Supporting Information

Guanosine-assisted synthesis of core-shell $Mo_2N/Mo_2C/C$ structure for enhanced hydrogen evolution reaction

*Miao Xia[a,b], Shuchun Li[a], Xuefei Zhang[a], and Zailai Xie[a]**

Address: a. Key Laboratory of Advanced Carbon-Based Functional Materials (Fujian Province University) Fujian Provincial Key Laboratory of Electrochemical Energy Storage Materials, Fuzhou University, Fuzhou 350016, Fujian, China; b. Changzhou Centers for Disease Control and Prevention, Changzhou, China

Email: zlxie@fzu.edu.cn; Tel: 0086-59122866102

Experimental

3 g guanosine and 570 μL sulfuric acid were dissolved in 35 mL deionized water in an oil bath at 80 °C, and then 1 g, 2 g and 3 g ammonium molybdate were added respectively. The solution was transferred to a polyteflon reactor and then placed in a stainless steel shell at 180 °C for 12 h. After cooling to room temperature, the samples were filtered through a Brinell funnel by deionized water, and then dried and ground at 80 °C. Samples after grinding were labeled as HTC-Mo-Guo-1, HTC-Mo-Guo-2, HTC-Mo-Guo-3 according to the amount of ammonium molybdate respectively. HTC-Mo-Guo-1, HTC-Mo-Guo-2, HTC-Mo-Guo-3 were annealed under a H_2/Ar (volume content of H_2: 5%) atmosphere. It was heated to 800 °C for 2 h at a heating rate of 5 °C /min. After cooling down to room temperature, samples after pyrolysis were labled as Mo-Guo-1, Mo-Guo-2, Mo-Guo-3 which were obtained from HTC-Mo-Guo-1, HTC-Mo-Guo-2, HTC-Mo-Guo-3 respectively.

Electrochemical test

The three-electrode system was used for HER testing, with 4.0 mm glassy carbon electrode as the working electrode, Ag/AgCl (saturated KCl) electrode as the reference electrode, and graphite rod as the counter electrode. The electrode potential of the reference electrode at 25 ºC is 0.1989 V. According to Nernst equation and the selection of three electrodes, the obtained potential should be converted into the electrode potential of reversible hydrogen electrode by the following formula:

E (RHE) =E+0.1989+0.0591pH

The sample preparation method was as follows: 3.0 mg sample was weighed and dispersed in 300 μL absolute ethanol and 100 μL deionized water, then 40 μL Nafion solution of 5 wt% was added, and then ultrasonic treatment was carried out for 15 min. Then 5.5 μL of the mixed solution was evenly added to the surface of the working electrode, and then placed in the drying oven for drying. Then the loading capacity of the active material on the working electrode is about 0.3 $mg \cdot cm^{-1}$.

Polarization curve test

Polarization curves were tested using 1 M KOH and 0.5 M H_2SO4 as electrolytes, and linear scanning voltammetry was used at a scanning rate of 5 $mV \cdot s^{-1}$. The LSV curves were obtained for iR drop compensation. The solution resistance required for iR drop compensation is measured by AC impedance method.

Tafel curve test

The Tafel equation, η=a+blgj, describes the semilog relationship between the overpotential (η) of hydrogen evolution reaction and the current density (j) of the reaction. Therefore, through the measurement of the polarization curve, we took the current density as the abscess coordinate and the overpotential as the ordinate coordinate to make the curve to get the Tafel curve, and calculated the slope of the curve to infer the possible reaction process.

Electrochemical Active Area Test (ESCA)

The electrochemical active area was measured by cyclic voltammetry in 1 M KOH solution to calculate the double layer capacitance value. The CV curves of the samples at different scanning rates were measured by gradually increasing the scanning rate from 20 $mV \cdot s^{-1}$ to 200 $mV \cdot s^{-1}$.

Electrochemical AC Impedance spectroscopy (EIS)

The surface electron transfer resistance of the characterized material was measured by AC impedance method in 1 M KOH solution. The overpotential in the test was set to 100 mV, with a frequency range from 100,000 Hz in the high frequency region to 0.01 Hz in the low frequency region and an amplitude of 10 mV.

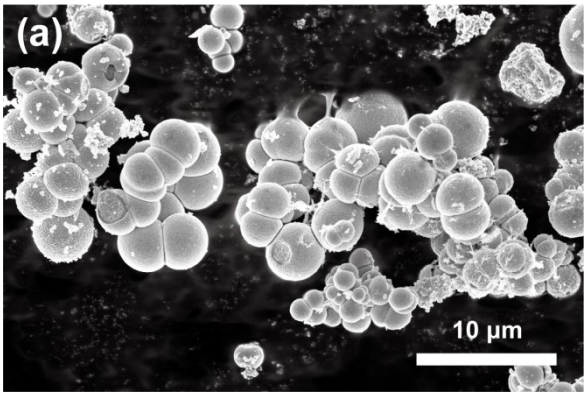

Figure S1. SEM images of Mo-Guo-2.

