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Supplementary Information

Efficient hydrogen evolution reaction by molybdenum carbide and molybdenum nitride nanocatalysts synthesized *via* the urea glass route

Liang Ma[a], Louisa Rui Lin Ting[a], Valerio Molinari[b], Cristina Giordano[b], Boon Siang Yeo*[a]

[a] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

[b] Max-Planck-Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, D-14424 Potsdam, Germany

S1: Size Distribution and High Resolution Transmission Electron Micrographs (HRTEM) of Mo_2C and Mo_2N Nanoparticles

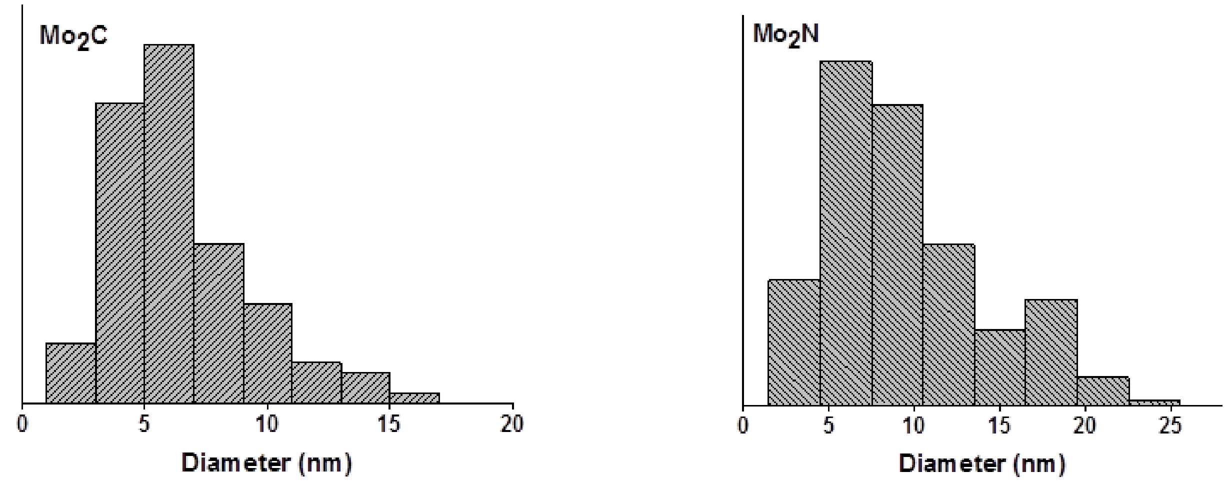

Figure S1: Particle size distribution of Mo_2C and Mo_2N nanoparticles synthesized in this work.

