Electronic Supplementary Information

Vertically Oriented MoS_2 and WS_2 Nanosheets Directly Grown on Carbon Cloth as Efficient and Stable 3-Dimensional Hydrogen-Evolving Cathode

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Experimental details

Synthesis procedure: Nanostructured carbon cloth (CC) supported MoS_2 and WS_2 sheets were synthesized by a simple solvothermal method. In a typical procedure, 30mg ammonium thiomolybdate ($(NH_4)_2MoS_4$, Sigma-Aldrich) was dispersed in the mixture (15 mL) of *N, N*-Dimethylformamide (DMF) and water (H_2O) with volume ratio of 2:1 by stirring for 15min whereas 30mg ammonium tetrathiotungstate ($(NH_4)_2WS_4$, Sigma-Aldrich) was only dissolved in 15 mL of DMF to form a clear solution. Then two pieces of carbon cloth (CC, Gashub) (2 cm × 2 cm) were cleaned by sonication sequentially in acetone, water and ethanol for 10 min each to remove the surface impurities. The above well-dispersed $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$ solution and the CC (against the wall) were transferred to two 25 mL Teflon-lined stainless-steel autoclave, respectively, which was sealed, maintained at 200 °C for 12 h, and then allowed to cool to room temperature naturally. Dark thin films were taken out from the autoclave and subsequently rinsed with distilled water, ethanol, and oven-dried. The weight of nanostructured MoS_2 sheets and WS_2 sheets was accurately measured by weighing the CC before and after hydrothermal process, the loading masses for MoS_2 and WS_2 on CC are ~0.19 mg cm^{-2} and ~1.5 mg cm^{-2}, respectively. The annealed MoS_2/CC and WS_2/CC samples

was prepared by further treating the as-prepared nanostructured MoS_2/CC and WS2/CC materials at 350 ^oC in an atmosphere of H_2 (5%) mixed with N_2 (95%) for 2 h at a heating rate of 1 ^oC min^{-1}.

Flat carbon cloth (CC) supported MoS_2 and WS_2 films were synthesized also prepared by a simple solvothermal method. Briefly, 30mg $(NH_4)_2MoS_4$ was dispersed in 15 mL of DI-water (H_2O) whereas 30mg $(NH_4)_2WS_4$ was dissolved in 15 mL of DMF/ H_2O mixture with volume ratio of 2:1. Then the solutions were transferred into two Teflon-lined stainless autoclaves (25 mL), respectively and a piece of cleaned CC (2 cm × 2 cm) was immersed into the solution, respectively. The autoclave was sealed and maintained at 200 °C for 12 h, and then allowed to cool to room temperature naturally and washed and dried as above mentioned procedure.

Characterization: All transmission electron microscopy (TEM), high-resolution (HR) TEM images and element mapping were taken from JEOL JEM 2100F, while the field emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDX) spectra were taken on a JEOL JSM 6700F. X-ray photoelectron spectroscopy (XPS) spectrum was measured on a VG Escalab 250 spectrometer equipped with an Al anode (Al Kα = 1846.6 eV).

All electrochemical measurements were conducted on an Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands) in a three-electrode cell at room temperature. Linear sweep voltammetry with scan rate of 2 mV s^{-1} was conducted in 0.5 M H_2SO_4 solution using saturated calomel electrode as the reference electrode. A graphite rod was used as the counter electrode and the MoS_2/CC and WS_2/CC samples as the working electrode. In all experiments, the electrolyte solutions were purged with N_2 for 15 min prior to the experiments in order to remove oxygen. During the measurements, the headspace of the electrochemical cell was continuously purged with N_2. AC impedance measurements were carried out in the same configuration at η= 0.15 V from 10^5-0.1 Hz with an AC voltage of 5 mV. In all measurement, the saturated calomel electrode was used as the reference, it was calibrated with respect to reversible hydrogen electrode (RHE).

