

Supporting Information for

In-situ CO₂-emission Assisted Synthesis of Molybdenum Carbonitride Nanomaterial as Hydrogen Evolution Electrocatalyst

Yong Zhao, Kazuhide Kamiya, Kazuhito Hashimoto^{}, Shuji Nakanishi^{*}*

Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. *e-mail: hashimoto@light.t.u-tokyo.ac.jp, nakanishi@light.t.u-tokyo.ac.jp

Experimental Section

Synthesis of MoCN materials

(1) Synthesis of polydiaminopyridine-2H⁺/MoO₄²⁻ (PDAP-2H⁺/MoO₄²⁻(CO₂)) complex
Typically, 0.01 mol Na₂MoO₄ and 0.02 mol diaminopyridine (DAP) were dissolved in 200 ml distilled water, and aqueous hydrochloric acid (HCl, pH 1) was then added dropwise under magnetic stirring at room temperature until a white precipitate was obtained at pH 5-6. The final pH value was adjusted to 4, and no additional precipitate was formed during the addition of HCl solution. After stirring of the solution for 5 h at 50 °C, the precipitate changed in color from white to yellow, indicating that the DAP-2H⁺/MoO₄²⁻ complex was obtained. The resulting yellowish suspension was filtered and then washed three times with distilled water. The washed DAP-2H⁺/MoO₄²⁻ complex was re-dispersed in 200 ml distilled water, to which an aqueous solution of 0.01 mol (NH₄)₂S₂O₈ and 0.02 mol NaHCO₃ was added.²⁰ In the resulting solution, the yellowish solid changed to brown in color, was then washed three times with distilled water before being dispersed in 100 ml distilled water. The precipitate solution was ultrasonically dispersed for 30 min, and was then freeze-dried at -45 °C for 24 hours to obtain the PDAP-2H⁺/MoO₄²⁻(CO₂) precursor.

(2) Synthesis of PDAP-2H⁺/MoO₄²⁻ complex The synthesis procedure of PDAP-2H⁺/MoO₄²⁻ was similar to that used for PDAP-2H⁺/MoO₄²⁻(CO₂), although NaHCO₃ was substituted for sodium hydroxide during the polymerization of DAP-2H⁺/MoO₄²⁻.

(3) Synthesis of polyaniline-H⁺/MoO₄²⁻ (PANI-H⁺/MoO₄²⁻/PANI-H⁺) complex The synthesis procedure of PANI-H⁺/MoO₄²⁻/PANI-H⁺ was similar to that used for PDAP-2H⁺/MoO₄²⁻ complex, although diaminopyridine was replaced with aniline as the starting monomer for the formation of ANI-H⁺/MoO₄²⁻/ANI-H⁺.

(4) Synthesis of pyrolyzed MoCN materials All polymer/molybdate complex solids were placed into the bottom of a half-closed quartz tube in an argon atmosphere. The tube was inserted into a muffle furnace preheated to 800 °C and the samples were then pyrolyzed for 1 h, unless otherwise specified.²⁸ The heat-treated products were ultrasonically treated in concentrated hydrochloride acid for 12 h, and were then washed three times with distilled water before vacuum drying at 60 °C. The PDAP-MoCN samples were pyrolyzed at 800 °C for different durations to obtain optimized catalysts. Commercial Pt/C powder Pt/C (Pt: 20 wt%) powder was purchased from Tanaka Kinzuko Co., Japan.

Measurement of electrocatalytic HER activity

Electrocatalytic HER activity was measured using a bipotentiostat (Pine Instrument Co.) equipped with a rotating ring disk electrode (RRDE). A saturated calomel electrode (SCE) was used as a reference electrode and calibrated with respect to a reversible hydrogen electrode (RHE) (RHE=SCE*+0.244+0.591×pH at 25 °C). A glassy-carbon disk electrode loaded with catalyst/naion was used as the working electrode and Pt wire was used as the counter electrode. The working electrode was prepared by loading catalyst ink (0.4 mg cm⁻²; catalyst to naion: 8:1) on a glassy carbon electrode. RRDE tests were conducted in an argon-gas bubbled H₂SO₄ and Na₂SO₄ (0.5 M) solution (pH 1) at 25 °C. A scan rate of 5 mV s⁻¹ and rotational speed of 1000 rpm were used for the HER activity test. The poised potential of the Pt ring was 0.30 V vs. RHE. The Pt counter electrode was replaced with a

titanium wire to exclude the possible contribution of the dissolved Pt species originating from the Pt counter electrode to HER activity during long-term operation.

