# Ultra-small Ni(HCO<sub>3</sub>)<sub>2</sub> as Water Dissociation Promoter Boosting the

# Alkaline Hydrogen Electrocatalysis Performance of MoS<sub>2</sub>

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# **Experimental Section**

### Synthesis of MoS<sub>2</sub>/CC

Commercial carbon cloth (CC, 1 cm×1 cm) was cleaned by sonication sequentially in acetone, water and ethanol for 10 min each to remove the surface impurities. The clean CC was submerged into the Teflon-lined stainless autoclave containing 30 mL aqueous solution of 0.05 M thiourea and 0.015 M Na<sub>2</sub>MoO<sub>4</sub>•2H<sub>2</sub>O. The autoclave was sealed and maintained at 210 °C for 18 h. After that, the autoclave was cooled down to room temperature naturally. The synthesized MoS<sub>2</sub>/CC was repeatedly washed with DI water and ethanol in sequence, and dried in air.

# Synthesis of Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC

Typically, Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (1, 2 or 4 mmol) and CO(NH<sub>2</sub>)<sub>2</sub> (4, 8 or 16 mmol) were dissolved in ethylene glycol solution (volume ratio between DI water and ethylene glycol of 1:7) was added to form a homogeneous solution. Afterwards, the resultant mixture and the prepared MoS<sub>2</sub>/CC were transferred into a 30 mL Teflon-lined stainless steel autoclave and heated at 140 °C for 12 h. Finally, the obtained catalysts were washed with DI water and ethanol several times, then dried at 60 °C for 6 h. The obtained catalysts were denoted as 0.5-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC, Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC

#### Synthesis of Ni(HCO<sub>3</sub>)<sub>2</sub>/CC

 $Ni(HCO_3)_2/CC$  as the contrast catalyst was obtained by the same process as  $Ni(HCO_3)_2/MoS_2/CC$  with CC as the substrate. The prepared  $Ni(HCO_3)_2/CC$  was washed with DI water and ethanol several times, then dried at 60 °C for 6 h.

# Characterization

Scanning electron microscope (SEM) images and their corresponding energy dispersive X-ray (EDX) data and EDX mapping images were obtained on a Quanta 200 FEI. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images, and their corresponding EDX mapping images were obtained on an FEI TENAI G2 F20 at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Fisher K-Alpha

instrument and XPS spectra were referenced to the C 1s peak (284.8 eV). X-ray diffraction (XRD) patterns were recorded in the range of  $5-100^{\circ}$  (20) on an X-ray diffractometer (Bruker, AXS D8) with Cu K $\alpha$  radiation operated at 40 kV and 30 mA.

#### **Electrochemical measurements**

Electrochemical measurements were performed with a standard three-electrode system on an electrochemical workstation CHI 660e in 1.0 M KOH solution. The Hg/HgO (1.0 M KOH) electrode and graphite rod were respectively used as the reference electrode and the counter electrode. The obtained catalytic electrode was directly used as the working electrode. All reported potentials were calibrated to the RHE, and were converted using the equation  $E_{RHE}$  =  $E_{Hg/HgO}$  + 0.098 + 0.059  $\times$  pH (1.0 M KOH, pH = 14). To prepare the Pt/C electrode, Pt/C (20 wt %) was dispersed in a mixed solution (water: ethanol: 5 wt % Nafion solution=49:49:2) to obtain a catalyst ink under ultrasound. Then the catalyst ink was dropcast on the surface of CC (1 cm×1 cm). For HER activity, linear sweep voltammetry (LSV) curves were recorded at the scan rate of 5 mV s<sup>-1</sup>. All LSV curves were corrected for ohmic losses unless stated. The ohmic losses that constitute the series resistance  $(R_s)$  can be obtained from the electrochemical impedance spectroscopy (EIS) measurements. The correction was performed using the following equation:  $E_{corrected} = E - IR_s$ , where E is the potential and I is the current. The Nyquist plots for the electron transfer efficiency investigation were obtained by the EIS measurement recorded at the overpotential of 263 mV in the frequency range of 100 kHz to 10 mHz. Chemical double-layer capacitance (C<sub>dl</sub>) was acquired through CV curves conducted at the non-faradaic current region ranging from 0 to 0.1 V (vs. RHE) at various scan rates of 40, 80, 120, 160 and 200 mV s<sup>-1</sup>. Long-term durability tests were conducted by employing Amperometric measurements at 300 mV overpotential for 15 h and cyclic voltammetry with the scan rate of 100 mV s<sup>-1</sup> for 5000 cycles from -0.23 to -0.13 V (vs. RHE).

## **Computational methods**

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package.<sup>1, 2</sup> The generalized gradient approximation

with the PBE functional<sup>3</sup> was used to describe the exchange and correlation energy. Electron-ion interactions were treated by the projector augmented wave method.<sup>4</sup> In all calculations, the energy cutoff of the plane-wave basis set was 400 eV. Optimized structures were obtained by minimizing the forces on each ion until they fell below 0.05 eV/Å.