We performed the calibration in the high purity H_2 saturated electrolyte with a Pt wire as the working electrode. In 0.5 M H_2SO_4, E(RHE) = E(SCE) + 0.259 V. All the potentials reported in our manuscript were referenced to a reversible hydrogen electrode (RHE) by adding a value of 0.259 V. The stability testing of the nanostructured MoS_2/CC electrode and the annealed WS_2/CC electrode were examined by continuously cycling the potential between +0.1 and −0.5 V vs. RHE at a scan rate of 50 mV/s while the time-dependent stability were operated at constant overpotential of 0.2 V.

Table S1 Comparison of HER performance in acidic media of MoS_2/CC and WS_2/CC electrode with other non-noble metal electrocatalysts.

Catalyst	Loading amount (mg cm^{-2})	Current density (j, mA cm^{-2})	Overpotential at the corresponding j (mV)	Exchange current density (mA cm^{-2}	Ref.
MoS_2/CC	0.19	86	250	9.2×10^{-3}	*This work*
WS_2/CC	1.50	15	250	-	
MoS_2/Ti	0.12	~30	250	3.87×10^{-4}	*Adv. Mater. 2014, 26, 2683*
WS_2/rGO	0.40	~5	250	-	*Angew. Chem. Int. Ed. 2013, 52, 13751*
double-gyroid MoS_2/FTO	0.06	~12	250	6.9×10^{-4}	*Nat. Mater., 2012, 11, 963*
MoS_2 nanoparticles/CC	2.60	25	250	-	*Int. J. Hydrogen Energy 2013, 38, 12302*
WS_2 nanoparticles /CC	14.0	20	250	-	
$MoSe_2$/CFP	-	10	250	3.80×10^{-4}	*Nano Lett. 2013, 13, 3426*
WSe_2/CFP	-	~3	250	-	
interconnected network of MoP nanoparticles	0.36	~260	250	0.086	*Adv. Mater., 2014, 26, 5702*
bulk MoP	0.86	30	180	0.034	*Energy Environ. Sci., 2014, 7, 2624*
Ni_2P hollow nanoparticles	1.00	100	180	0.033	*J. Am. Chem. Soc., 2013, 135, 9267*
FeP nanosheets	0.28	~12	250	-	*Chem. Commun., 2013, 49, 6656*
Mo_2C/carbon paste electrode	-	19	250	-	*Angew. Chem. Int. Ed. 2012, 51, 12703*
NiMoNx/C	0.25	5	220	0.24	*Angew. Chem. Int. Ed., 2012, 51, 6131*

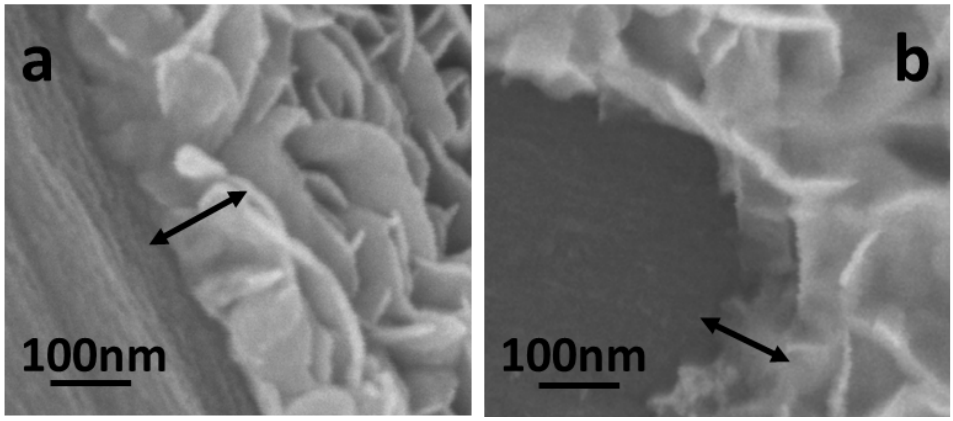

Figure S1. SEM images of the as-prepared nanostructured MoS_2/CC (a) and WS_2/CC (b) electrodes revealing the thickness of the films.

