Supporting information

Laser Induced MoS_2/Carbon Hybrids for Hydrogen Evolution Reaction Catalysts

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1. Experimental Section

1.1 Synthesis and pattering of the MoS_2/carbon hybrids

Ammonium molybdate, sodium sulfide, and citric acid with different molar ratio of CA: Mo: S were dissolved in deionized water homogeneously. Take a recipe with CA: Mo: S of 2:1:3 as an example, 192 mg 192 mg CA ($C_6H_8O_7$), 88 mg ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) and 113 mg sodium sulfide (Na_2S) were dissolved in 1.5 ml deionized (DI) water. After being mixed homogeneously in a bath sonicator, 0.2 ml solution was dropped on a glass slide with a size of 1 inch x 3 inch. The glass slide was then put into a vacuum oven and dried at a room temperature for 30 min. Direct laser writing (DLW) was then conducted on the surface of the precursor films using a Full Spectrum H-Series Desktop CO_2 Laser. The pulse width of the laser is 14 μs. The laser power was fixed at 4 W during processing. All experiments were performed under ambient conditions. For laser patterning, the patterns were first designed by AutoCAD, then DXF files were loaded onto the software to control the movement of the laser beams. After laser induction the obtained black

MoS_2/carbon hybrids were scraped from glass slide for further experiments, then was purified by a centrifuge in DI water at a speed of 4000 rpm for at least 3 times. To synthesize MoS_2 by the hydrothermal method, 19.2 g CA, 8.8 g ammonium molybdate, and 11.3 g Na_2S were dissolved in 100 ml DI water homogeneously. The molar ratio was the same to the ones in preparing films for DLW. Then the solution was put into a stain-less autoclave at 180 ℃ for 20 hours. The product was collected by the centrifuge in DI water at a speed of 4000 rpm.

1.2 Materials characterizations

Morphology analysis was conducted on a Hitachi S-4800 field emission scanning electron microscope (SEM). Elemental mapping and electron energy dispersive spectroscopy (EDS) were performed with an EDS detector equipped in the Hitachi S-4800 SEM. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were recorded on a JEOL-2100F microscope. X-ray diffraction (XRD) experiments were carried out on a Rigaku X-ray diffractometer having a Cu Kα radiation (λ = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) was recorded on a PHI Quantera equipped with monochromated Al Kα radiation. Raman spectra were collected from a Renishaw inVia Raman spectroscopy equipped with a 633 nm laser.

1.3 Electrochemical measurements

Electrochemical measurements were performed in a 708E electrochemical workstation (CH Instruments) in a typical three-electrode setup. In all the measurements, bulk MoS_2, MoS_2/carbon hybrid, hydrothermal MoS_2 and Pt/carbon had the same loading of ~0.2 mg cm^{-}

^{2} on the glassy carbon working electrode (3 mm in diameter). A graphite rod was used as the counter electrode, and a saturated silver chloride electrode as the reference electrode. An electrolyte solution consisting of 0.5 M H_2SO_4 was used for all the measurements. Before measurement, the reference electrode was calibrated with respect to the reversible hydrogen electrode (RHE) and all the potentials reported in this paper were versus RHE. Linear sweep voltammetry (LSV) measurements were conducted at a scan rate of 5 mV/s. The electrochemical impedance spectroscopy (EIS) was performed at an overpotential of 224 mV at frequencies from 0.1 Hz to 100k Hz.