We employed a triangular MoS<sub>2</sub> nanoparticle (NP) with 8 Mo atoms on each edge to represent the synthesized MoS<sub>2</sub> catalyst. The atomic structure of the employed MoS<sub>2</sub> NP can be viewed in Fig. s1a-b. The MoS<sub>2</sub> NP is terminated S dimers adsorbed on the Mo edge. The particular structure is found the most stable in previous STM study<sup>5</sup> and supported by DFT studies.<sup>6</sup> Ni(HCO<sub>3</sub>)<sub>2</sub> is simulated with a Ni bicarbonate complex as shown in Fig. s1c. A similar structure has been employed to study Mn bicarbonate complex in a previous study.<sup>7</sup> The potential of the electrode was calculated using U<sub>(V/SHE)</sub>= -4.6 + W/eV, where W is the work function of MoS<sub>2</sub>.



Fig. s1 Atomic models of (a)  $MoS_2$  NP top view, (b)  $MoS_2$  NP side view, and (c)  $Ni(HCO_3)_2$ .



Fig. s2 SEM images of (a, b)  $MoS_2/CC$  and (c, d)  $Ni(HCO_3)_2/MoS_2/CC$ 



Fig. s3 TEM image of Ni(HCO<sub>3</sub>)<sub>2</sub> nanosheets.



Fig. s4 XRD patterns of (a)  $MoS_2/CC$  and (b)  $Ni(HCO_3)_2/CC$ .



Fig. s5 XPS survey spectrum of Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC.



Fig. s6 (a) S 2p, (b) C 1s and (c) O 1s XPS spectra of  $Ni(HCO_3)_2/MoS_2/CC$ .



Fig. s7 LSV curves of Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC, 2-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC and 0.5-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC.



Fig. s8 TEM images of (a) 2-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC and (b) 0.5-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC.

As shown in the TEM image of 2-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC (Fig. s8a), large amount of Ni(HCO<sub>3</sub>)<sub>2</sub> nanosheets densely grew on MoS<sub>2</sub> with serious agglomeration, leading to significant decrease of the coupling interfaces between the two phases, thus unfavorable to the fast generation of H<sub>2</sub> gas. However, for 0.5-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC (Fig. s8b), Ni(HCO<sub>3</sub>)<sub>2</sub> nanosheets cannot be clearly observed. It may ascribed to the tiny size of Ni(HCO<sub>3</sub>)<sub>2</sub> and its sparse dispersion on MoS<sub>2</sub> due to the limited reactants employed during the synthesis. As a result, there are limited hydroxyl species adsorption sites on 0.5-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC, leading to the sluggish alkaline HER kinetics. In summary, Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC, with the appropriate ratio of Ni(HCO<sub>3</sub>)<sub>2</sub>:MoS<sub>2</sub> and proper distribution of Ni(HCO<sub>3</sub>)<sub>2</sub> on MoS<sub>2</sub>, exhibits the optimal HER activity.

Element (At %)	C K	O K	S K	Ni K	Mo L
0.5-Ni(HCO <sub>3</sub> ) <sub>2</sub> /MoS <sub>2</sub> /CC	92.02	5.00	1.90	0.09	0.99
Ni(HCO <sub>3</sub> ) <sub>2</sub> /MoS <sub>2</sub> /CC	87.89	6.47	3.62	0.14	1.88
2-Ni(HCO <sub>3</sub> ) <sub>2</sub> /MoS <sub>2</sub> /CC	91.10	4.96	2.56	0.08	1.30

Table s1 EDX results of 0.5-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC, Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC and 2-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC.

As shown in Table s1, the relative high percentage composition of C may be ascribed to the CC substrate, and the content of O can't be measured accurately. However, the almost 1:2 ratio for all the samples' Mo and S atomic ratios agree with that of MoS<sub>2</sub>, which demonstrates that the EDX results are reliable to reveal the molar ratio of Ni(HCO<sub>3</sub>)<sub>2</sub>:MoS<sub>2</sub>. Consequently, the molar ratios of Ni(HCO<sub>3</sub>)<sub>2</sub>:MoS<sub>2</sub> in 0.5-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC, Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC, and 2-Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC were calculated to be 1:16, 1:13 and 1:11 respectively. It is consistent with the tendency of the reactants' quantity.



Fig. s9 CV curves of (a)  $Ni(HCO_3)_2/MoS_2/CC$ , (b) $MoS_2/CC$  and (c) $Ni(HCO_3)_2/CC$  measured in a non-Faradaic region at the following scan rate: 40, 80, 120, 160 and 200 mV s<sup>-1</sup>.



Fig. s10 Linear fitting of the capacitive currents of the catalysts vs. scan rates.



Fig. s11 The relationship between TOF values and overpotential.



**Fig. s12** Nyquist plots measured at the overpotential of 376 mV for  $Ni(HCO_3)_2/CC$ . The equivalent circuit and zoom-in spectra are in the inset.



Fig. s13 (a) Time-dependent current density curve at overpotential of 300 mV for 15 h. (b) LSV curve of Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC without IR correction, and Ni(HCO<sub>3</sub>)<sub>2</sub>/MoS<sub>2</sub>/CC exhibited an overpotential of 300 mV to reach the current density of 100 mA cm<sup>-2</sup>.



Fig. s14 (a-b) SEM images and (c-d) TEM images of  $Ni(HCO_3)_2/MoS_2/CC$  after 15 h stability test.



Fig. s15 (a) Mo 3d, (b) S 2p, (c) Ni 2p and (d) (e) O 1s XPS spectra of  $Ni(HCO_3)_2/MoS_2/CC$  after 15 h stability test.



Fig. s16 LSV curves of  $Ni(HCO_3)_2/MoS_2/CC$  in 1.0 M KOH before and after 5000 CV cycles.

# References

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