Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Boosting Hydrogen Evolution Performance by Plasma-Sputtered Porous Monolithic $W_2C@WC_{1-x}$/Mo Film Electrocatalyst

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Figure S1 shows the internal layout of the sputtering system chamber attached by two targets located face-to-face. In this study, the two target positions are WC and Mo materials with the size of 60 cm× 12.5 cm × 1.2 cm. The carousel was rotating in the deposition process for constructing the $W_2C@WC_{1-x}$/Mo multilayer film on carbon cloth (CC) substrate. The maximum deposition zone is 1.1×10^4 cm^2 electrode (per batch).

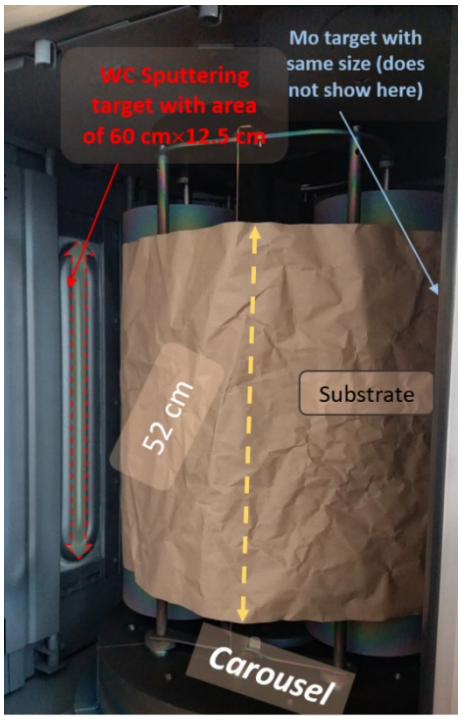

Figure S1 The optical picture of the chamber of the sputtering deposition system.

The dense $W_2C@WC_{1-x}$ film was deposited under Ar pressure of 0.5 Pa, DC bias voltage of -90 V on substrate, the sputtering power of 2.8 kW of WC target and deposition time of 120 min. **Figure S2** presents the FESEM image of the surface morphology of the dense $W_2C@WC_{1-x}$ film.

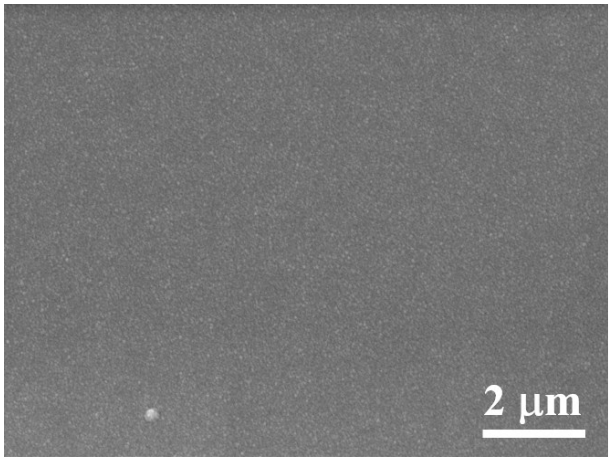

Figure S2 The FESEM image of the surface morphology of the dense $W_2C@WC_{1-x}$ film.

Figure S3 shows the FESEM image of the CC coated by the porous $W_2C@WC_{1-x}$ film. The cross-section of each carbon fibre of CC is approximate 14μm in diameter.

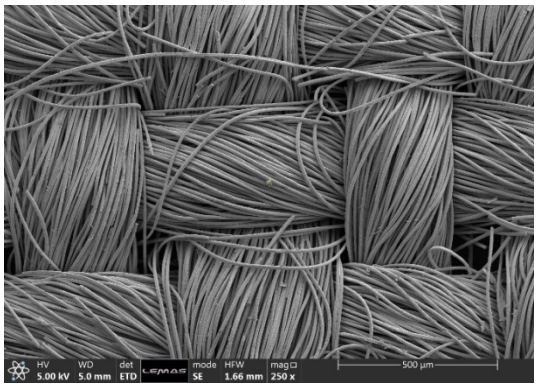

Figure S3 The FESEM image of $W_2C@WC_{1-x}$ film coated on CC.