2. Supplemental Figures

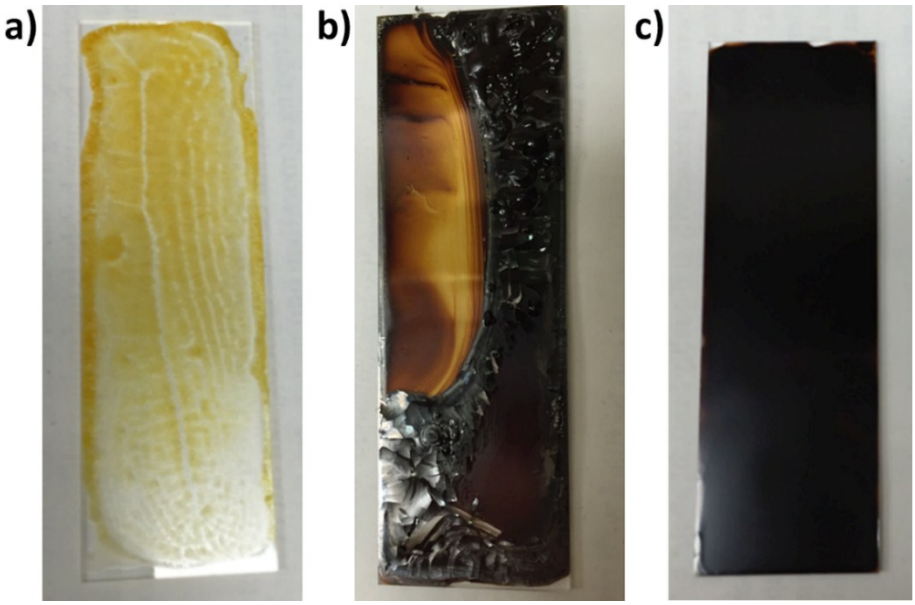

Figure S1. Optical images of precursor films with different molar ratios of Mo: S: CA. (a) Mo: S: CA ratio of 1:3:0; (b) Mo: S: CA ratio of 1:3:1; (c) Mo: S: CA ratio of 1:3:2.

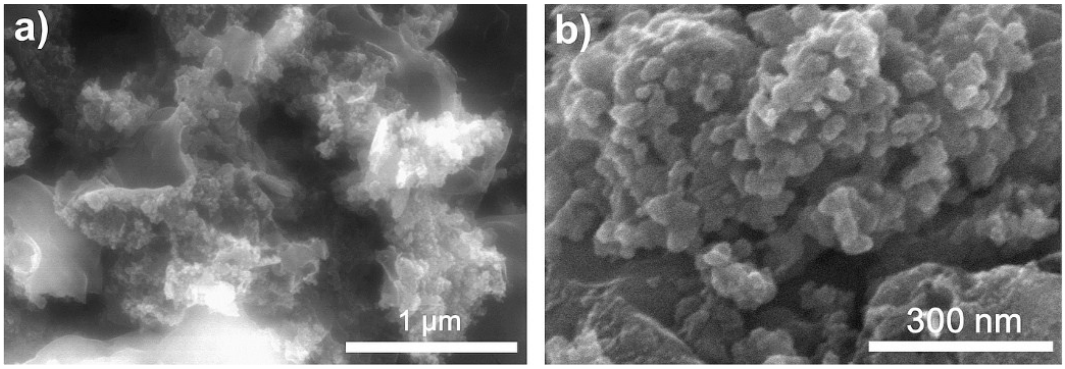

Figure S2. SEM images of laser-induced MoS_2/carbon hybrids, which show that the size of granule is around 30 nm.