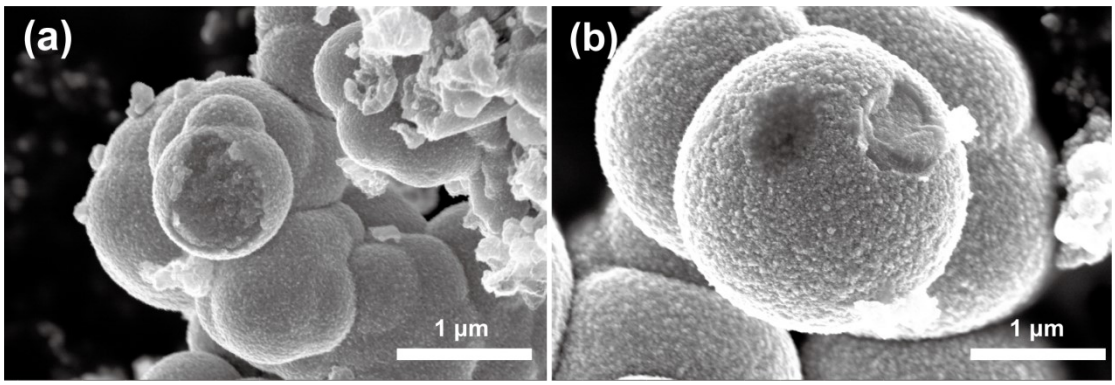

Figure S2. (a) SEM images of Mo-Guo-1, (b) SEM images of Mo-Guo-3.

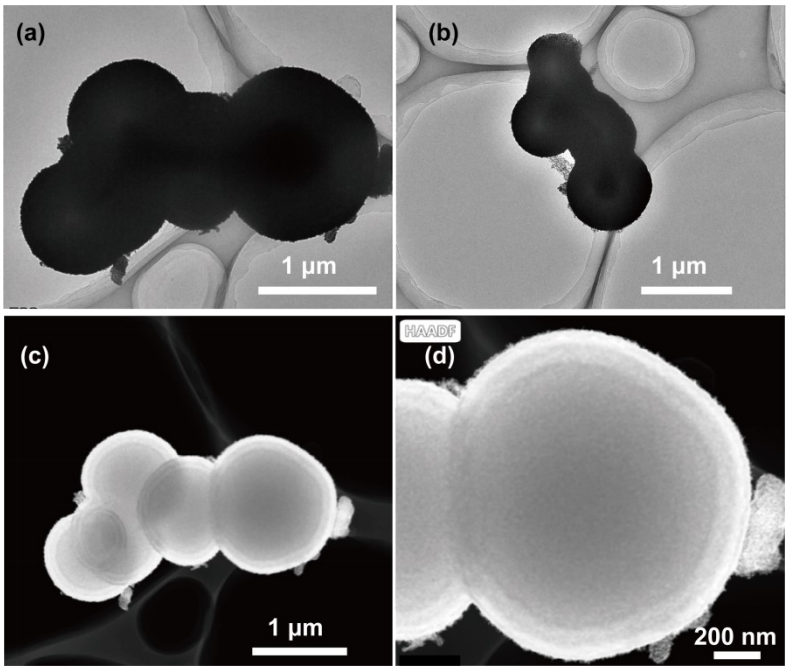

Figure S3. (a) -(b) TEM images of Mo-Guo-2, (c) -(d) HRTEM of Mo-Guo-2.

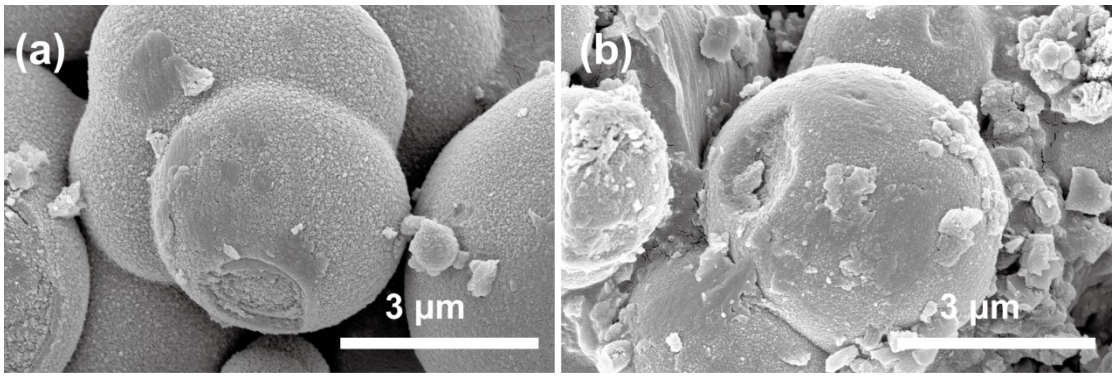

Figure S4. SEM images of (a) HTC-Mo-Guo-1, (b) HTC-Mo-Guo-3.