The cross-sectional FESEM image of the columnar $W_2C@WC_{1-x}$ film on CC and the EDS elemental mappings of W and C are shown in **Figure S4**. The loading mass per area of $W_2C@WC_{1-x}$ is 2.34 $mg \cdot cm^{-2}$ as calculated by weighting.

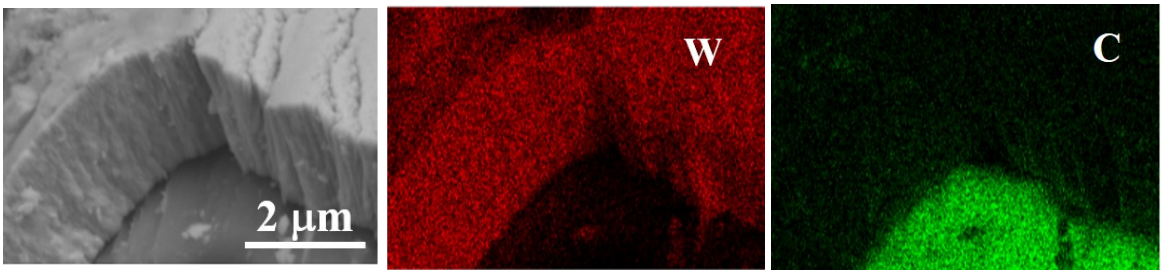

Figure S4 The cross-sectional FESEM image of $W_2C@WC_{1-x}$ film on CC and EDS elemental mappings of W and C.

The Ir/Pt coating was deposited on the $W_2C@WC_{1-x}$/Mo multilayer film to protect the original film structure from any damage by the high-power focused ion beam in the preparation process of cross-sectional sample. **Figure S5** shows FESEM image of original sampling position of the as-made cross-sectional FIB sample. The took-off FIB sample was welded at the end of the tungsten tip before it was put the TEM sample holder.

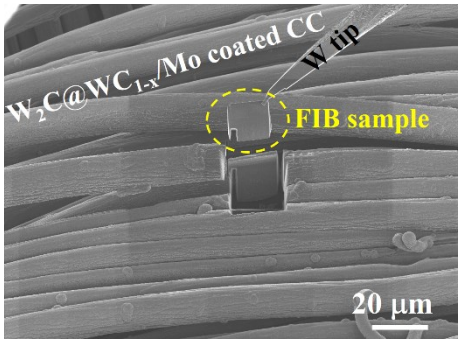

Figure S5 FESEM image of the FIB sample of $W_2C@WC_{1-x}$/Mo multilayer film on CC.

As shown in **Figure S6**, it can be obviously observed that each single column and pore channel is almost throughout the entire $W_2C@WC_{1-x}$/Mo multilayer film from the interface between film and substrate to the film top surface.

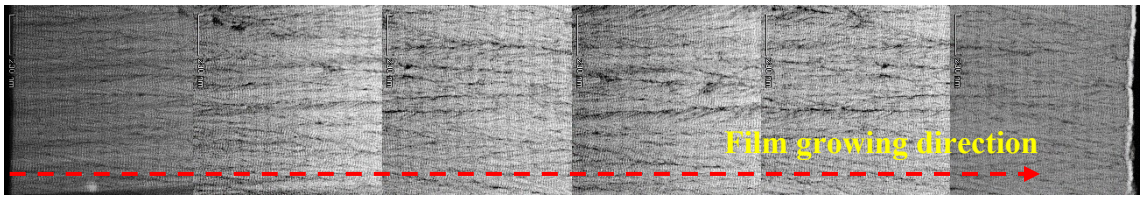

Figure S6 HAADF image of the entire cross-sectional $W_2C@WC_{1-x}$/Mo film on CC.

Figure S7a show the cross-sectional HAADF image of the $W_2C@WC_{1-x}$ film. The columnar platelets are marked by the blue color and the concominant pore channles are marked by the yellow color, both of which grew along the film thickness direaction. As shown in the HRTEM image in **Figure S7**b, it can be seen that the $W_2C@WC_{1-x}$ particles have big size over 30 nm.