Characterization methods

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of MoCN samples were recorded with JEOL JSM-6700 and Hitachi H-9000UHR microscopes, respectively. Surface elemental composition and content were analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos Ultra AXIS Spectrometer system equipped with a monochromatic Al-K α source. Surface concentrations of different elements were estimated from the peak area ratios of the species. BET surface area and pore distribution of the samples were measured using a Shimadzu Micromeritics Tristar 3000 instrument.

Figure S1

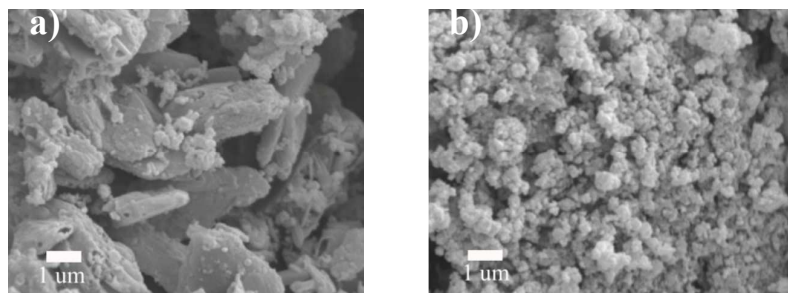


Figure S1 SEM images of polydiaminopyridine/MoO₄²⁻ (PDAP-2H⁺/MoO₄²⁻) complex synthesized (a) without and (b) with the addition of NaHCO₃.

Figure S2

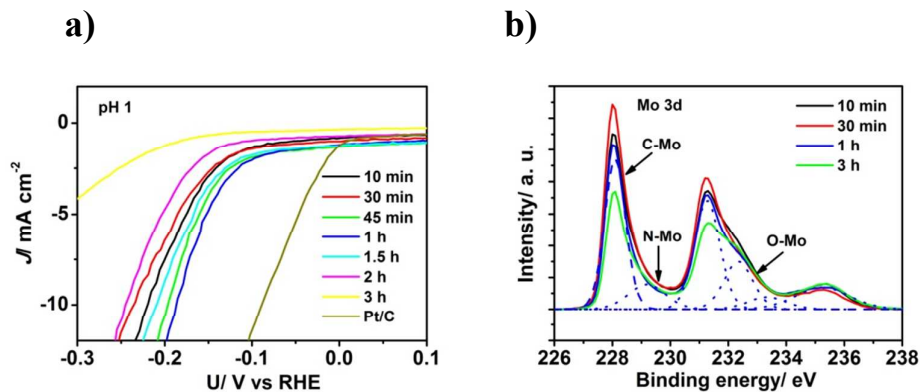


Figure S2 a) HER activity and b) XPS Mo 3d spectra of PDAP-MoCN materials synthesized at 800 °C with different pyrolysis times. Solid line: measured; Dotted line: simulated. (Note: With increasing pyrolysis time, the ratio of Mo^{6+} (O-bound Mo^{6+}) and $\text{Mo}^{2+}/\text{Mo}^{3+}$ (C-bound Mo^{2+} and N-bound Mo^{3+}) species changed. The optimized pyrolysis time was determined to be 1 h at 800 °C.)

