Supplementary data for:

Highly Efficient and Free-standing WS_2/C Electrocatalyst for Solar-cell-driven Hydrogen Evolution Reaction

Zexia Zhang,[a] Lina Shen,[a] Chen Qin,[a] Ruitao Lv*[b] and Feiyu Kang*[c]

[a]*Xinjiang Key Laboratory for Luminescence Minerals and Optical Functional Materials, School of Physics and Electronic Engineering, Xinjiang Normal University, Urumqi 830054, China*
[b]*Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*
[c]*Tsinghua Shenzhen International Graduate School, Shenzhen 518055, China*

*Corresponding author.
E-mail address: lvruitao@tsinghua.edu.cn (R. Lv); fykang@tsinghua.edu.cn (F. Kang)

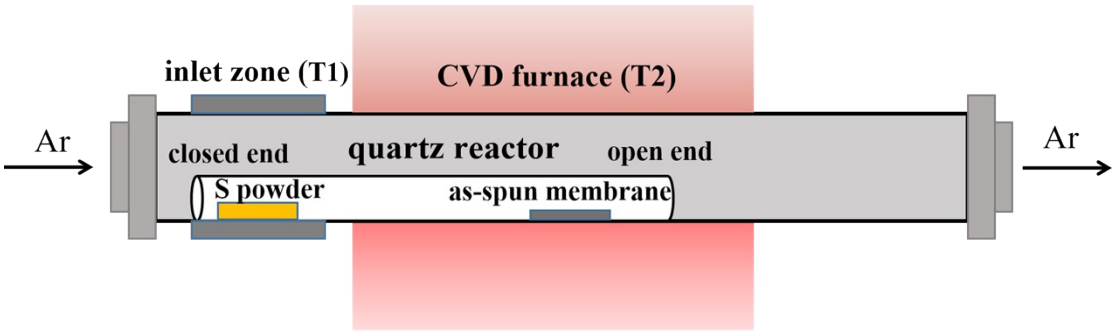

Fig. S1 Schematic illustration of the synthesis process of WS_2/C composites.

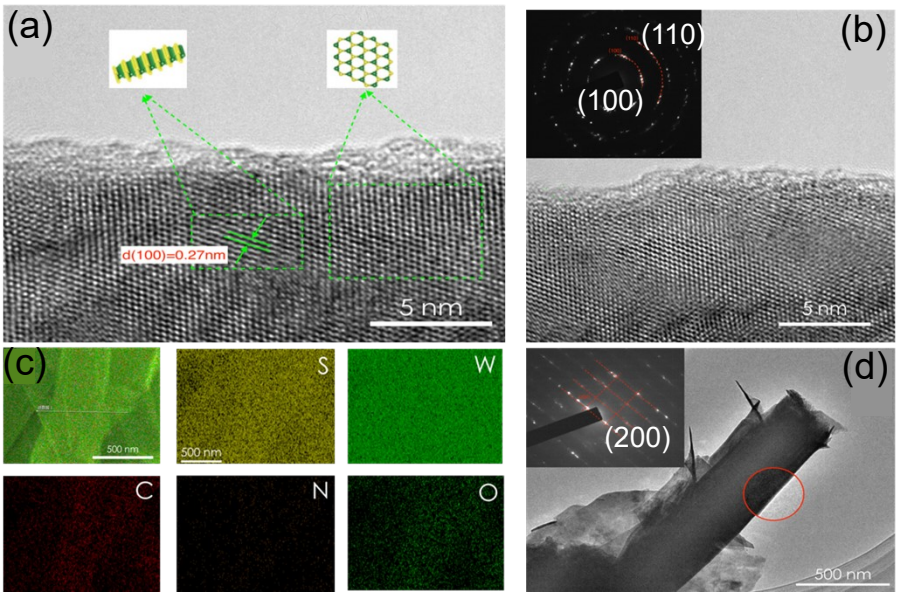

Fig. S2 (a) TEM images, (b) SAED pattern on nanoplates, (c) elemental mappings and (d) SAED pattern on fibers of 800-2h-O. On both the fiber surface and layered regions, S and W are distributed uniformly.