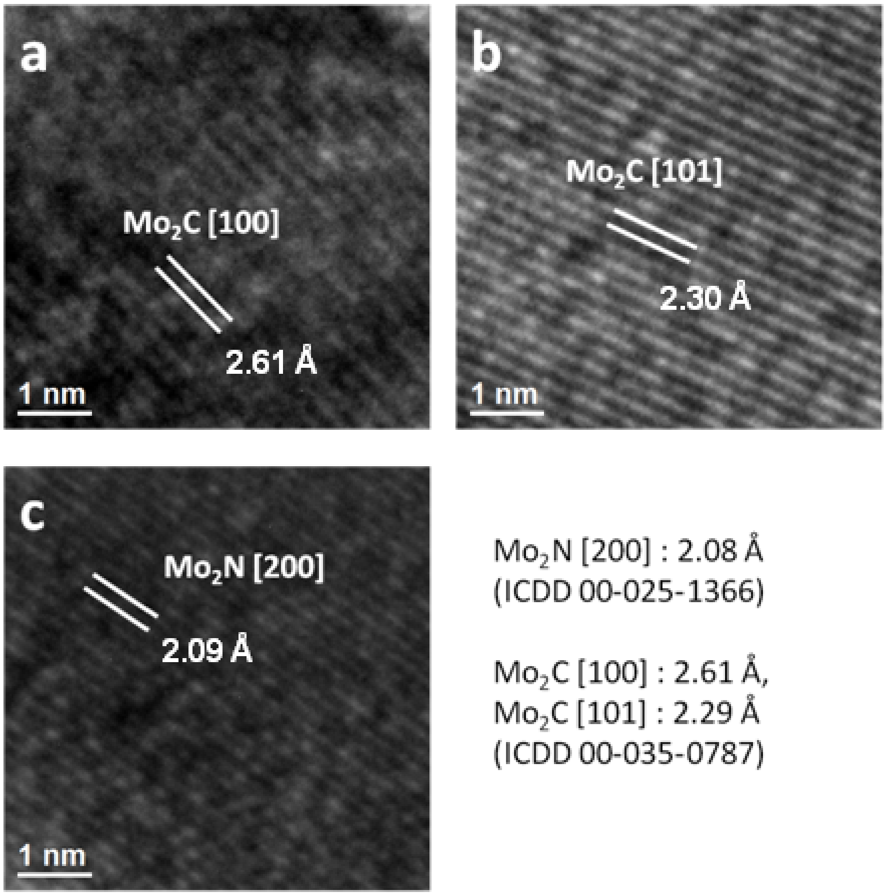

Figure S2: Representative high resolution TEM micrographs of (a-b) Mo_2C and (c) Mo_2N. The d-spacings measured are indicated in the respective TEM micrographs. The expected d-spacings of Mo_2C and Mo_2N as obtained from the ICDD-PDF4+ database are shown at the bottom right of the figure.

S2: Online Gas Chromatography (GC) for Quantifying Hydrogen Evolution

Experimental procedure:

A custom-made, gas-tight two compartment polytetrafluoroethylene cell was used for online gas chromatography.[1] The cathodic compartment was filled with 32 ml electrolyte, leaving ~3 ml of headspace. Before each measurement, the electrolyte was saturated with N_2 gas (Chemgas) for at least 30 minutes. All experiments were performed at 298 K. Using a mass flow controller (MC-100SCCM-D, Alicat Scientific), N_2 was continuously pumped into the electrolyte at a flow rate of 20 sccm. The gas outlet of the cathodic compartment was connected to a gas chromatograph (GC-7890A, Agilent Technologies) for periodical sampling. A thermal conductivity detector (TCD) was used for detecting H_2. The carrier gas for the TCD was N_2.

A typical online GC experiment at a constant applied voltage spanned over 28.3 min. A gas aliquot (0.5 cm^3) was automatically injected into the GC every 4 minutes. The first injection was 240 seconds after the start of the HER. This is to ensure adequate flushing of the transfer line of atmospheric contaminants. Six gas aliquots were measured. The GC data collected in this work were translated to current efficiencies. It is assumed that the detected H_2 gas originate solely from electrochemical reactions, and that two electrons are required to form one H_2 molecule.

The current efficiency for HER using Mo_2C or Mo_2N is ~100%. We present here representative data of HER catalyzed by α-Mo_2C nanoparticles in 1M KOH electrolyte (Figure S3 and Table S1).