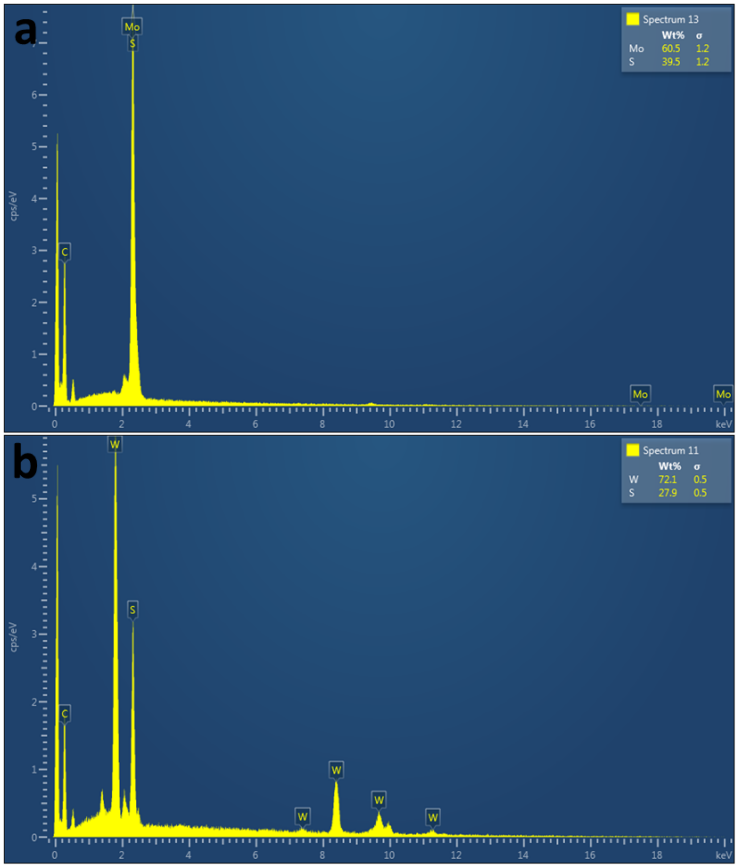

Figure S2. EDX spectrum of the nanostructured MoS_2/CC and WS_2/CC.

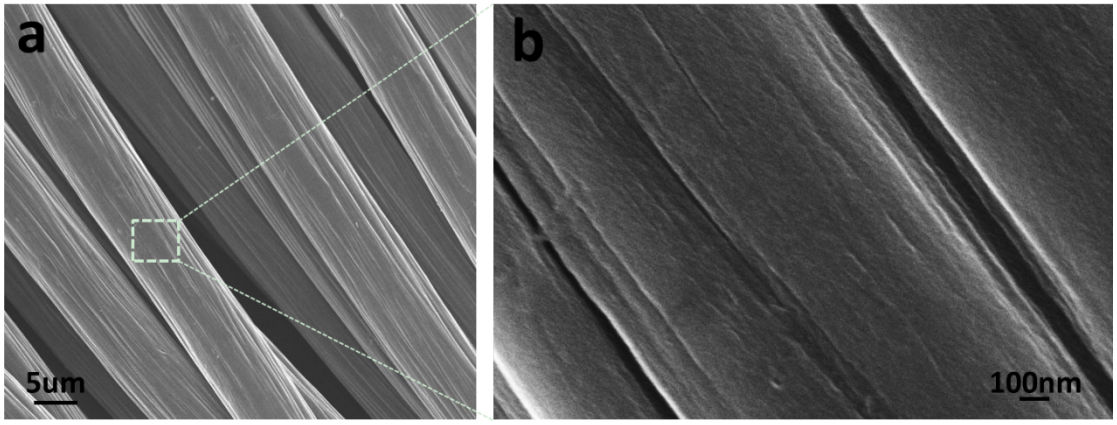

Figure S3. SEM images of carbon cloth revealing the highly textured surface of carbon microfibers.