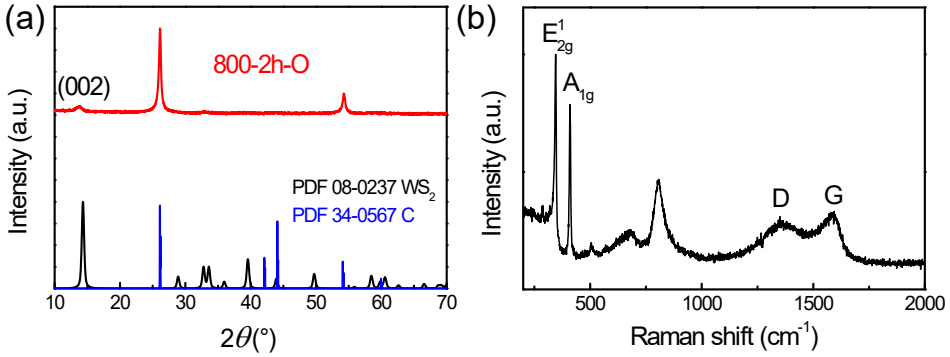

Fig. S3 (a) XRD patterns and (b) Raman spectrum of 800-2h-O. 2H-phase WS_2 and carbon matrix composite structure is validated.

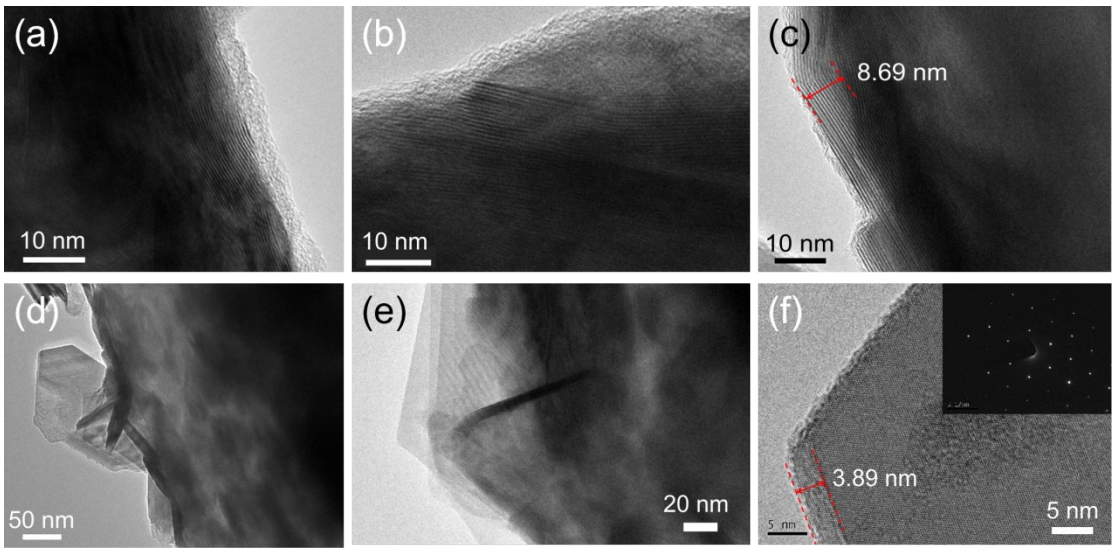

Fig. S4 TEM images of different areas for S600-1000. (a) (b) (c) The WS_2 nanosheets embeded in surface of S600-1000; (d) (e) (f) The WS_2 nanosheets protruding out from the surface of S600-1000.