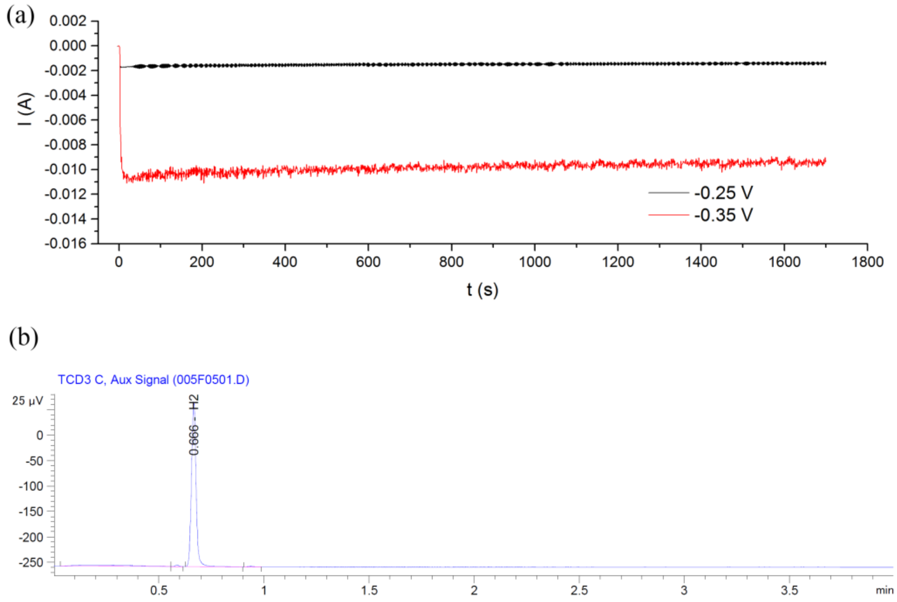

Figure S3: (a) Chronoamperogram of Mo_2C recorded at -0.25 and -0.35 V respectively in N_2-saturated 1 M KOH. (b) A representative gas chromatogram of the gas products emitted during water electrolysis using Mo_2C catalyst. Only a single peak belonging to H_2 gas was observed.

Voltage (V vs. RHE)	**Average Current (mA)**	**Average H_2 concentration (mol ppm)**	**Average current efficiency (%)**
-0.25	-1.4	539.3	100.8
-0.35	-10.6	4052.4	98.3

Table S1: Online GC measurements of gas products produced during HER using α-Mo_2C catalyst.

S3: Calculations of Turnover Frequencies (TOF) of H_2 Production

S3.1 Calculation of TOF using the surface areas of the Mo_2C catalysts as determined by XRD data

The structural data of Mo_2C from the ICDD-PDF-4+ (ICDD 00-035-0787) database was used. Density of Mo_2C = 9.098 g cm^{-3}. Average size of Mo_2C nanoparticle (as determined from the Scherrer equation) = 11 nm. The shapes of the nanoparticles are approximated to spherical.

Total volume of Mo_2C particles present on the electrode = $(2\times10^{-5}) / (9.098) = 2.198 \times10^{-6}$ cm^3

Total number of Mo_2C nanoparticles present on the electrode

$= [2.198\times10^{-6}] / [(4/3)(\pi)(r^3)]$

$= [2.198\times10^{-6}] / [(4/3)(\pi)(5.5 \text{ nm})^3]$

$= 3.15\times10^{12}$ particles

Surface area of 1 Mo_2C nanoparticle

$= (4)(\pi)(r^2)$

$= (4)(\pi)(5.5 \text{ nm})^2$

$=3.80\times10^{-16}$ m^2

Hence, the total surface area of all the Mo_2C nanoparticles present

$= (3.80\times10^{-16} \text{ m}^2) \times(3.15\times10^{12})$

$= 1.197\times10^{-3}$ m^2.

The surface of the Mo_2C catalysts is assumed to be (100)- and Mo atom- terminated. The area per surface unit cell is = 602.8 pm × 519.7 pm = 3.13×10^{-19} m^2.[2] There are 3.5 Mo atoms in this cell.

Hence, the total number of surface Mo atoms present

$= [3.5 / (3.13\times10^{-19} \text{ m}^2)] \times (1.197\times10^{-3} \text{ m}^2)$

$= 1.338\times10^{16}$ atoms

We assume that all the surface Mo atoms participate in the HER. Hence, the turnover frequency of H_2 production at η= 176 mV (current density measured = 10 mA cm^{-2}, electrolyte = 1 M KOH).

$= [(10 \text{ mA/cm}^2) (10^{-3}) (0.196 \text{ cm}^2) (6.02\times10^{23})] / [(96485.3 \text{ C/mol}) (2) (1.338\times10^{16})]$

$= 0.5$ s^{-1}

The factor ½ is derived by assuming that two electrons are required to form one H_2 molecule.

This TOF is a lower bound value, as it does not take into consideration agglomeration of the catalyst particles. Analogous calculations can be performed to obtain the TOFs occurring at other electrode potentials. These values are presented in Table 2.

S3.2 Calculation of TOF using the surface areas of the Mo_2N catalysts as determined by XRD data

The structural data of Mo_2N from the ICDD-PDF-4+ (ICDD 00-025-1366) database was used. Density of Mo_2N = 9.477 g cm^{-3}. Average size of Mo_2N nanoparticle (as determined from the Scherrer equation) = 16 nm. The shapes of the nanoparticles are approximated to spherical.