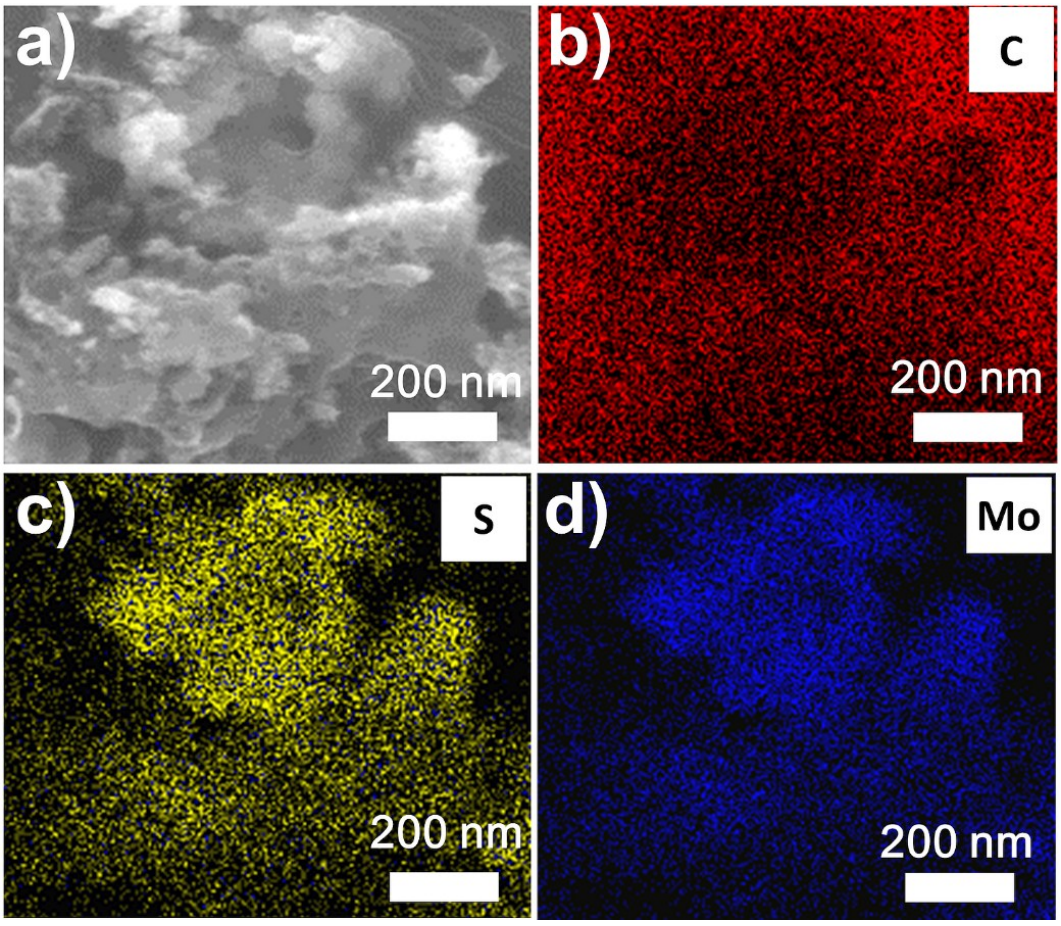

Figure S3. (a) SEM image of laser-induced MoS_2/carbon hybrids; (b-d) Energy dispersive X-ray (EDS) elemental mapping images of elemental C, S, and Mo from the sample shown in (a)

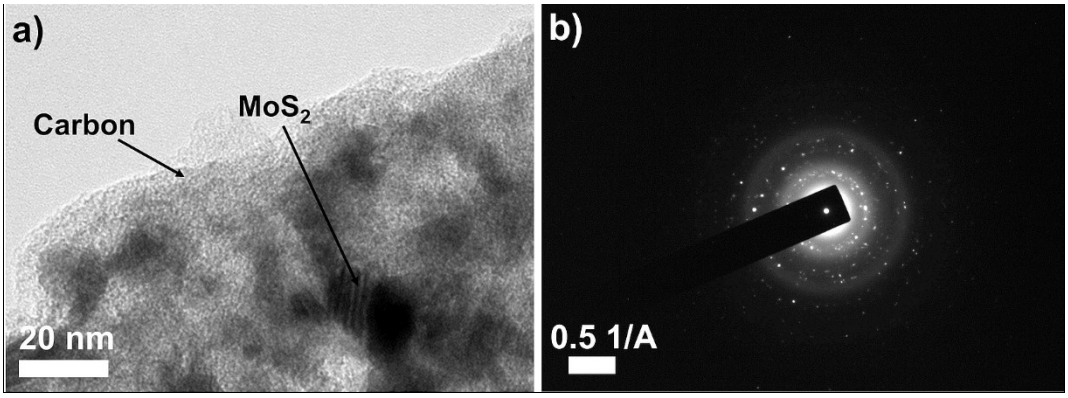

Figure S4. (a) TEM image and (b) Selected area electron diffraction (SAED) pattern of laser induced MoS_2/carbon hybrids. In the electron diffraction pattern, the halo rings are due to amorphous carbon, and bright spots represent MoS_2 nanocrystals.