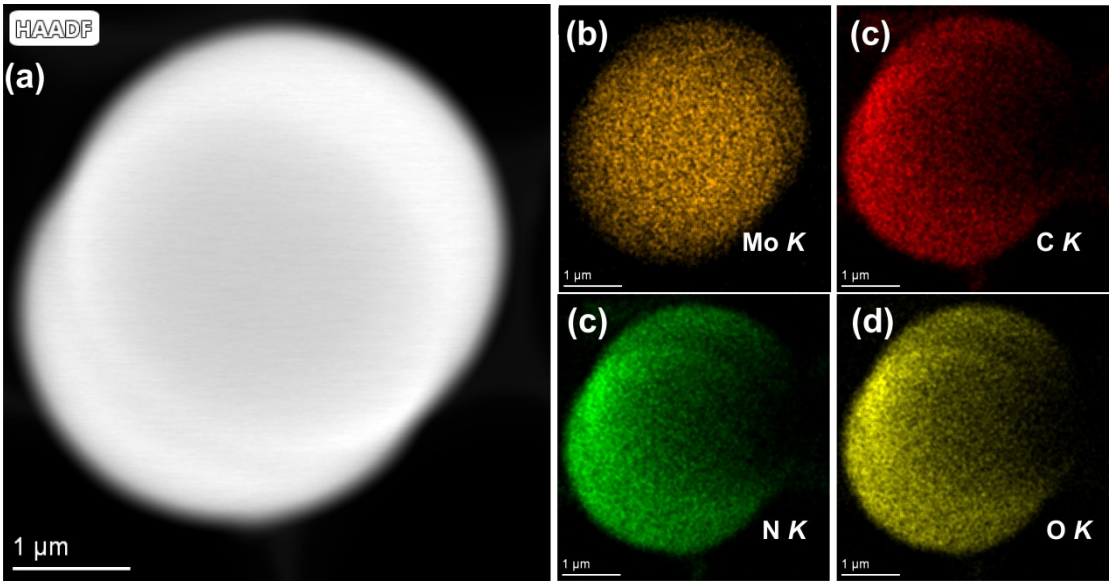

Figure S5. (a)HAADF of Mo-Guo-2 at 2 h and EDS mapping of Mo, C, N and O.

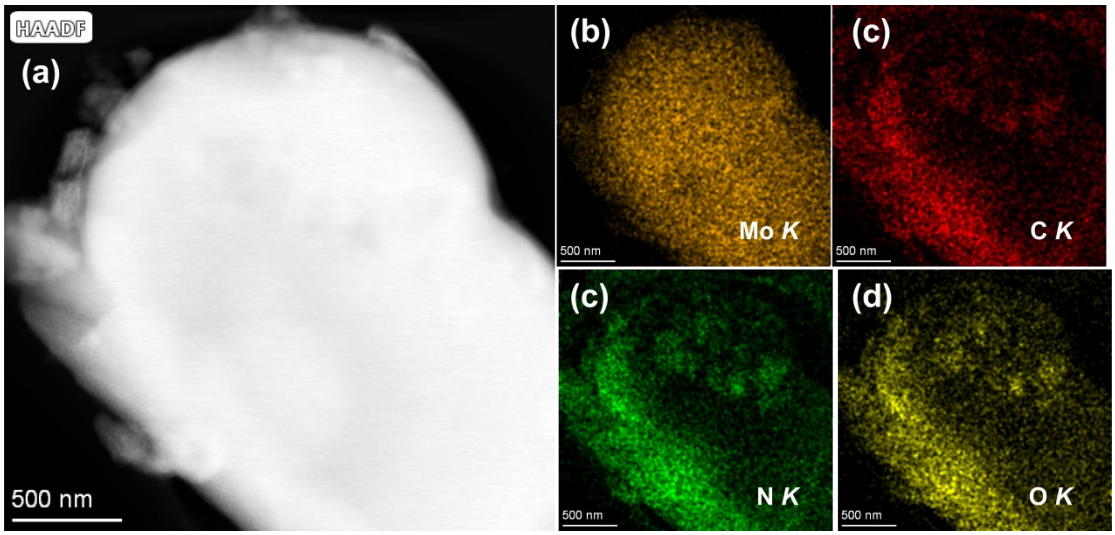

Figure S6. (a)HADDF of Mo-Guo-2 at 12 h and EDS mapping of Mo; C; N and O.