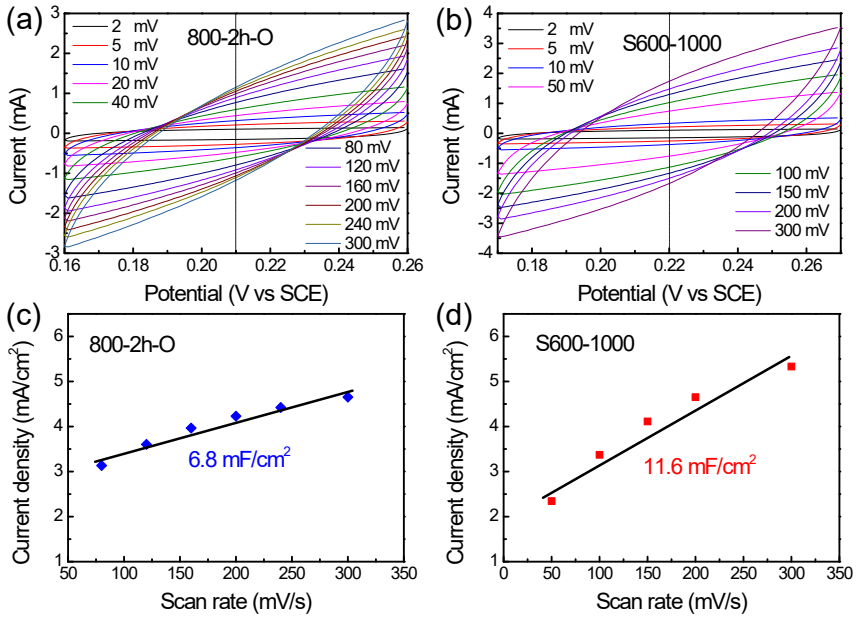

Fig. S5 CV curves within non-Faradaic regions of (a) 800-2h-O and (b) S600-1000. Non-faradaic current densities at 0.21 V (vs. RHE) as a function of the potential scan rate for (c) 800-2h-O and (d) S600-1000. The corresponding double-layer capacitance (C_{dl}) are approximately 6.8 mF/cm^2 and 11.6 mF/cm^2.

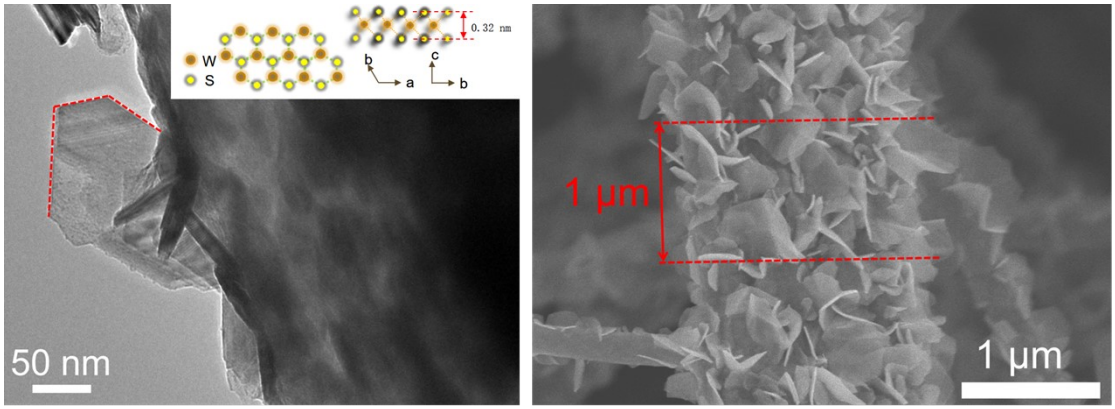

Fig. S6 (a) TEM and (b) SEM images of S600-1000 used to estimate the amount of edge active sites. Inset of (a) is the schematic of WS_2.

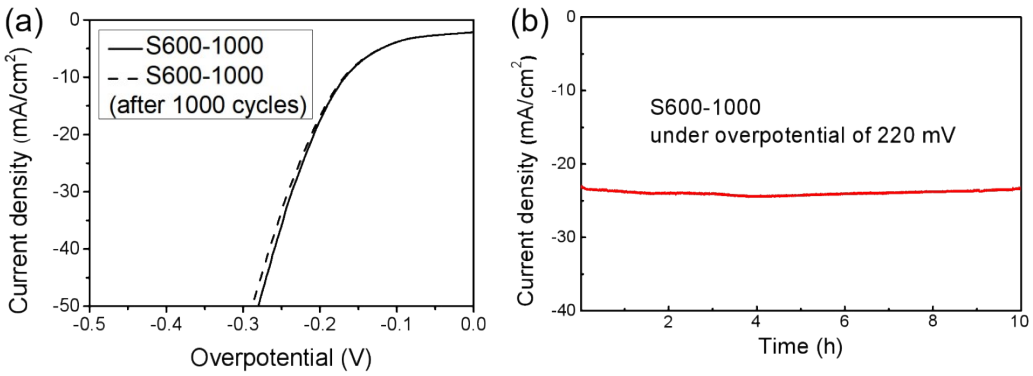

Fig. S7 (a) Polarization curves of S600-1000 in the initial scan and after 1000 cycles; (b) Current density versus time (*i*-*t*) curves over 10 h for S600-1000 under static overpotential of 220 mV.