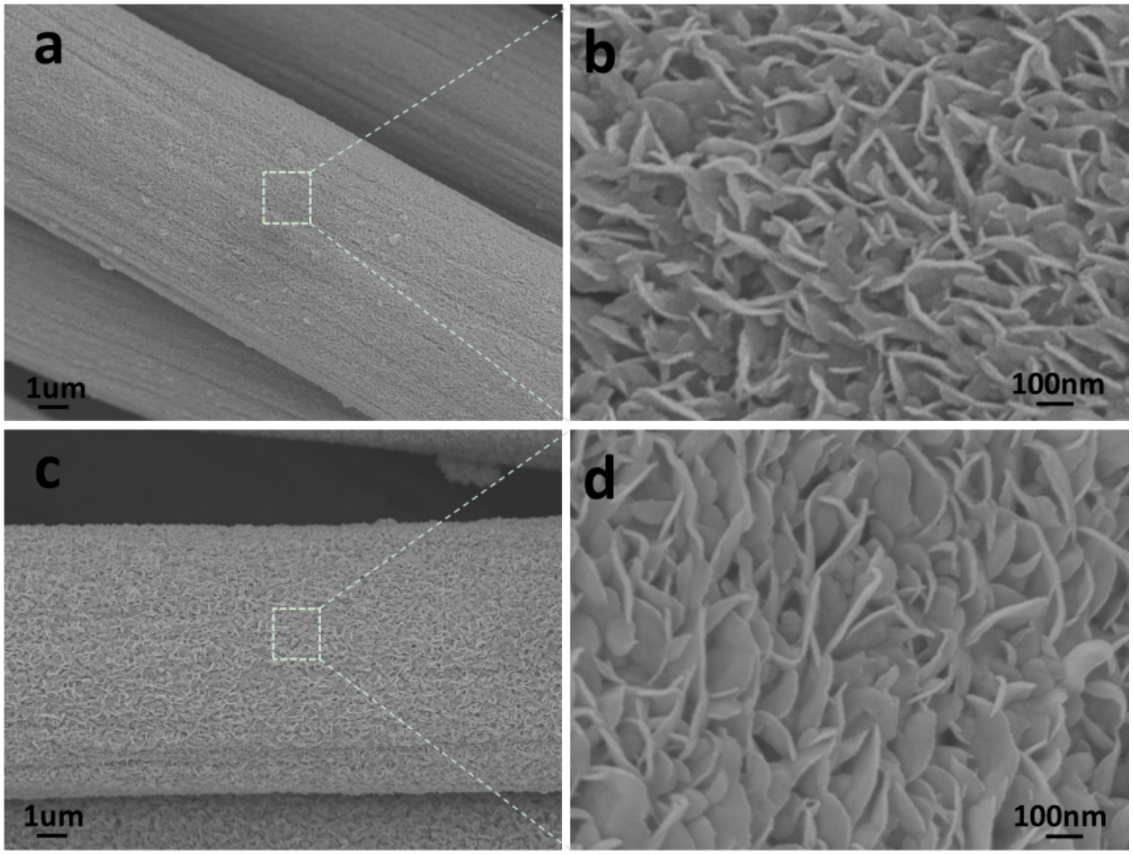

Figure S4. SEM images of the as-prepared nanostructured MoS_2/CC (a&b) and WS_2/CC (c&d) electrodes annealed at 350 ^oC for 2 h under (5%)H_2/(95%)Ar.

