Electronic Supporting Information

Mo_2C quantum dots embedded chitosan-derived nitrogen-doped carbon for efficient hydrogen evolution in a broad pH range

Zonghua Pu,[a] Min Wang,[a] Zongkui Kou,[a] Ibrahim Saana Amiinu,[a] and Shichun Mu[a] *

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, China

* E-mail: msc@whut.edu.cn

Experimental Section

Materials: Chitosan, ammonium molybdate ($(NH_4)_6Mo_7O_{24}•4H_2O$) and sulfuric acid (H_2SO_4) were purchased from Beijing Chemical Works. Commercial Mo_2C, potassium hydroxide (KOH), potassium phosphate (KH_2PO_4, K_2HPO_4) and ethanol were purchased from Aladdin Reagent. Nafion (5 wt%) and Pt/C (20 wt%) were purchased from Sigma-Aldrich. All the reagents in the experiment were analytical grade and used without further treatments. Deionized Mini-Q water was used as solvent.

Preparation of Mo_2C QDs/NGCLs: 1.0 g $(NH_4)_6Mo_7O_{24}•4H_2O$ and 1.0 g chitosan were dissolved in water via ultrasonication for 20 min. The solution was dried at 80 ℃ form homogeneous powder. The solid mixture was annealing at 900 °C for 2 h in Ar atmosphere. After cooled to room temperature naturally, the resulting products of Mo_2C QDs/NGCLs were obtained.

Preparation of NGCLs: NGCLs were derived from pyrolysis of chitosan powder with the same temperature under Ar flow.

Characterizations: X-ray diffraction (XRD) patterns were collected on a Rigaku X-ray diffractometer equipped with a Cu K_α radiation source. The morphology and structure were characterized by transmission electron microscopy (TEM, HITACHI H-8100). X-ray photoelectron spectroscopy (XPS) was obtained on an ESCALABMK

II X-ray photoelectron spectrometer. Raman shifts were recordedon aLabRAMAramis Raman spectrometer instrument using the Ar ion laser with an excitation wavelength of 633 nm.

Electrochemical characterization: The electrochemical tests for HER were carried out with a CHI 660E electrochemical workstation using a three-electrode configuration cell. The Ag/AgCl (3.0 M KCl) and graphite rod were used as reference electrode and auxiliary electrode, respectively. Glass carbon electrode (GCE: diameter = 3 mm) modified by catalyst was used as working electrode. 10 mg catalyst and 10 μl 5 wt% Nafion solution were dispersed in 990 μl ethanol/water (v/v=1:1) mixed solvent by sonication 30 min. Then 14 μl of the catalyst ink was loaded on a GCE (loading: 2.0 mg cm^{-2}). The polarization curves were recorded in 0.5 M H_2SO_4 (pH = 0), 1.0 M phosphate buffered solution (PBS, pH = 7) and 1.0 M KOH (pH = 14) with a scan rate of 2 mV s^{-1} at room temperature (~25 ℃), respectively. In all measurements, the Ag/AgCl reference electrode was calibrated with respect to reversible hydrogen electrode (RHE) by adding a value of (0.197 + 0.059 pH) V. EIS measurements were carried out in the frequency range of 100 kHz–0.01 Hz. All measured polarization curves were corrected for iR loss.