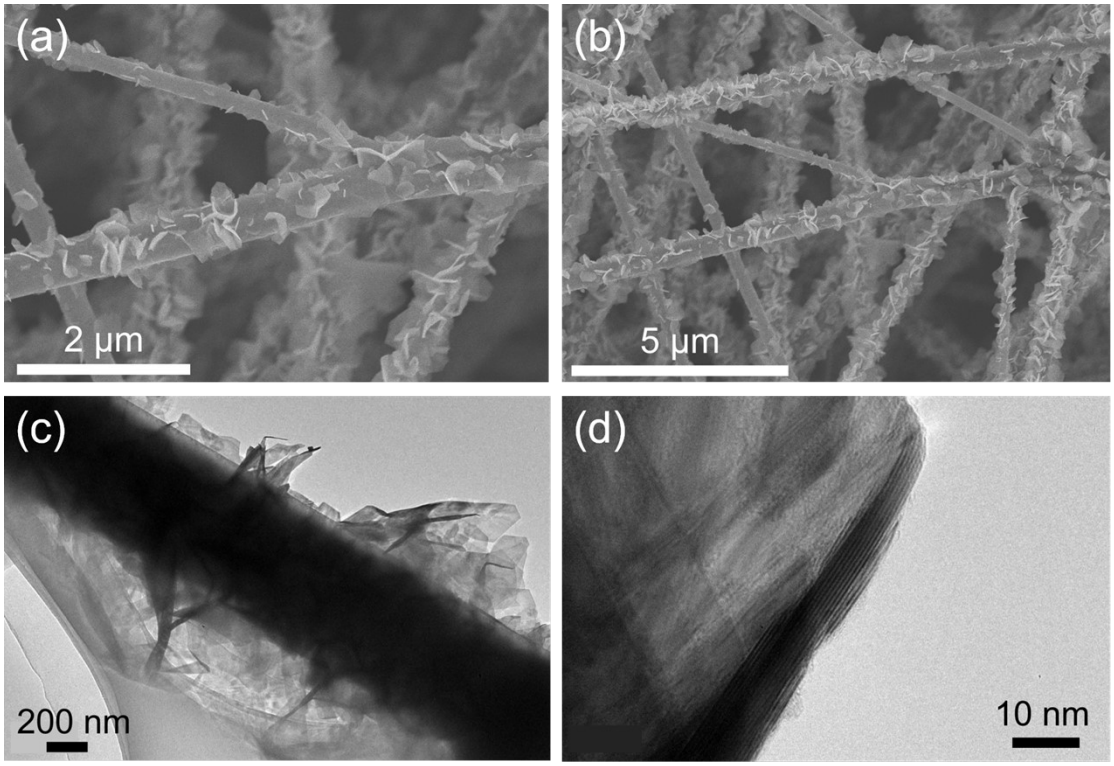

Fig. S8 SEM (a) (b) and TEM (c) (d) images of S600-1000 after 1000 cycles.

