Supplementary Information for

Robust and selective electrochemical reduction of CO₂: the case of integrated

3D TiO₂@MoS₂ architectures and Ti-S bonding effect

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1. Experimental and calculation details

1.1. Materials synthesis. All chemicals used in this study and Ti foil with purity of 99.98% were purchased from Shanghai Guoyao Chemicals Ltd. Co. The chemicals were analytical reagents and used without further purification. Deionized water was used for the preparation of all aqueous solutions. In this study, TiO2 nanosheet arrays were synthesized via the minor modification of our reported hydrothermal method.¹ In a typical procedure, after sonication in alcohol and acetone for three times, a piece of Ti foil $(50 \times 20 \times 0.2 \text{ mm}^3)$ was placed against the wall of polyphenyl (PPL)lined stainless-steel autoclave (100 mL) containing 60 mL 1M NaOH solution. Then it was held in the oven at 180 °C for 14 h, followed by being immersed in a dilute HCl solution (0.5 M) for 30 mins to replace Na⁺ with H⁺. The film was subsequently calcined at 500 °C for 1 h to synthesize crystallized TiO₂ nanosheet arrays. For the preparation of TiO₂@MoS₂ composites, as-prepared TiO_2 nanosheet was put in the autoclave with the solution of 0.93 g ammonium molybdate tetrahydrate ((NH)₄Mo₇O₂₄·4H₂O), 1.71 g thiourea (CS(NH₂)₂) and 40 mL deionized water. The autoclave was heated at 260 °C and had been kept for 24 h. Different amount of (NH)₄Mo₇O₂₄·4H₂O and CS(NH₂)₂ was also applied to control the loading amount of MoS₂. Specifically, 0.31 g (NH)₄Mo₇O₂₄·4H₂O + 0.57 CS(NH₂)₂, 0.62 g (NH)₄Mo₇O₂₄·4H₂O + 1.14 $CS(NH_2)_2$, 0.93 g (NH)₄Mo₇O₂₄·4H₂O + 1.71 CS(NH₂)₂, and 1.24 g (NH)₄Mo₇O₂₄·4H₂O + 2.28 CS(NH₂)₂ was dissolved in 40 mL deionized water respectively, had been kept in an oven at 260 °C for 24 h, and the corresponding obtained composites were successively labeled with TM1, TM2, TM3, and TM4. For comparison, direct growth of pure MoS_2 on the Ti substrate was performed with 0.93 g (NH)₄Mo₇O₂₄·4H₂O and 1.71 CS(NH₂)₂ dissolved in 40 mL deionized water at 260 °C for 24 h. After that, all the samples were thoroughly rinsed with deionized water and ethanol, dried at 70 °C for 24 h and then transferred to a tube furnace for annealing at 500 °C for 2 h under Ar

atmosphere.

1.2. Materials characterization. The morphology of the prepared samples was detected with scanning electron microscopy (SEM, JEOL JSM-6700) and transmission electron microscopy (TEM, JEM-2010FEF, 200kV) coupled with an energy dispersive X-ray spectroscopy (EDS). X-ray powder diffraction (XRD) patterns of the samples were analyzed by using a PANalytical diffractometer (D/max 40kv) using Cu K α radiation (λ =0.154598 nm) for crystalline phase. The surface chemical analysis of the samples was achieved with X-ray Photoelectron Spectroscopy (XPS) (VG Multiab-2000) using a PHI Quantum 2000 XPS system with a monochromatic Al K α source and charge neutralizer. All spectra were calibrated to C1s peak at 284.6 eV. Raman spectra were collected at room temperature using a LabRAMHR Raman system under Ar⁺ (532 nm) laser excitation. The nitrogen adsorption-desorption isotherms and the Barrett-Joyner-Halenda (BJH) methods were detected on a Bel Sorp-mini (S/N-00230) analyzer (accelerated surface area and porosimetry system). Thermogravimetric analysis (TG) was performed with an STA 449C thermal analyzer at a heating rate of 15 °C/min in air atmosphere. CO₂ adsorption isotherms were measured at room temperature using a BEL SORP-mini II (BEL Japan).

1.3. Electrochemical measurements. Electrochemical measurements were conducted on an electrochemical station (CHI 660, CH Instruments, Inc.) in a standard three electrode system with the prepared samples as working electrodes, a platinum plate as the counter and standard Ag/AgCl electrode as the reference, and 0.1 M KHCO₃ aqueous solution as the electrolyte. Linear sweep voltammetry (LSV) measurements were carried out in aqueous KHCO₃ solution (0.1 M) saturated with N₂ or CO₂ by bubbling N₂ or CO₂ for 30 min, and the scan rate was 2 mV s⁻¹. CV was tested in CO₂-saturated KHCO₃ solution with a scan rate of 20 mV/s. Chronoamperometry was measured under a constant potential. Electrochemical impedance spectroscopy (EIS) was carried out when

the working electrode was biased at a constant potential of 0.15 V while the frequency was swept from 100 kHz to 0.01 Hz with a 10 mV AC dither. All the potentials were calibrated to the RHE by adding a value of 0.714 V ($E_{RHE} = E_{Ag/AgCl} + 0.0592 \times pH + 0.198$), and all the potentials used here were referred to RHE.