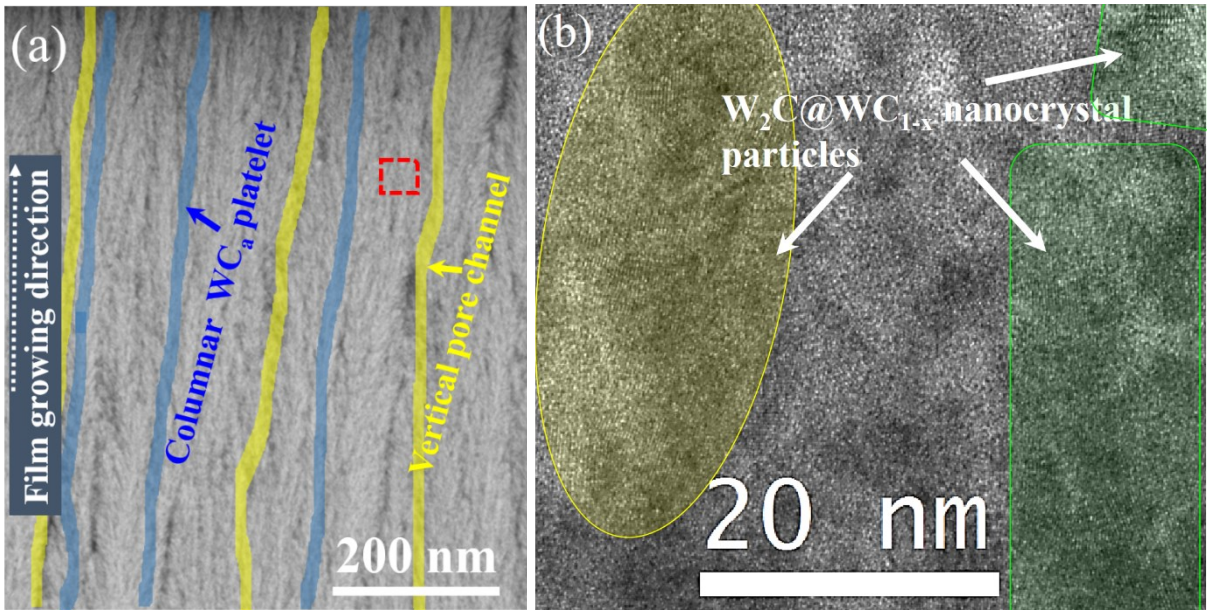

Figure S7 (a) HAADF image of cross-sectional $W_2C@WC_{1-x}$ film on CC, and (b) HRTEM image of the representative zone from the selected red square in (a).

Figure S8a presents the full scan XPS spectrum of $W_2C@WC_{1-x}$ film. The W/C ratio was 0.73, much lower than that of the initial target of WC (stoichiometric ratio of 1). **Figure S8**b shows the high-resolution XPS W *4f* spectrum of $W_2C@WC_{1-x}$ film. The fitting peaks at 31.7 eV and 33.7 eV can be assigned to features of W-C bonds in W_2C, while the doublet of 32.3 eV and 34.3 eV is attributed to the features of W-C bonds in WC_{1-x}, indicating that WC_{1-x} and W_2C co-exist in the deposited film.