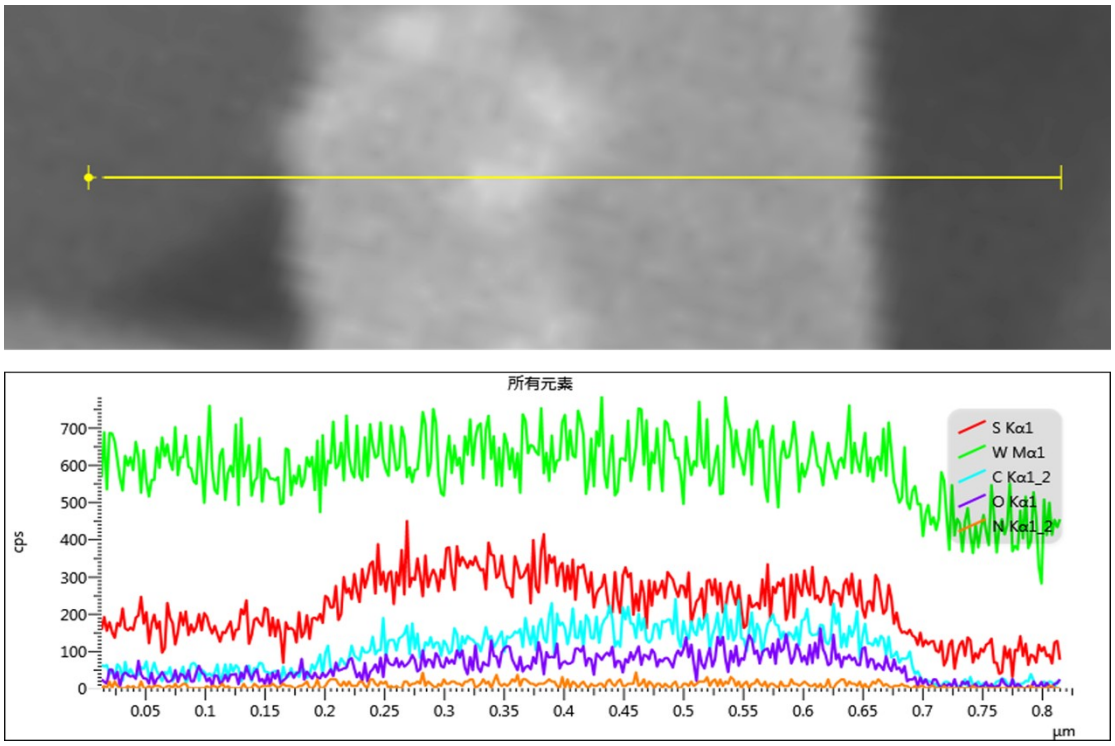

Fig. S9 Elemental line scanning of the WS_2/C composite materials after 1000 cycles.

Table S1 Comparison of overpotential at 10 mA/cm^2 and tafel slopes for some reported carbon-based WS_2 HER catalysts in literature.

Catalysts	Electrolytes	η_{10}/mV	Tafel Slope /mV dec^{-1}	Ref.
WS_2/CNF	0.5 M H_2SO_4	160	95	this work
WS_2@graphene	0.5 M H_2SO_4	117	56	*Adv. Mater.*, 2020, 32: e2002584
WS_2/N-rGO/carbon cloth	0.5 M H_2SO_4	175	85.23	*Nano Res.*, 2023, 17: 1267-1280
WS_2/C	0.5 M H_2SO_4	179	98	*J. Fuel Chem. Technol.*, 2021, 49: 1362-1370
WS_2	0.5 M H_2SO_4	166	82.2	*FlatChem*, 2021, 29: 100278.

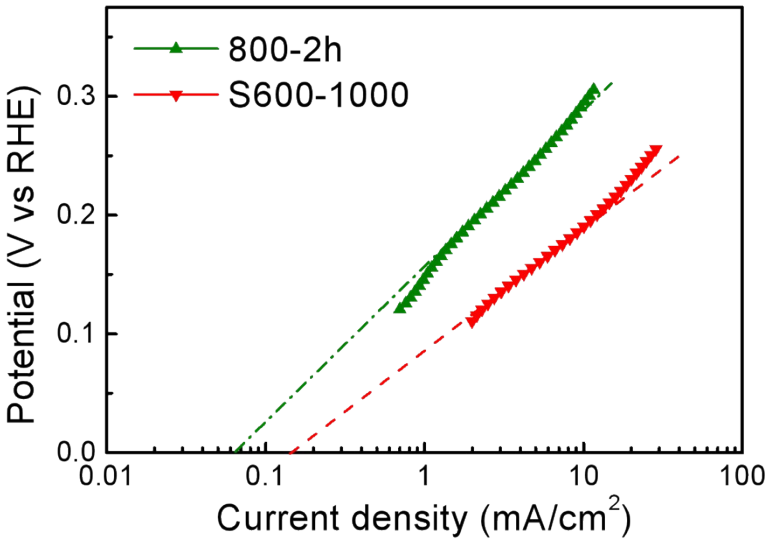

Fig. S10 Exchange current densities of 800-2h and S600-1000.