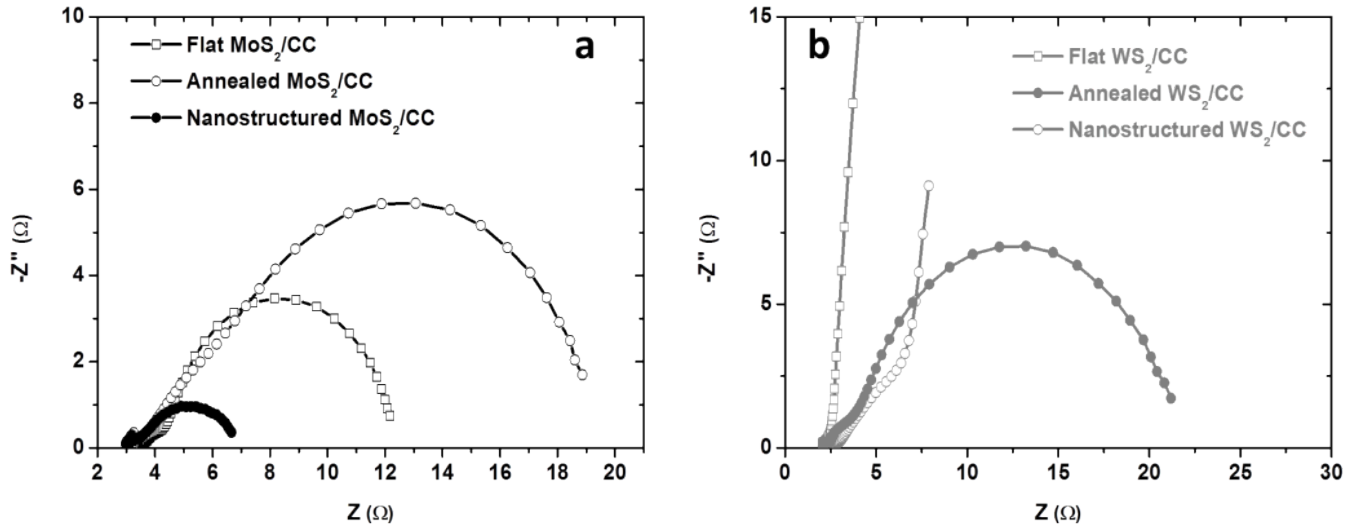

Figure S5. Nyquist plots of different samples. The electrochemical impedance spectroscopies (EIS) further reveal similar system resistance (Rs, 2.5 ± 0.3Ω) for all the tested electrodes and low charge-transfer resistance (Rct) for the nanostructured MoS_2/CC (a) and the annealed WS_2/CC (b). *i*R correction to data with the series resistance (Rs) is performed by $\eta_{corr} = \eta$ *i*R.