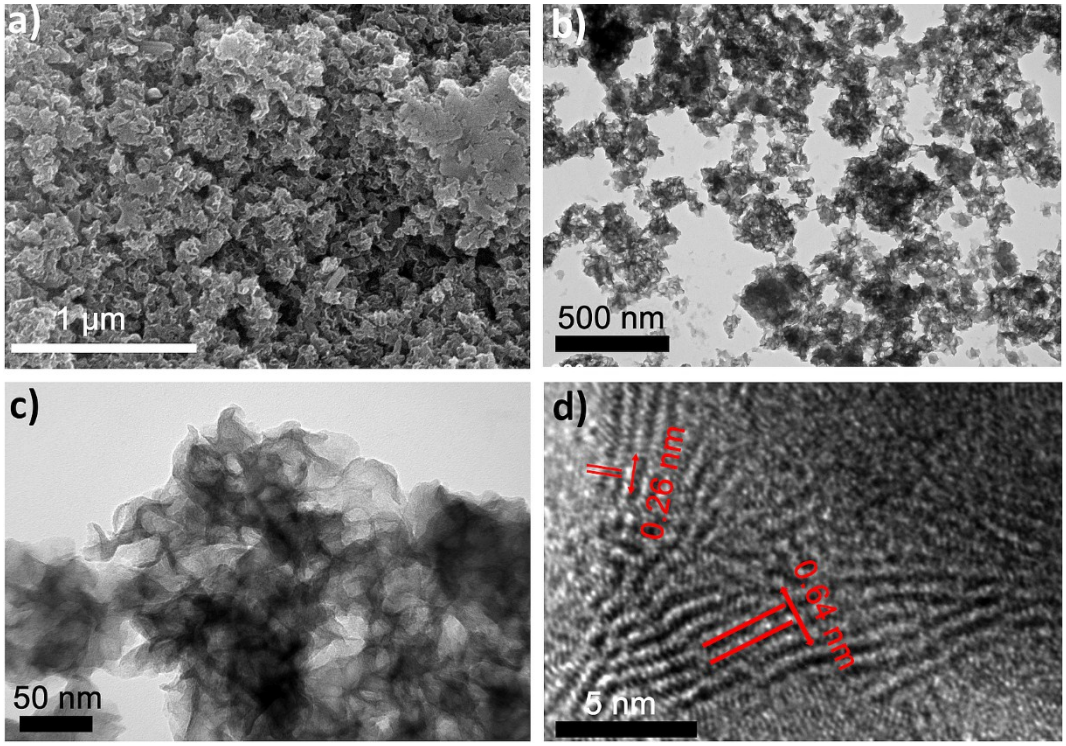

Figure S5. (a) SEM image of hydrothermal MoS_2 showing aggregated MoS_2 crystals. (b) and (c) TEM images of hydrothermal MoS_2; (d) HRTEM image of hydrothermal MoS_2 with layered structures. Lattice spacing of 0.26 nm and 0.64 nm correspond to the (002) and (100) planes of MoS_2 crystals.