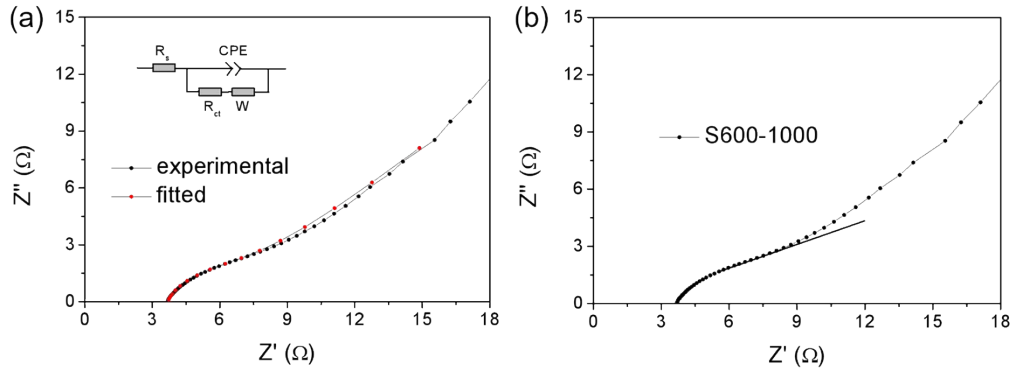

Fig. S11 (a) Electrochemical impedance spectra of S600-1000; (b) Slope of diffusion area in electrochemical impedance spectra spectra of S600-1000.

Table S2 The kinetic parameters obtained from fitted electrochemical impedance spectra curves. (R_s: solution resistance, R_{ct}: charge transfer resistance, R_p: the sum of R_{ct} and Warburg impedance)

Sample	R_s (Ω)	R_{ct} (Ω)	R_p (Ω)
S600-1000	3.8	0.14	16.1

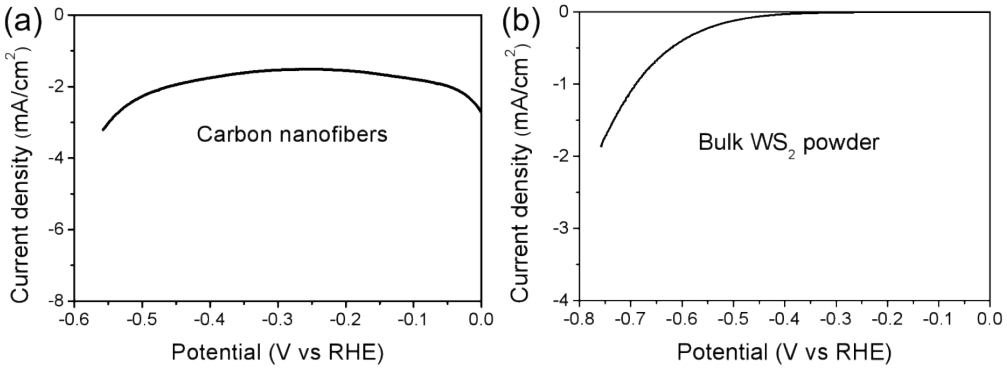

Fig. S12 Linear sweep voltammogram polarization curves of (a) CNF membrane and (b) bulk WS_2 powder in 0.5 M H_2SO_4.

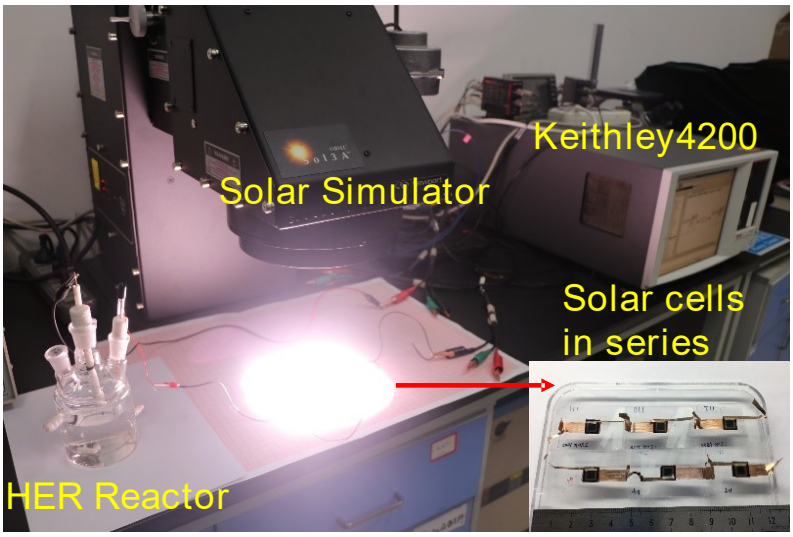

Fig. S13 Photograph of the carbon-based non-precious metal photovoltaic hydrogen production system constructed by integrating six series-connected carbon-based hybrid solar cells with a HER cell using WS_2/C as the working electrode. Inset showing the corresponding 6-serial solar cell module.