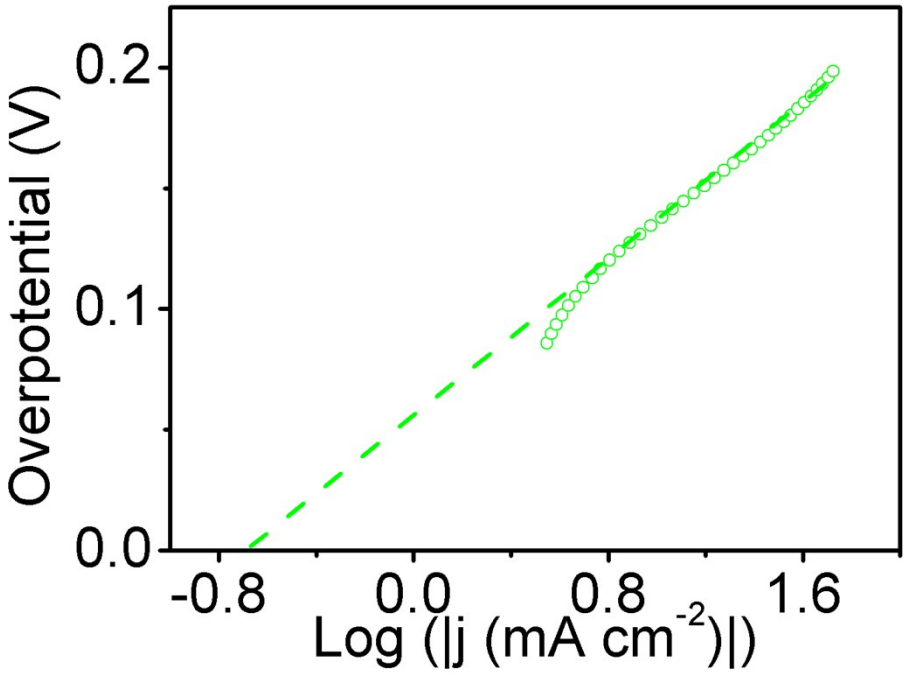

Fig. S1. Tafel plot of Mo_2C QDs/NGCLs.

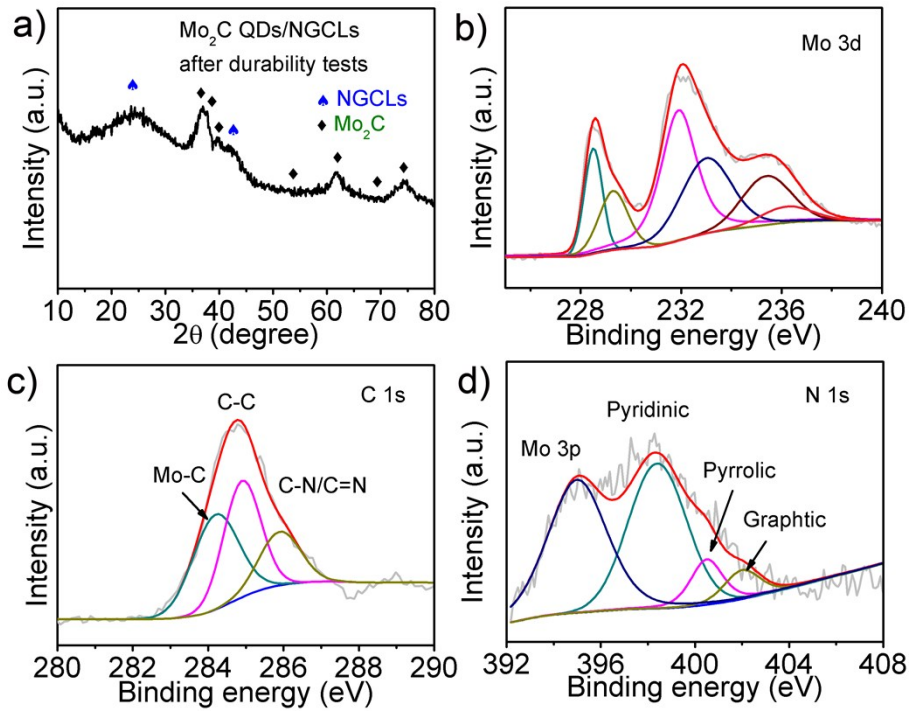

Fig. S2 (b) XRD pattern and (b-c) the high-resolution XPS spectra of Mo_2C QDs/NGCLs after the durability tests.