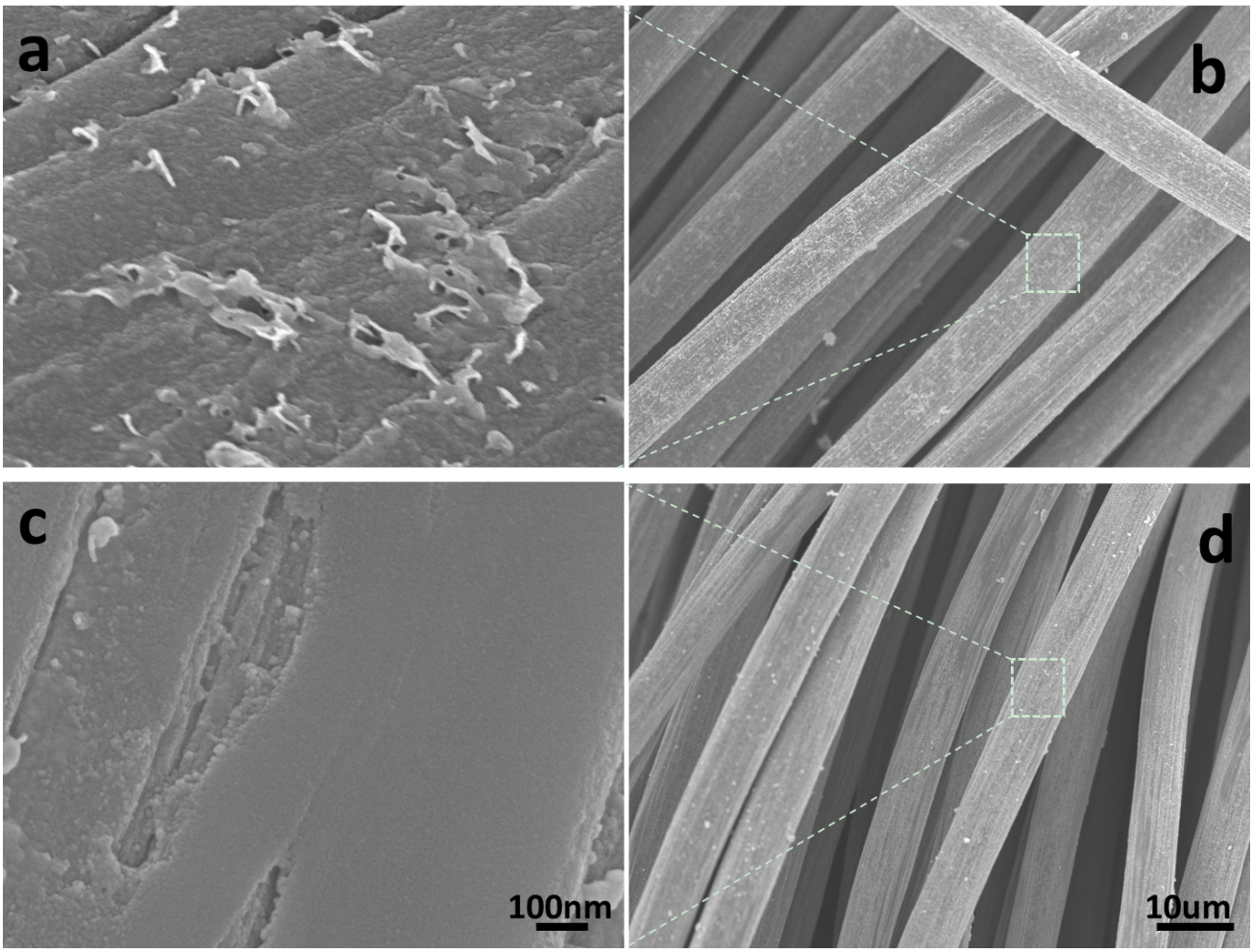

Figure S6. SEM images of flat MoS_2/CC (a &b) and WS_2/CC electrode (c &d).