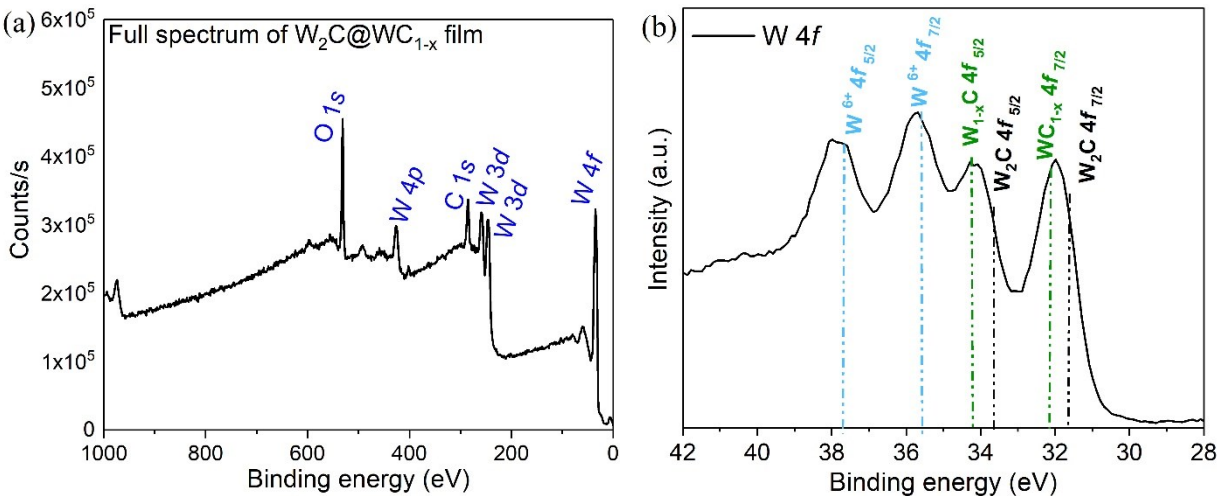

Figure S8. The full scan (a) and high-resolution XPS W *4f* spectra (b) of the $W_2C@WC_{1-x}$ film.

Figure S9 shows the high-resolution XPS Mo *3d* spectrum of the $W_2C@WC_{1-x}$/Mo multilayer film. The peaks located at 228.3 eV and 231.4 eV (**Figure S9**) are attributed to be metallic Mo, indicating that additional Mo sublayer didn't react with other W and C ions in plasma and has potential to benefit for the improved electron transport properties of the $W_2C@WC_{1-x}$/Mo multilayer film electrocatalyst.

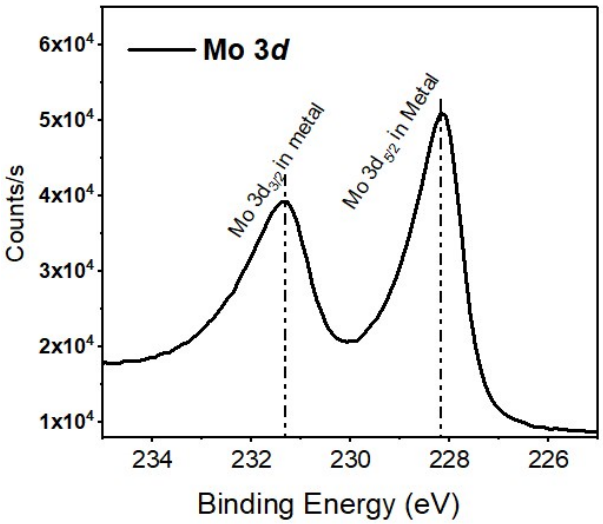

Figure S9. The high-resolution XPS Mo *3d* spectrum of the $W_2C@WC_{1-x}$/Mo multilayer film.

Figure S10a,b present the TEM image of the cross-sectional $W_2C@WC_{1-x}$/Mo multilayer film and the SAEDs localized at the red circles, respectively. It can be seen that the all the SAEDs show the constant diffraction. It indicates that the deposited entire film possesses the homogenous structure of W_2C and WC_{1-x} and Mo phases.