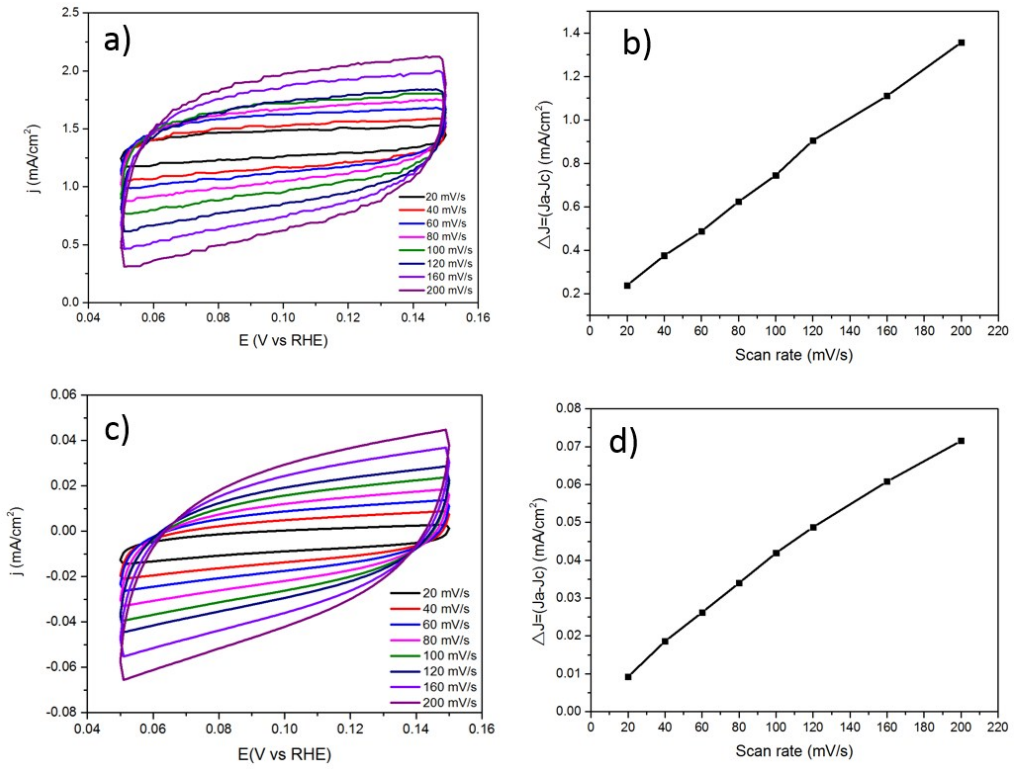

Figure S6. Cyclic voltammetry curves of (a) DLW MoS_2/carbon hybrids and (c) hydrothermal MoS_2 at scan rates (V_b) from 20 to 200 mV·s^{-1}. Scan rate dependence of the current densities of (b) DLW MoS_2/carbon hybrids and (d) hydrothermal MoS_2.

Electrochemically active surface areas (ECSA**)**: The ECSA of a material with similar composition is proportional to its electrochemical double-layer capacitance (C_{dl}), which was measured by CV in a non-Faradaic region at different scan rates (V_b) of 20, 40, 60, 80, 100, 120, 160 and 200 mV s^{-1} (Fig. S6a and c). Then the double-layer capacitance (C_{dl}) was estimated by plotting the $\Delta j = (j_a - j_c)$ at 0.1 V vs RHE as a function of the scan rate (Fig. S6b and d). It can be calculated using the equation:

$$C_{dl} = \frac{d(\Delta j)}{2dV_b}$$

The ECSA can be calculated from the C_{dl} according to:

$$ECSA = \frac{C_{dl}}{C_s}$$

Where C_s is the specific capacitance of a flat surface with 1 cm^2 of real surface area. Here we assume its value is 40 μF·cm^{-2} per cm^2_{ECSA} for the flat electrode. The calculated value of ECSA for DLW MoS_2/carbon hybrid was ~70 cm^2_{ECSA}, while the value for the hydrothermal MoS_2 is ~5 cm^2_{ECSA}.

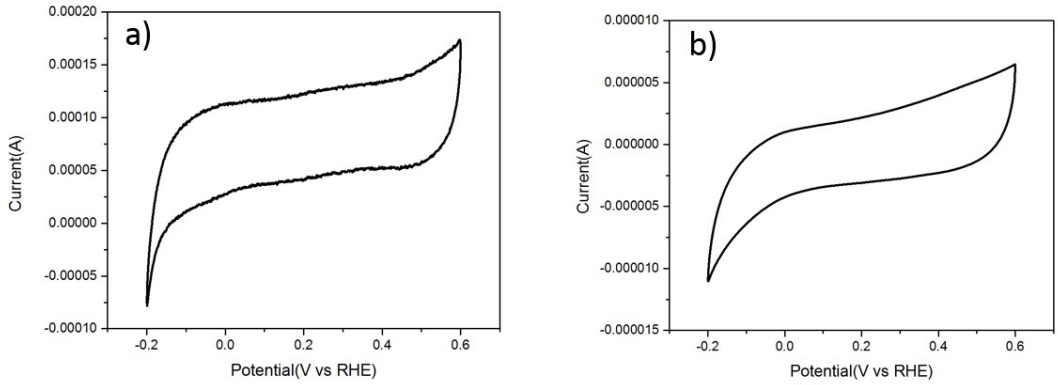

Figure S7. Cyclic voltammetry curves of (a) DLW MoS_2/carbon hybrids and (c) hydrothermal MoS_2 in 0.5 M H_2SO_4 vs. RHE at a scan rate of 50 mV/s.