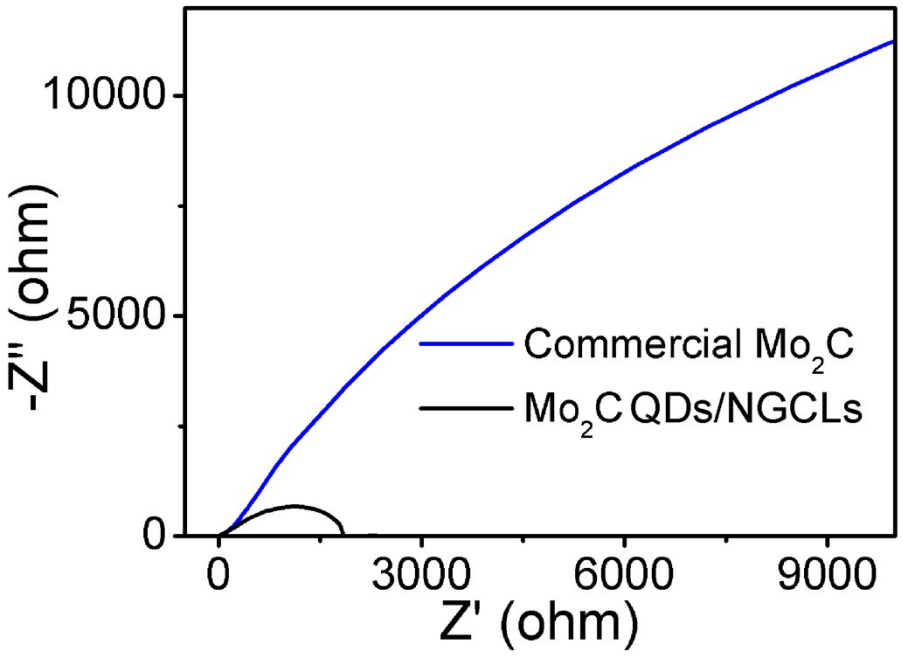

Fig. S3 Nyquist plots of Mo_2C QDs/NGCLs and commercial Mo_2C in 0.5 M H_2SO_4 at overpotential of 200 mV.