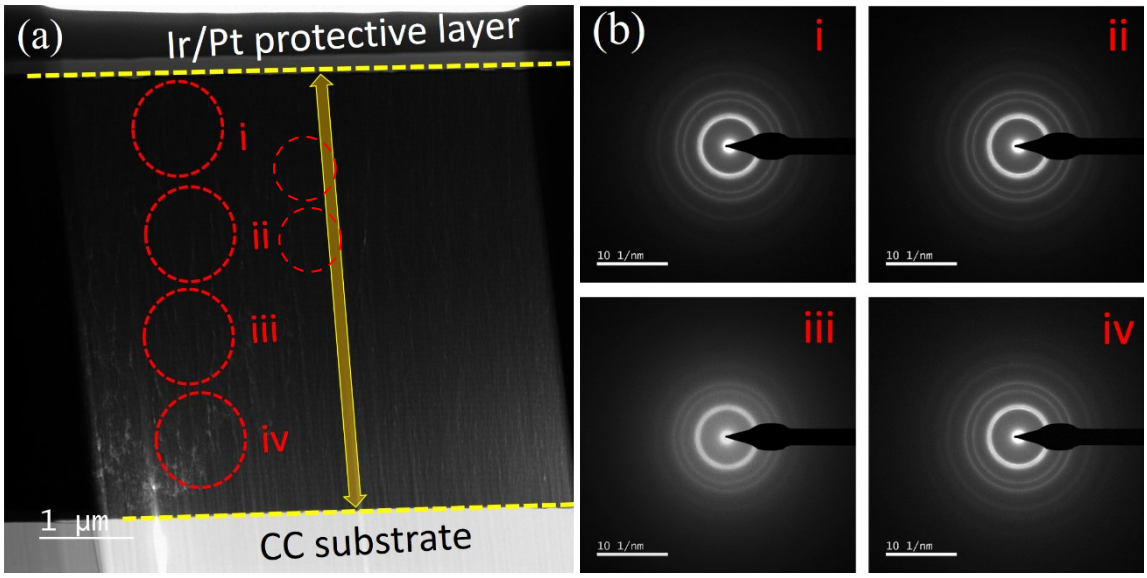

Figure S10. The TEM image of the cross-sectional $W_2C@WC_{1-x}$/Mo multilayer film on CC (a) and the SAED patterns through the entire cross-section (b).

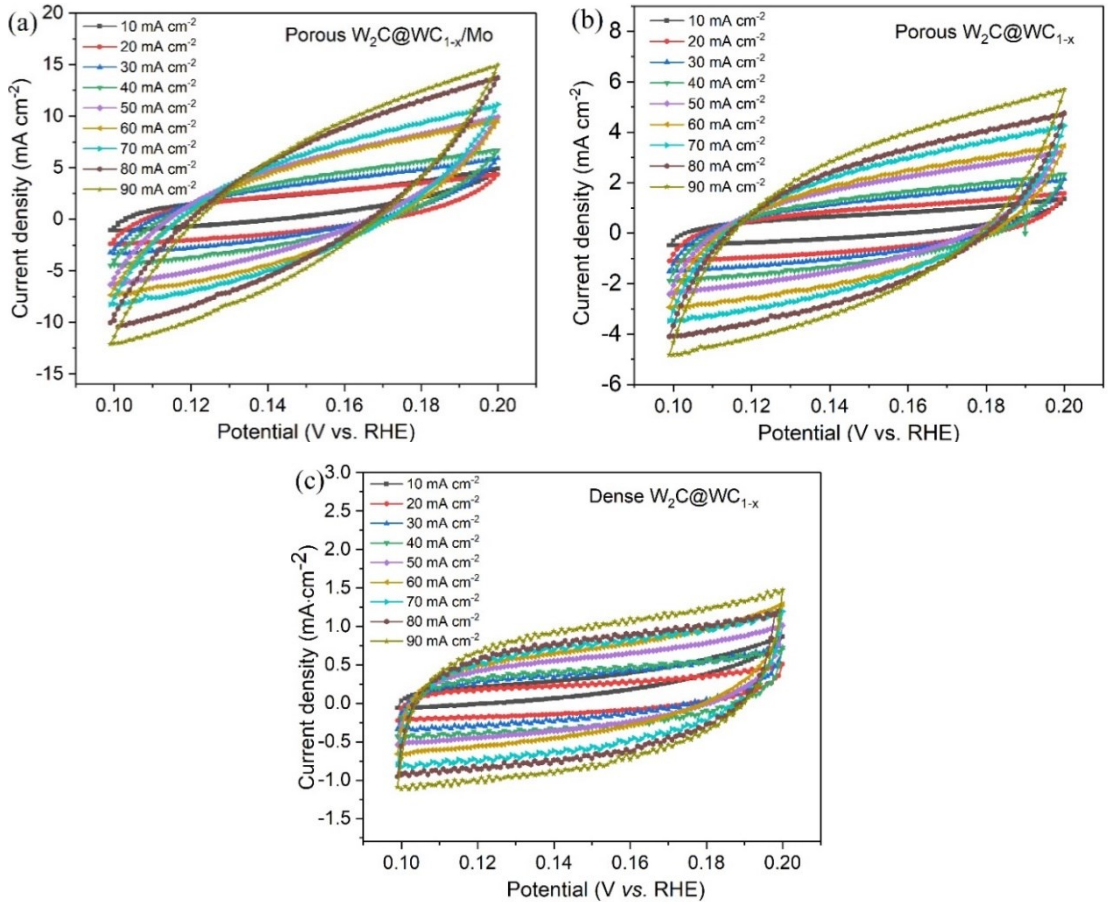

Figure S11 Cyclic voltammograms (CV) curves of (a) $W_2C@WC_{1-x}$/Mo film, (b) $W_2C@WC_{1-x}$ film and (c) dense $W_2C@WC_{1-x}$ film electrodes with different scan rates from 10 to 90 mV·s^{-1}.