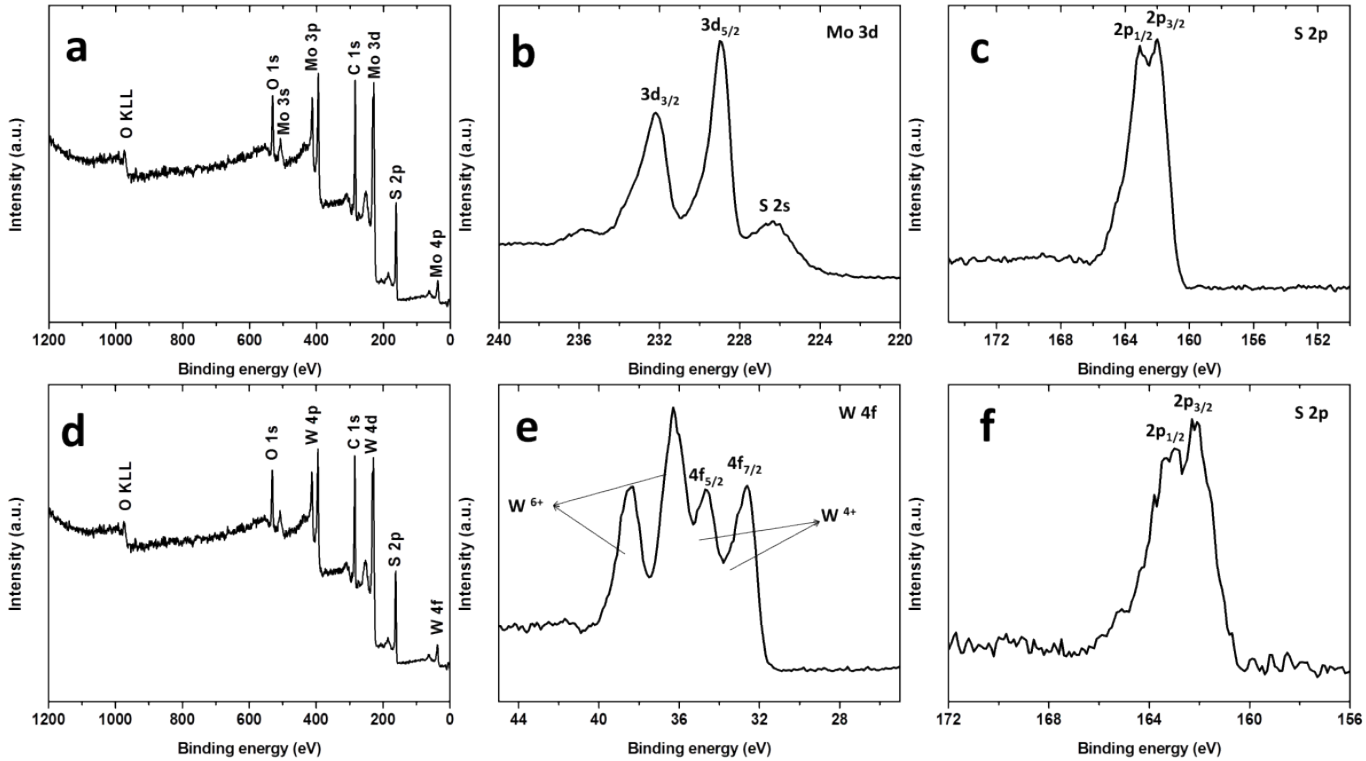

Figure S7. The XPS spectra of the flat MoS_2/CC (a-c) and flat WS_2/CC electrode (d-f).

X-ray photoelectron spectroscopy (XPS) showed above confirms the predominant signals of Mo, S, C and O for the flat MoS_2/CC (Figure S4a) and W, S, C and O for the flat WS_2/CC (Figure S4d). The O should come from the oxidized Mo or W species. Furthermore, the +4 oxidation state of Mo (Mo $3d_{5/2}$, ~229.1 eV, Figure S4b) and –2 oxidation state of S (S $2p_{3/2}$, ~162.3 eV, Figure S4c) with an atomic ratio of Mo:S ≈ 1:2 in the surface region indicate the formation of MoS_2. For the flat WS_2/CC, the W 4f mainly contains two doublets W 4+ (32.8~32.0 eV) as in WS_2 and W 6+ (35.9~38.0 eV) at oxygen-rich surrounding for tungsten atoms as in WO_3, this is quite similar to the as-prepared nanostructured WS_2/CC.

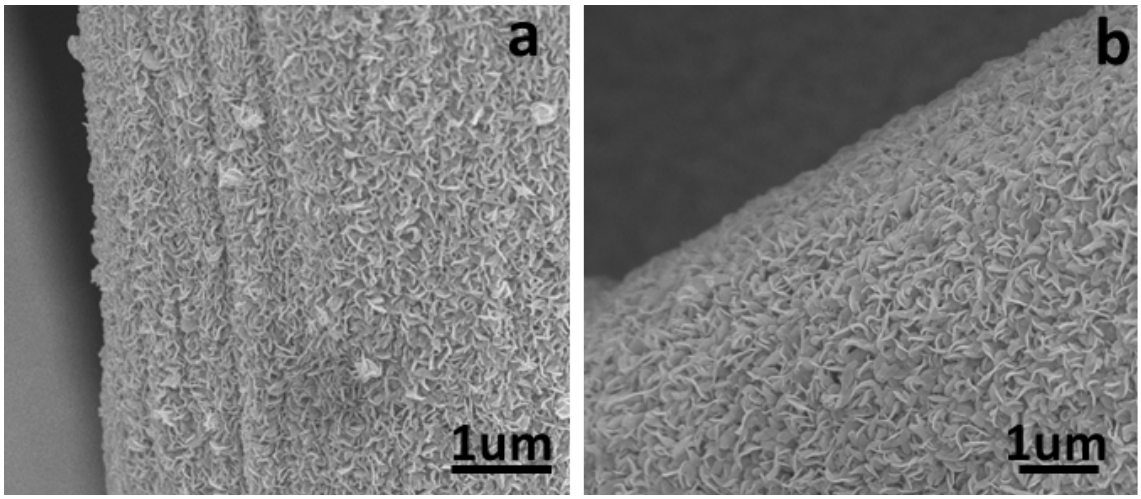

Figure S8. SEM image of MoS_2/CC (a) and WS_2/CC (b) after sonication for 30 min