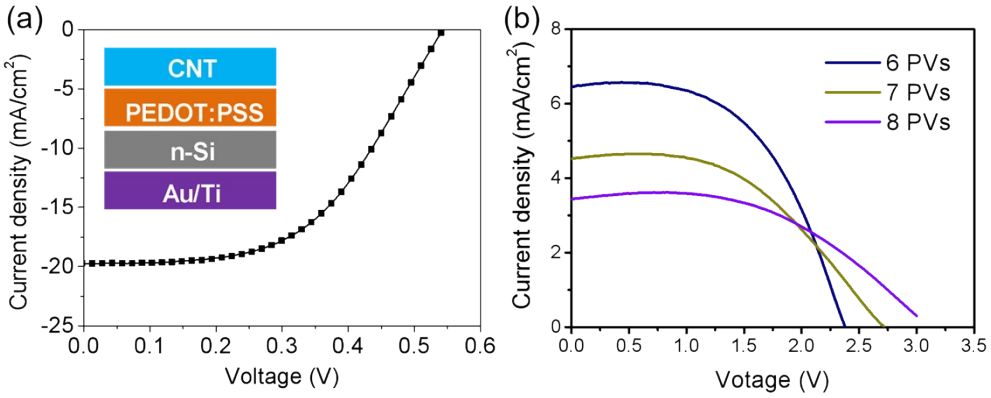

Fig. S14 Light current density (*J*)-voltage (*V*) curves of (a) a carbon-based hybrid solar cell (inset is the schematic of the cell structure) and (b) series connection of six, seven and eight carbon-based hybrid solar cells.

Table S3 Photovoltaic parameters of the carbon-based hybrid solar cells (CNT/PEDOT:PSS/Si). V_{OC}, J_{SC}, FF and PCE refer to open-circuit voltage, short-circuit current density, fill factor and power conversion efficiency, respectively.

Cell No.	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
1	480.0	19.3	29.8	3.4
2	510.1	20.8	37.0	4.9
3	525.2	20.0	47.6	6.2
4	540.2	19.8	52.4	7.0
5	480.0	19.1	34.2	3.9
6	630.7	19.9	20.0	3.1
7	480.0	14.3	45.2	3.9
8	472.4	19.2	27.9	3.2

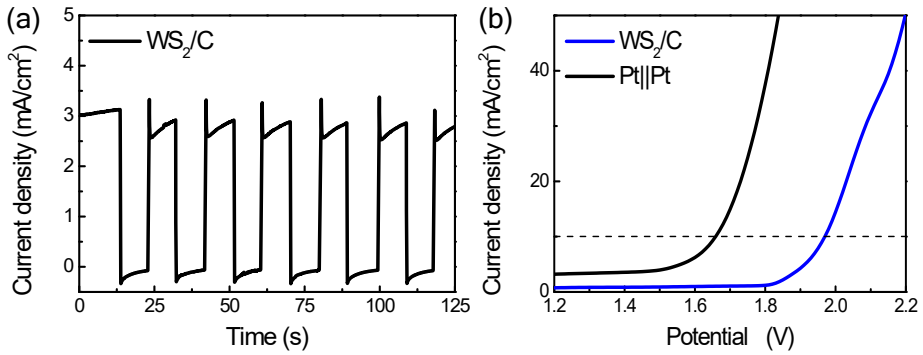

Fig. S15 (a) Photoelectric response curve and (b) LSV curves for two-electrode system of S600-1000. The η_{10} of Pt and WS_2/C are 1.66 V and 1.97 V, respectively. The corresponding solar-to-hydrogen conversion efficiency are 5.2% and 4.4%.