Figure S12 shows the time-dependent current density curve of $W_2C@WC_{1-x}$/Mo film electrode at 170 mV *vs* RHE. The high current density of approximate 104 mA·cm^{-2} was close to the industrial H_2 production and its stabilization was over 52 hours even though the hydrogen production process was interrupted at the running time of 7.2 and 28.2 hours.

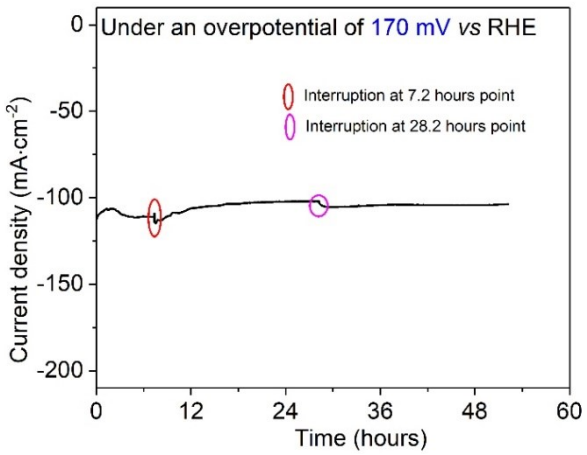

Figure S12 Time-dependent current density curve of $W_2C@WC_{1-x}$/Mo film electrode under a static overpotential of 170 mV *vs* RHE for running 52 hours, with twice interruption moments of running 7.2 hours and 28.2 hours.

The turnover frequency (TOF) is the number of H_2 molecules evolved per second per active site. It is a crucial index to evaluate the intrinsic catalytic activities of the electrocatalysts. To further estimate the activities of the films, the TOF value was investigated using the most reported method, the detail was described as below [S1]:

$$\text{TOF}=\frac{\text{Total number of } H_2 \text{ molecules per second}}{\text{Total number of active sites per unit area}}=\frac{j}{2qN}$$

where j is current density, N is the active site density, q is the elementary charge as 1.6×10^{-19}, 2 accounts for 2 electrons transfer per one H_2 molecule generation. The active sites per unit area can be obtained from the ECSA measurement, and the ECSA of the electrocatalyst can be calculated from the C_{dl}/C_s. C_s is the sample capacitance of an atomically smooth planar surface of material per unit area under identical electrolyte conditions. The C_s as general specific capacitance was 0.04 mF/cm^2 in 0.5M H_2SO_4 based on typical reported values [S1]. The number of active site was estimated to be 7.91×10^{14} W atoms per cm^2 [S2]. So the active site density is calculated according to equation:

$$\text{TOF}=\frac{j}{2qN}=\frac{j}{2\times(1.6\times10^{-19})\times(7.91\times10^{14})\times(C_{dl}/0.04)}$$

The porous $W_2C@WC_{1-x}$/Mo film still anchors on the CC substrate even after 3,000 sweeps between 0 to -0.25 V *vs.* RHE in 0.5 M H_2SO_4 solution, as shown in **Figure S13**a and b. It suggests that this porous film on flexible possesses the remarkable integrity of film structure.

