃ −0.95 V vs RHE</td>
<td>15.1</td>
<td>4.8</td>
<td>7</td>
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<tr>
<td>Cu-C₃N₄</td>
<td>0.1 M KHCO₃ −1.6 V vs Ag/AgCl</td>
<td>10</td>
<td>0.8</td>
<td>8</td>
</tr>
<tr>
<td>Nitrogen-doped mesoporous carbon</td>
<td>0.1 M KHCO₃ −0.56 V vs RHE</td>
<td>77</td>
<td>0.5</td>
<td>9</td>
</tr>
<tr>
<td>B and N-co-doped nanodiamond</td>
<td>0.1 M NaHCO₃ −1.0 V vs RHE</td>
<td>93.2</td>
<td>0.6</td>
<td>10</td>
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<tr>
<td>TiO₂/MoS₂</td>
<td>0.5 M KHCO₃ −0.6 V vs RHE</td>
<td>50</td>
<td>1.2</td>
<td>This work</td>
</tr>
</tbody>
</table>
Reference