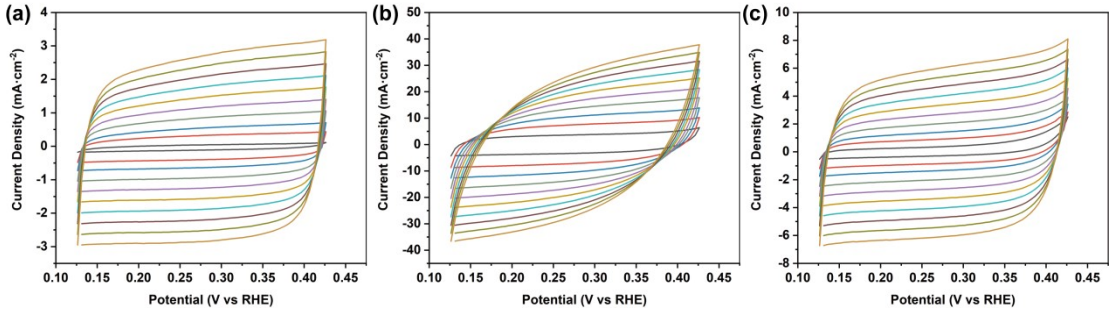

Figure S7. The cyclic voltammetry curve of Mo-Guo in the sweep speed range of 20 $mV \cdot s^{-1}$-200 $mV \cdot s^{-1}$. (a) Mo-Guo-1, (b) Mo-Guo-2, (c) Mo-Guo-3.

Table S1. Textural properties of Mo-Guo samples.

Samples	BET Surface Area ($m^2 \cdot g^{-1}$)	V_{total} ($m^3 \cdot g^{-1}$)	V_{meso} ($m^3 \cdot g^{-1}$)	V_{micro} ($m^3 \cdot g^{-1}$)
Mo-Guo-1	48.14	0.074	0.007	0.063
Mo-Guo-2	43.82	0.065	0.004	0.055
Mo-Guo-3	21	0.023	0.003	0.017

Table S2. HER Performance of Various Mo-Based Electrocatalysts under alkaline condition.

Samples	PH	Tafel slope/mV	η_{10} (mA cm^2)	Reference
$Mo_2N/Mo_2C/C$	14	62	79	This work
Mo_2C@NCS	14	83	147	[1]
Mo_2C-NCSs	14	115	140	[2]
Mo_2C@NC/Mo_2C-12	14	38	86	[3]
MoC-Mo_2C	14	42	120	[4]
Fe_3C-Mo_2C/NC	14	92	170	[5]
Fe_3C-Mo_2C/NC	14	57	180	[6]
Mo_2C microparticles	14	54	190	[7]

References

1. J.-T. Ren, L. Chen, D.-D. Yang and Z.-Y. Yuan, Molybdenum-based nanoparticles (Mo_2C, MoP and MoS_2) coupled heteroatoms-doped carbon nanosheets for efficient hydrogen evolution reaction, *Applied Catalysis B: Environmental*, 2020, **263**.
2. Y. Xu, J. Yang, T. Liao, R. Ge, Y. Liu, J. Zhang, Y. Li, M. Zhu, S. Li and W. Li, Bifunctional water splitting enhancement by manipulating Mo-H bonding energy of transition Metal-Mo_2C heterostructure catalysts, *Chemical Engineering Journal*, 2022, **431**.
3. X. Zhang, T. Lei, M. Xia, Q.-H. Wei and Z. Xie, Core–shell Mo_2C@NC/Mo_2C hollow microspheres as highly efficient electrocatalysts for the hydrogen evolution reaction, *Dalton Transactions*, 2023, **52**, 6267-6272.
4. H. Lin, Z. Shi, S. He, X. Yu, S. Wang, Q. Gao and Y. Tang, Heteronanowires of MoC–Mo_2C as efficient electrocatalysts for hydrogen evolution reaction, *Chemical Science*, 2016, **7**, 3399-3405.
5. T. Ouyang, Y. Q. Ye, C. Y. Wu, K. Xiao and Z. Q. Liu, Heterostructures Composed of N-Doped Carbon Nanotubes Encapsulating Cobalt and β-Mo_2C Nanoparticles as Bifunctional Electrodes for Water Splitting, *Angewandte Chemie International Edition*, 2019, **58**, 4923-4928.
6. H. Lin, W. Zhang, Z. Shi, M. Che, X. Yu, Y. Tang and Q. Gao, Electrospinning Hetero-Nanofibers of Fe_3C-Mo_2C/Nitrogen-Doped-Carbon as Efficient Electrocatalysts for Hydrogen Evolution, *ChemSusChem*, 2017, **10**, 2597-2604.
7. H. Vrubel and X. Hu, Molybdenum Boride and Carbide Catalyze Hydrogen Evolution in both Acidic and Basic Solutions, *Angewandte Chemie International Edition*, 2012, **51**, 12703-12706.