Total volume of Mo_2N particles present on the electrode = $(2\times10^{-5}) / (9.477) = 2.110 \times10^{-6}$ cm^3

Total number of Mo_2N nanoparticles present on the electrode

$= [2.110\times10^{-6}] / [(4/3)(\pi)(r^3)]$

$= [2.110\times10^{-6}] / [(4/3)(\pi)(8 \text{ nm})^3]$

$= 9.84\times10^{11}$ particles

Surface area of 1 Mo_2N nanoparticles

$= (4)(\pi)(r^2)$

$= (4)(\pi)(8 \text{ nm})^2$

$=8.04\times10^{-16}$ m^2

Hence, the total surface area of all the Mo_2N nanoparticles present

$= (8.04\times10^{-16} \text{ m}^2) \times (9.84\times10^{11})$

$= 7.91\times10^{-4}$ m^2.

We assume that the surface of the Mo_2N catalysts consists of low index planes. The number of Mo atoms present is 1.09×10^{15} Mo cm^{-2}.[3]

The total number of surface Mo atoms present

$= (7.91\times10^{-4} \text{ m}^2) \times (1.09\times10^{15} \text{ Mo/cm}^2)$

$= 8.62\times10^{15}$ atoms

We assume that all the surface Mo atoms participate in the HER. The turnover frequency of H_2 production at η= 250 mV (current density measured = -0.94 mA cm^{-2}, electrolyte = 1 M KOH).

$= [(0.94 \text{ mA/cm}^2) (10^{-3}) (0.196 \text{ cm}^2) (6.02\times10^{23})] / [(96485.3 \text{ C/mol}) (2) (8.62\times10^{15})]$

$= 0.07$ s^{-1}

This TOF is a lower bound value, as it does not take into consideration agglomeration of the catalyst particles. Analogous calculations can be performed to obtain the TOFs occurring at other electrode potentials. These values are presented in Table 2

S3.3 Calculation of TOF using BET surface area

We give a sample calculation for the TOF of H_2 production by Mo_2C in 1 M KOH. The overpotential is η= 176 mV, which gives a current density of 10 mA/cm^2. The surface area of Mo_2C was determined by BET measurements to be 9.1 m^2 g^{-1}. The surface of the Mo_2C catalysts is assumed to be (100)- and Mo atom terminated. The area per surface unit cell is = 602.8 pm × 519.7 pm = 3.13×10^{-19} m^2.[2] There are 3.5 Mo atoms in this cell.

Hence, the total number of surface Mo atoms present

$= [3.5 / (3.13\times10^{-19}\ \text{m}^2)] \times (2\times10^{-5}\ \text{g}) \times (9.1\ \text{m}^2\ \text{g}^{-1})$

$= 2.04 \times 10^{15}$ atoms

We assume that all the Mo sites are involved in the HER process. The factor ½ is derived by assuming that two electrons are required to form one H_2 molecule.

Turnover frequency of H_2 production at η= 176 mV (measured current density = 10 mA cm^{-2})

$= [(10\ \text{mA/cm}^2)\ (10^{-3})\ (0.196\ \text{cm}^2)\ (6.02 \times 10^{23})] / [(96485.3\ \text{C/mol})\ (2)\ (2.04\times10^{15})]$

$= 3\ \text{s}^{-1}$

The TOF calculated here is higher than that determined in S3.1. This is because the surface area of Mo_2C as determined by the BET method is lower than that determined by XRD and TEM data. This can be attributed to agglomeration of the catalysts powder which reduces the effective surface areas that can be probed by N_2 sorption (the BET method). Analogous calculations and findings can be made for the TOFs of Mo_2N.

In this work, we shall use the more conservative TOF values as determined in S3.1-3.2 for comparison with other works.