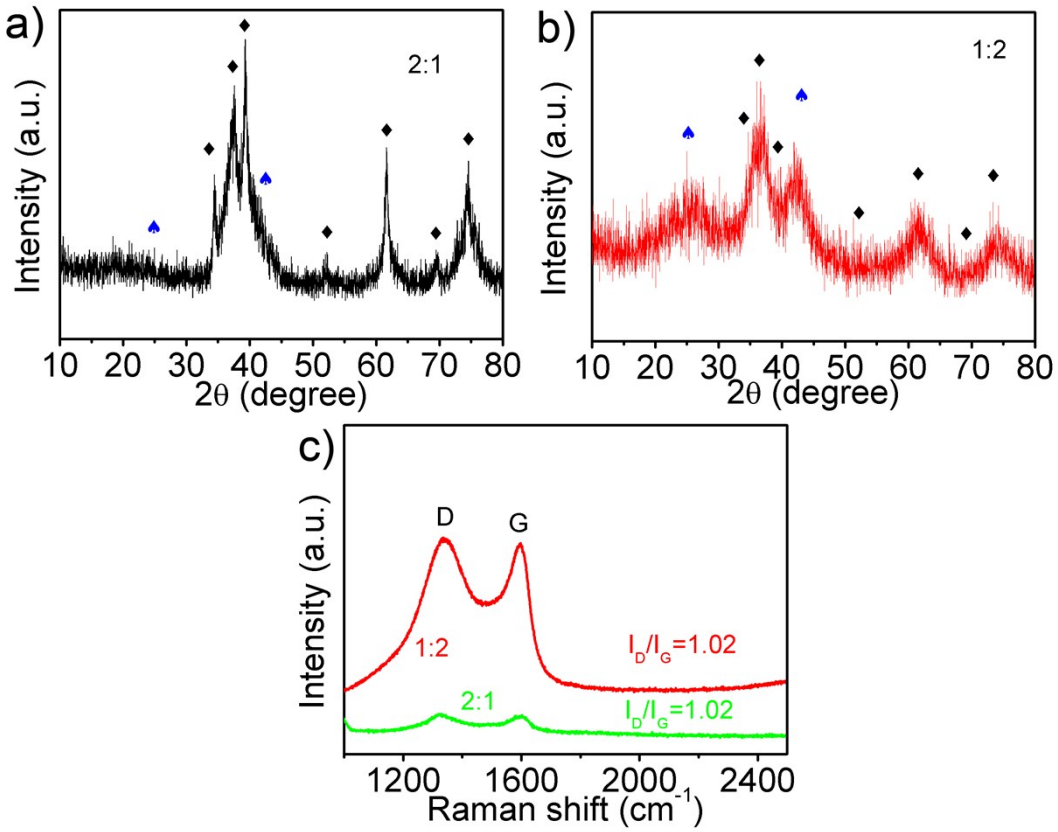

Fig. S4 (a, b) XRD patterns and (c) Raman spectra for samples obtained from $(NH_4)_6Mo_7O_{24}•4H_2O$ and chitosan with different initial mass ratios (2:1 and 1:2).

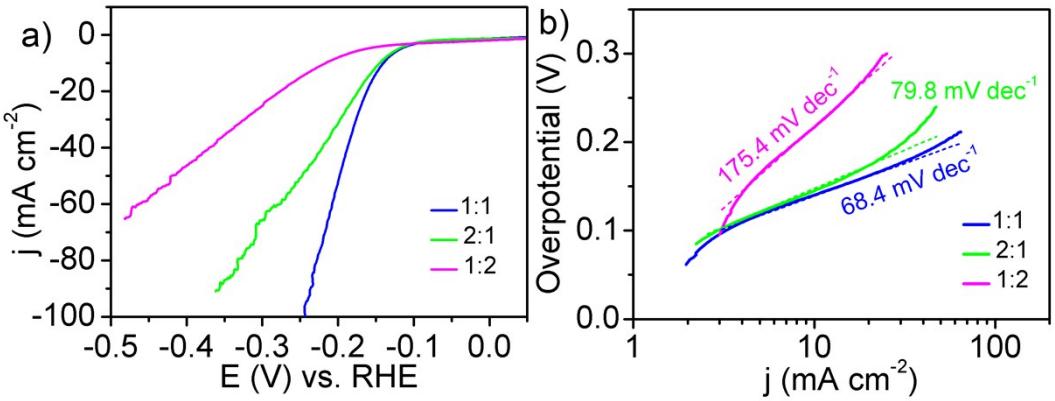

Fig. S5. (a) Polarization curves and (b) Tafel plots of the catalysts derived from ammonium molybdate and chitosan with different initial mass ratios.