1.4. Electrocatalytic performance tests. The electroreduction of CO₂ was conducted in a homemade 250 mL sealed cell with 170 mL of 0.1 M KHCO₃ as electrolyte solution, which ran by an electrochemical station (CHI 660, CH Instruments, Inc.). The prepared sample was working electrode, a platinum plate as the counter and standard Ag/AgCl electrode as the reference. Before reduction, high purity CO₂ (99.99%) gas was passed through the electrolyte solution for 30 min until the CO₂ concentration reached saturation. All the experiments were performed at room temperature and ambient pressure. The evolved gaseous products were collected by a 1µm syringe and then immediately analyzed by a gas chromatograph. The GC model was GC-2014 (Serial No. C11485013433 SA, SHIMADZU, Japan) with a thermal conductivity detector (TCD), and a packed column (C36880-14, Restek, 2 m × 1 mm) was used. The carrier gas was nitrogen (N₂). The amount of the evolved products was the average value of three measurements. The Faradaic efficiency of CO and H₂ was calculated as follows: FE-CO, H₂ = 2F ·n_{gas}/I·t, where F is the Faraday constant, n_{gas} (in moles) the amount of CO or H₂, I (in amperes) the reduction current at a specific applied potential and t the time (in seconds) for the constant reduction current.

1.5. Density Functional Theory (DFT) calculations. DFT calculations were carried out using the Vienna *ab-initio* simulation package (VASP, version 5.3.3) code.²⁻⁵ The PBE functional was employed for electronic exchange and correlation.⁶ The plane wave pseudopotential with a kinetic cutoff energy of 450 eV and Gaussian smearing method with an electronic temperature of $k_{\rm B}T = 0.05$ eV were used in all our calculations.

In our models, single-layer MoS₂ and TiO₂@MoS₂ were used for the charge density calculations, and single-layer Mo exposed nanoribbons were used for the free energy calculations of the reaction. For the monolayer slabs, each MoS₂ layer included 4 × 4 unit cells with 32 S atoms and 16 Mo atoms, and each Ti-O layer contained 16 O atoms and 16 Ti atoms. A ~ 10 Å thick vacuum space was added to avoid inter-layer interactions. Brillouin-zone integration was conducted using a $8 \times 8 \times 1$ Monkhorst-Pack grid.⁷ Mo exposed nanoribbons was modeled by a 6 layer 1 × 4 unit cell with 24 S atoms and 12 Mo atoms for MoS₂ nanoribbon and additional 12 Ti atoms and 12 O atoms for TiO₂@MoS₂ nanoribbon. A vacuum layer of ~ 10 Å thick was applied on the top of the Mo edges to avoid artificial interactions between the nanoribbon and its periodic images. The Brillouin-zone integration on MoS₂ and TiO₂@MoS₂ nanoribbons were performed using a $3 \times 1 \times 1$ Monkhorst-Pack gird. The bottom three layers of the nanoribbon unit cell were fixed in the geometrical optimization while the top three layers and the associated adsorbates were allowed to relax. The binding energy (E_{BE}) of the adsorbates is defined as: $E_{BE} = E_{tot} - E_{sub} - E_{ads}$, where E_{tot} , E_{sub} and E_{ads} is the total energy of optimized adsorbate + substrate, clean substrate and gas phase adsorbate respectively, and they can be directly obtained from DFT calculations. The free energies (G) of the CO₂ reduction intermediates are calculated as $G = E_{ele} + ZPE - TS$, where E_{ele} is the electronic energy, ZPE the zero point energy, T the temperature (20 °C in all our calculations) and S the entropy. In our practical calculations, the changes of free energy (ΔG) relative to the gas phase CO₂ and clean substrate are more illustrative.

2. Supplementary Figures



Figure S1. Top-view SEM images of obtained TiO_2 nanosheet arrays calcinated at different temperatures: (a) 400 °C, (b) 500 °C, and (c) 600 °C. (d) XRD patterns of different TiO_2 nanosheet arrays.

We studied the effect of calcination temperature on the morphology and phase of TiO_2 nanosheet arrays. From the SEM images, we can see that over a range of calcination temperatures from 400 to 600 °C, the morphology of TiO_2 nanosheet arrays remained invariant regardless of the calcination temperatures, confirming the high thermal stability of TiO_2 nanosheets. Further, we can observe that the size of the nanosheets became smaller when increasing the calcination temperature, and the one calcinated at 500 °C was the most uniform. The XRD results showed that all the three samples were pure TiO_2 phase, and samples calcined at higher temperature displayed stronger diffraction peaks, indicating the improved crystallinity.



Figure S2. Top-view SEM image of MoS₂ grown on Ti substrate.