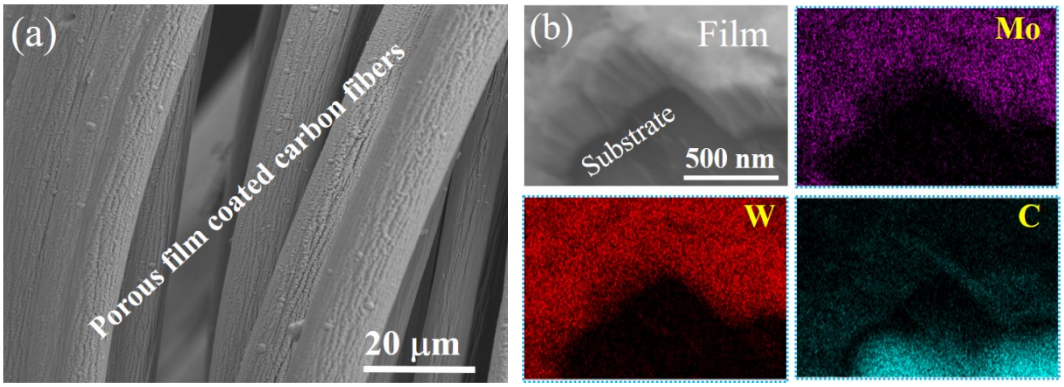

Figure S13 (a) The FESEM images and (b) the EDS elemental mappings of W, Mo and C of the cross-sectional $W_2C@WC_{1-x}$/Mo film on CC after 3,000 sweeps between 0 to -0.25 V *vs.* RHE in 0.5 M H_2SO_4 solution.

Figure S14a,b show the XPS C1*s* and Mo 3*d* spectra of the $W_2C@WC_{1-x}$/Mo multilayer film on CC after 3,000 sweeps between 0 to -0.25 V *vs.* RHE, respectively. The main peak at 283.4 eV in C1*s* profile is indexed to the C-metal bonds, and the two peaks at 284.4 and 285.5 eV are attributed to sp^2 and sp^3 C-C bonds of contaminate carbon, respectively. The peaks at 228.3 eV and 231.4 eV in Mo 3*d* profile are attributed to be metallic Mo of sublayer in the $W_2C@WC_{1-x}$/Mo film. As shown in **Figure 5**b, the fitting peaks at 31.6 eV and 33.7 eV can be assigned to features of W-C bonds in W_2C, while the doublet of 32.3 eV and 34.4 eV is attributed to the features of W-C bonds in WC_{1-x}. The aforementioned analysis results suggest the high chemical composition stability of the $W_2C@WC_{1-x}$/Mo film electrode.

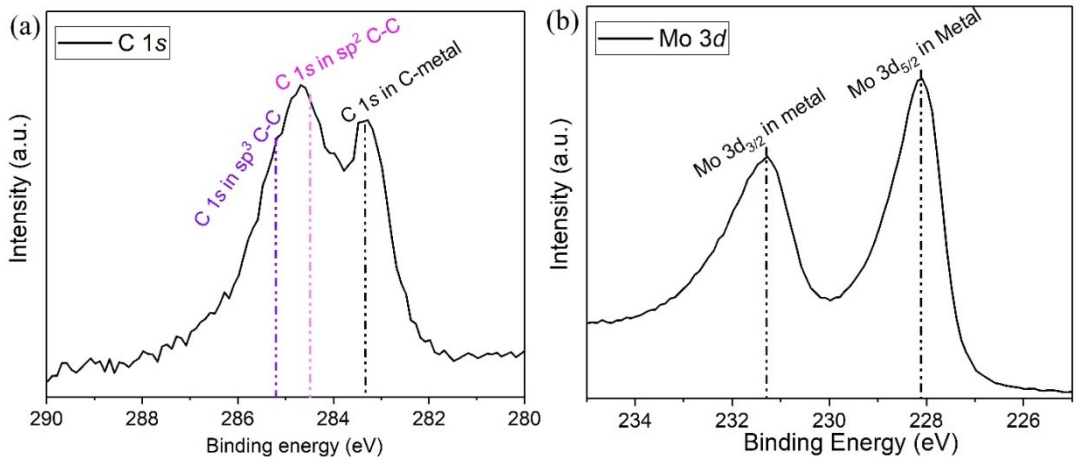

Figure S14 The high-resolution XPS (a) C1*s* and (b) Mo 3*d* spectra of the $W_2C@WC_{1-x}$/Mo multilayer film on CC after 3,000 sweeps between 0 to -0.25 V *vs.* RHE in 0.5 M H_2SO_4 solution.

References

S1. J. Hu, B. L. Huang, C. X. Zhang, Z. L. Wang, Y. M. An, D. Zhou, H. Lin, M. K. H. Leung, S. H. Yang, *Energy Environ. Sci.* **2017**, *10*, 593.

S2. Y. J. Ko, J. M. Cho, I. Kim, D. S. Jeong, K. S. Lee, J. K. Park, Y. J. Baik, H. J. Choi, W. S. Lee, *Appl. Catal. B: Environ.* **2017**, *203*, 684.