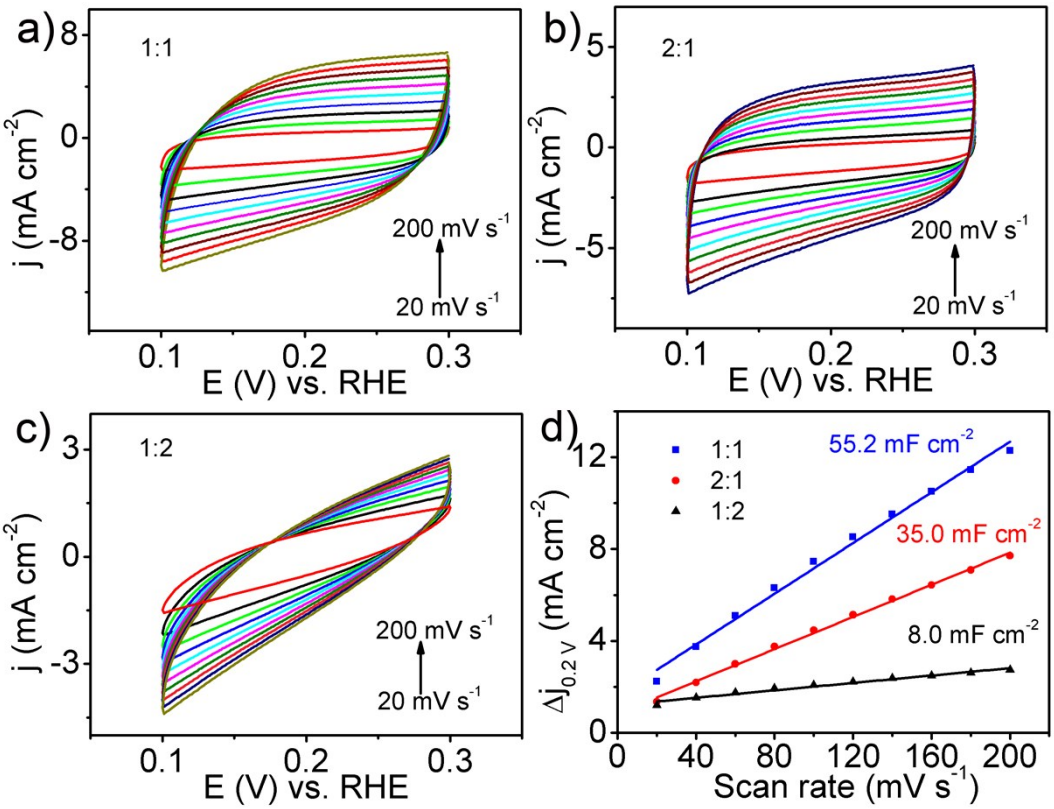

Fig. S6 (a, b and c) CVs for samples obtained from $(NH_4)_6Mo_7O_{24}$•$4H_2O$ and chitosan with different initial mass ratios (1:1, 2:1 and 1:2). (d) The capacitive current density at 0.2 V as a function of scan rate for samples in 0.5 M H_2SO_4.

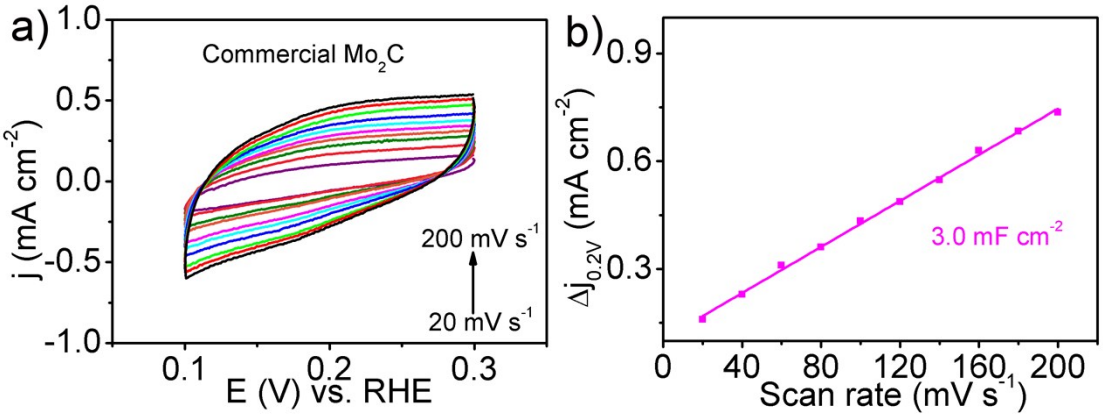

Fig. S7 (a) CVs and (b) the capacitive current density at 0.2 V as a function of scan rate for commercial Mo_2C in 0.5 M H_2SO_4.

Table S1 Comparison of HER performance in acidic media for Mo_2C QD NCs/NGCLs with other Mo_2C-based electrocatalysts.