Figure S3. Top-view SEM images for (a1 and a2) TM1, (b1 and b2) TM2, and (c1 and c2) TM4 with different magnification.



Figure S4. Side-view SEM image of TM3.



Figure S5. XRD patterns of TM1, TM2 and TM4.



Figure S6. Raman spectra of TM1, TM2 and TM4.



Figure S7. N_2 adsorption-desorption isotherm curves for (a) TiO₂ and (b) TM3. The insets show the corresponding pore size distribution.



Figure S8. N_2 adsorption-desorption isotherm curves for (a) TM1, (b) TM2, and (c) TM4. The insets show the corresponding pore size distribution.



Figure S9. Thermogravimetric (TG) curves of TiO₂, MoS₂ and TM3.

Thermogravimetric (TG) analysis was carried out in an air atmosphere to inspect the thermal stability of the integrated architectures. The TiO₂ nanosheet arrays showed a slight weight loss of about 3.18%, proving the superior chemical stability of TiO₂ scaffold. For pure MoS₂ and TM3, both had a distinct weight loss in the range of 200-500°C, which was attributed to the transformation of MoS₂ into MoO₃ via the following reaction: $2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2$. However, pure MoS₂ started weight loss at about 220°C while TM3 started at almost 400°C, implying much better thermal stability. This was because that part of the heat was absorbed by the TiO₂ scaffold, and the formation of Ti-S bonds between TiO₂ and MoS₂ endowed the composite with stable and integrated 3D structures.



Figure S10. Top-view SEM image of TM3 after stability test for 14 h.



Figure S11. XRD patterns of TM3 before and after stability test for 14 h.



Figure S12. High-resolution XPS spectra of (a) Ti, (b) Mo and (c) S for TM3 before and after stability test for 14 h.



Figure S13. (a) Photographs of TM3 (more than 14 h) and the control of MoS₂ (less than 5 h) after stability test. (b) Schematic illustration for the structure superiority of TM3 architectures.



Figure S14. Calculated partial density of states (PDOS) of the edge Mo atoms for MoS_2 monolayer and $TiO_2@MoS_2$ interface.

To illuminate the changes of the adsorption energy of CO_2 , we further calculated the d-band partial density of states (PDOS) of the edge Mo atoms. According to the results, we can find that the center of PDOS of MoS_2 is much close to the fermi level. However, the formation of $TiO_2/$ MoS_2 interface shifts the d-band center towards lower energy. Therefore, the CO_2 adsorptivity of MoS_2 on the Mo edges is stronger than that of the $TiO_2@MoS_2$.



Figure S15. High-resolution XPS spectra of S for TMx (x=1, 2, 3, 4), and the peak area of Ti-S is presented on the top right corner.



 $\rm R_{s}$: series resistance; $\rm R_{ct}$: charge transfer resistance

Figure S16. Equivalent circuit for EIS Nyquist plots.

3. Supplementary Table

Catalyst	Electrolyte	FE _{max} (%) ^[a]	$\eta_{max}^{[b]}$	j _{CO} (mA cm ⁻²) ^[c]	Ref.
3D TiO ₂ @MoS ₂	0.1 M KHCO ₃	82	-0.7 V vs. RHE	-68	This work
layered MoS_2	EMIM-BF ₄ in water	98	-0.77 V vs. RHE	-120	8
rGO-PEI-MoS _x	0.5 M NaHCO ₃	85	-0.65 V vs. RHE	-5.1	9
Cu NPs-MoS $_2$	0.1 M NaHCO ₃	44	-1.4 V vs. SCE	-1.76	10
WSe ₂ nanoflake	EMIM-BF ₄ in water	88	-0.76 V vs. RHE	-290	11
Au NPs (7.7 nm)	0.1 M KHCO ₃	45	-1.2 V vs. RHE	-23	12
Ag NPs (5 nm)	0.5 M KHCO ₃	88.4	-0.75 V vs. RHE	-4	13
Ag nanoplates	0.1 M KHCO ₃	97	-0.85 V vs. RHE	-1.3	14
Cu NPs (1.9 nm)	0.1 M KHCO ₃	28	-1.1 V vs. RHE	-13	15
Pd NPs (3.7 nm)	0.1 M KHCO ₃	91.2	-0.89 V vs. RHE	-8.5	16
Hexagonal Zn	0.5 M KHCO ₃	85.4	-0.95 V vs. RHE	-21	17
Dendritic Zn	0.5 M NaHCO ₃	80	-1.1 V vs. RHE	-14	18
Au ₃ Cu NPs	0.1 M KHCO ₃	65	-0.73 V vs. RHE	-2.9	19

Table S1. Comparison of the electrocatalytic performance for CO_2 reduction to CO over different catalysts with the presence of different electrolytes.

[a] Maximum FE CO; [b] Overpotential for the maximum FE of CO; [c] Partial current density of CO. (j_{CO} is obtained by multiplying the total current density at the potential by the corresponding FE of CO.)

4. References

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