S4: Electrochemical Impedance Spectroscopy

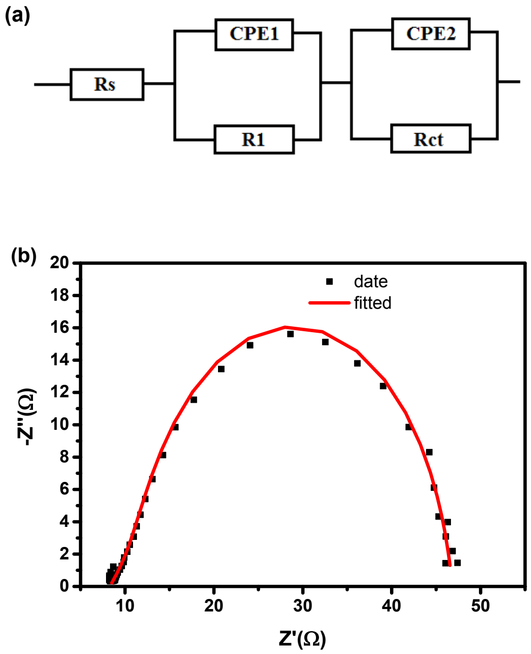

Figure S4: (a) Two-time constant model and (b) Nyquist plot of the Mo_2C electrode at $\eta = 200$ mV with amplitude of 5 mV in 1 M KOH solution.

Catalyst	**Electrolyte**	**Tafel slope from LSV (mV dec^{-1})**	**Tafel slope from EIS (mV dec^{-1})**
α-Mo_2C	0.5 M H_2SO_4	56	56
	1 M KOH	58	57
γ-Mo_2N	0.5 M H_2SO_4	100	104
	1 M KOH	108	126

Table S2: Tafel slopes of the as-synthesized Mo compounds.

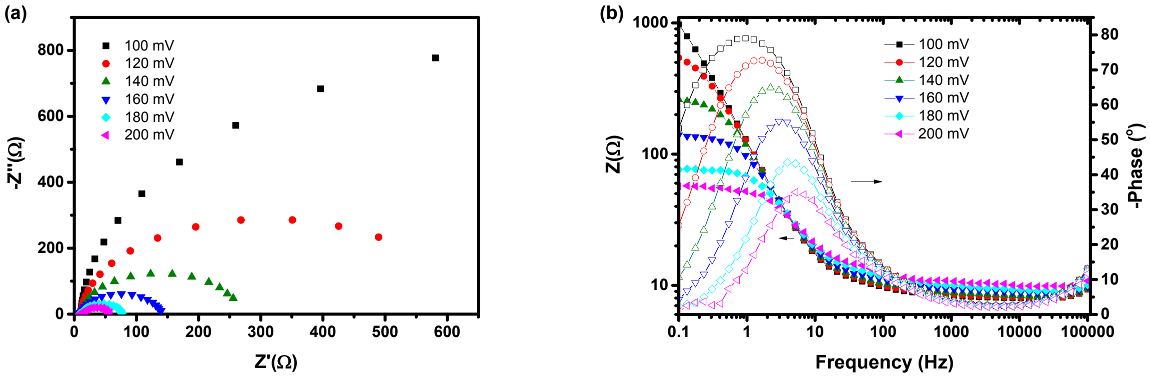

Figure S5 (a) Nyquist and (b) corresponding Bode plots of the Mo_2C recorded at selected overpotentials in N_2-saturated 0.5 M H_2SO_4 solution.

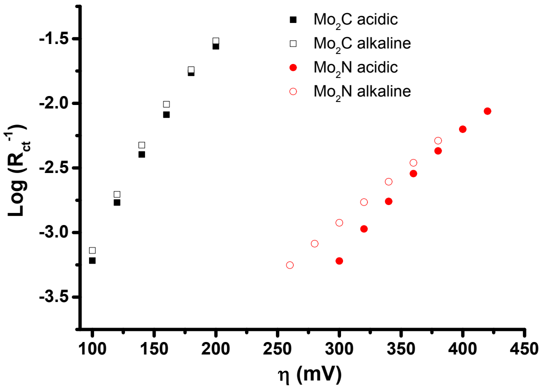

Figure S6: Plots of log (R_{ct}^{-1}) vs overpotential for the Mo_2C (square), and Mo_2N (circle) catalysts in N_2-saturated 0.5 M H_2SO_4 (solid) and N_2-saturated 1 M KOH (open).

References

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