Figure S3

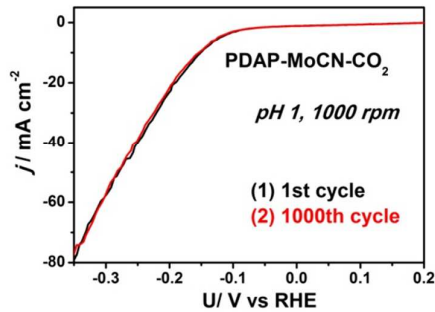


Figure S3 Electrocatalytic HER stability of PDAP-MoCN-CO₂ materials

Figure S4

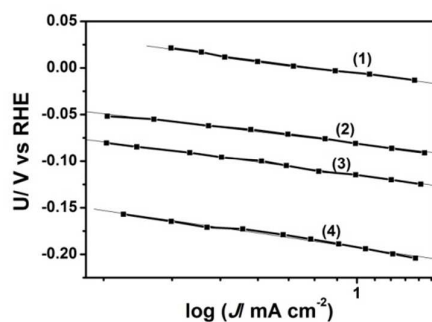


Figure S4 Tafel plots of (1) commercial Pt/C; (2) PDAP-MoCN-CO₂; (3) PDAP-MoCN and (4) PANI-MoCN electrodes from the analysis of Figure 1.

Figure S5

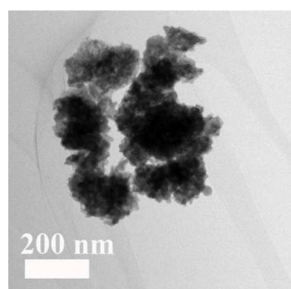


Figure S5 TEM image of the PDAP-MoCN material

Figure S6

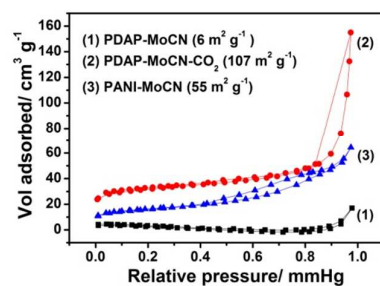


Figure S6 Measured BET surface areas of (1) PDAP-MoCN, (2) PDAP-MoCN-CO₂ and (3) PANI-MoCN based on low-temperature N₂ absorption/desorption tests.

Figure S7

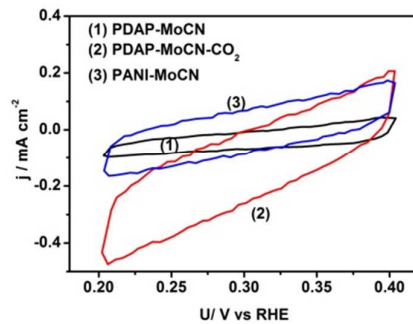


Figure S7 Measured capacitor currents of (1) PDAP-MoCN; (2) PDAP-MoCN-CO₂ and (3) PANI-MoCN materials.

Figure S8

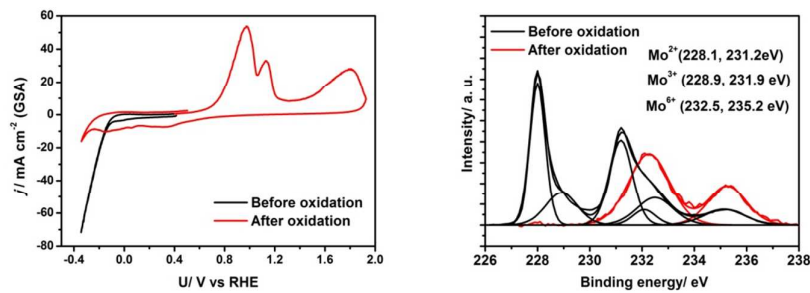


Figure S8 a) Linear sweep voltages of PDAP-MoCN-CO₂ catalysts in the range of 0.32 V_{RHE} to 1.90 V_{RHE}. b) XPS Mo 3d spectra of PDAP-MoCN-CO₂ before and after in-situ electrochemical oxidation. (Both of the measured and simulated curves are presented.)

Note: The forward and backward curves of HER process (black line) were well-overlapped, which indicated that the electrolyte was very conductive in the electrochemical test.