Calculation of ctive sites: The absolute number of active sites (n) for both types of MoS_2/carbon was examined using CV curves at a scan rate of 50 mV/s (Fig. S7). n (mol) was calculated with the equation: n=Q/(2F); where Q is the absolute voltammetry charges derived from the CV curves using equation: $Q = \frac{1}{V_b}\int_{E_1}^{E_2} IdE$ (E: the potential, V_b: scan rate); and F is the Faraday's constant (96480 C/mol). For the sample of DLW MoS_2/carbon hybrid, n (mol) is $1.34*10^{-8}$ mol. For hydrothermal MoS_2/carbon, n (mol) = $5.51*10^{-10}$ mol. If normalized to mass loading of them on the glass carbon, they are $9.33*10^{-7}$ mol/mg and $3.83*10^{-8}$ mol/mg, respectively.

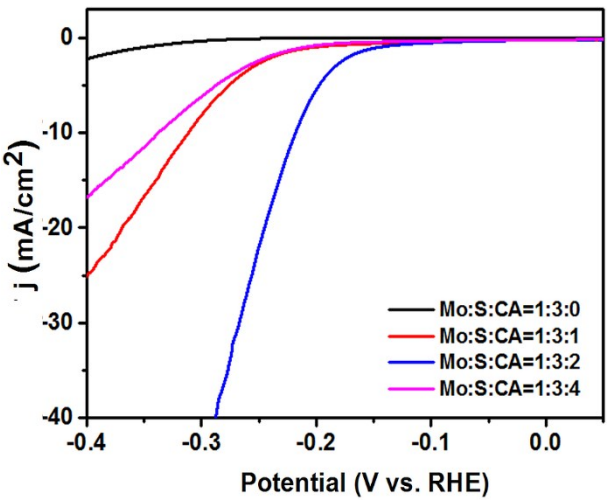

Figure S8. Polarization curves of laser induced MoS_2/carbon hybrids obtained with the different mass ratios of citric acid in Mo: S: CA. The optimal ratio of Mo: S: CA is 1:3:2.

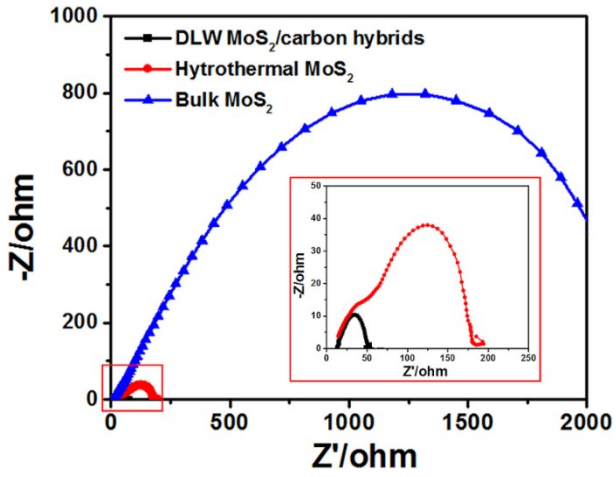

Figure S9. Comparison Nyquist plots of bulk MoS_2, hydrothermal MoS_2, and laser induced MoS_2/carbon hybrids. Inset image is enlarged from the area indicated in the red rectangle. Laser-induced MoS_2/carbon hybrids have the smallest charge transfer resistance, indicating the fastest HER kinetic process.

Table S1 Summary of HER catalytic performances of bulk MoS_2, hydrothermal MoS_2 and DLW MoS_2/carbon hybrids

Samples	η_{10} (mV)	b_f (mV/dec)	J_0 (mA/cm^2)
Bulk MoS_2	N/A	97	$1.4663*10^{-3}$
Hydrothermal MoS_2	276	76	$3.9048*10^{-3}$
DLW MoS_2/carbon hybrids	216	64	$4.2049*10^{-3}$

η_{10}: overpotential at a current density of 10 mA/cm^2; b_f: Tafel slope; J_0: exchange current density.