Catalyst	Loading (mg cm^{-2})	Electrolyte/pH	j (mA cm^{-2})	Overpotential at the corresponding j (mV)	j_0 (mA cm^{-2})	Ref.
Mo_2C QDs/NGCLs	2	0.5 M H_2SO_4	10	136	0.2	This work
Mo_2C/GCNs	0.36	0.5 M H_2SO_4	10	200	0.0125	1
Bulk Mo_2C	1.4	1.0 M H_2SO_4	10	210	0.0013	2
Mo_2C/CNT	2	0.1 M $HClO_4$	10	152	0.014	3
Mo_2C/XC	2	0.1 M $HClO_4$	3	~150	0.013	3
Mo_1Soy/RGO	-	0.1 M $HClO_4$	10	177	0.037	4
β-Mo_2C	0.75	0.5 M H_2SO_4	10	172	0.017	5
Mo_2C@NC	0.28	0.5 M H_2SO_4	10	124	0.096	6
Mo_2C nanowires	0.21	0.5 M H_2SO_4	10	130	-	7
MoC_x nano-octahedrons	0.8	0.5 M H_2SO_4	10	142	0.23	8
MoCN	0.4	pH=1	10	145	-	9
Mo_2C/NCNT	3	0.5 M H_2SO_4	10	147	0.1146	10
3D Mo_xC/Ni network	-	0.5 M H_2SO_4	10	150	0.1	11
Mo_2C nanowires	~0.28	0.5 M H_2SO_4	10	200	-	12
Mo_2C nanoparticles	0.102	0.5 M H_2SO_4	10	198	-	13

Table S2 Comparison of HER performance in neutral media for Mo_2C QDs/NGCLs with other Pt-free HER electrocatalyst.

Catalyst	Electrolyte/pH	*j* (mA cm^{-2})	Overpotential at the corresponding *j* (mV)	Ref.
Mo_2C QDs/NGCLs	1.0 M PBS	2	73	This work
		10	136	
Bulk Mo_2C	pH= 7	1	200	2
Mo_2C@NC	1.0 M PBS	10	156	6
Mo_2C/NCNT	1.0 M PBS	10	645	10
MoP/CF	1.0 M PBS	1	~300	14
MoS_2/Mo	1.0 M PBS	2	172	15
WP NAs/CC	1.0 M PBS	2	95	16
CoP/CC	1.0 M PBS	2	65	17
Co-NRCNTs	0.1 M PBS	2	380	18
FeP/Ti	1.0 M PBS	10	102	19
H_2-CoCat/FTO	1.0 M PBS	2	385	20
Co-S/FTO	1.0 M PBS	2	83	20
$CuMoS_4$ crystals	1.0 M PBS	2	210	21

Table S3 Comparison of HER performance in basic media for Mo_2C QDs/NGCLs with other Pt-free HER electrocatalyst.

Catalyst	Electrolyte/pH	*j* (mA cm^{-2})	Overpotential at the corresponding *j* (mV)	Ref.
Mo_2C QDs/NGCLs	1.0 M KOH	2	73	This work
		10	111	
Bulk Mo_2C	1.0 M KOH	10	190	2
β-Mo_2C	0.1 M KOH	10	197	5
Mo_2C@NC	1.0 M KOH	10	60	6
MoC_x nano-octahedrons	1.0 M KOH	10	151	8
Mo_2C/NCNT	1.0 M KOH	10	257	10
Mo_2C nanoparticles	1.0 M KOH	10	176	13
MoS_2/Mo	1.0 M KOH	2	172	15
WP NAs/CC	1.0 M KOH	10	150	16
CoP/CC	1.0 M KOH	10	209	17
Co-NRCNTs	1.0 M KOH	10	370	18
Co-S/FTO	1.0 M KOH	1	480	20
Ni_2P nanoparticles	1.0 M KOH	20	250	22
Ni wire	1.0 M NaOH	10	350	23
Ni-Mo alloy/Ti foil	1.0 M NaOH	10	80	23

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