Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Multifunctional 2H-TaS$_2$ nanoflakes efficient for supercapacitors, electrocatalytic evolution of hydrogen and oxygen

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Experimental Section

Chemical and Materials: Tantalum powder (-22 mesh, 99.995 %) and sulfur powder (99.9 %) were purchased from Alfa Aesar. Potassium hydroxide (KOH), N, N-dimethylformamide (DMF), ethanol (C_2H_5OH), hydrochloric acid (HCl), and polytetrafluoroethylene (PTFE, 60 wt%) were purchased from Aladdin Company. Nickel foam was purchased from Suzhou jiashide metal foam Co., Ltd. Nafion solution (5 wt%) was purchased from DuPont, Inc. The super carbon (10 ~ 20 S/cm) was purchased from Tianjin Tianyi Chemical Products Technology Development Co., Ltd.

Material characterization: The powder samples were examined by X-ray powder diffraction (XRD) which was carried out on a Philips PW-1830 X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm). X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB 250 spectrometer with a hemispherical analyzer and a monochromatized Al Ka X-ray source (E = 1486.6 eV), operating at 15 kV and 15 mA. The morphology of the as-synthesized samples was determined by using field emission scanning electron microscopy (SEM) which was characterized by a JEOL JSM-6700F at an accelerating voltage of 5 kV. And energy-dispersive X-ray (EDX) and EDX mapping were recorded. Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDS) images were captured using a JEOL-2010 with an acceleration voltage of 200 kV. High resolution transmission electron microscopy (HRTEM) images were captured on a JEOL-2010F instrument at an accelerating voltage of 200 kV. Raman spectra were collected in a WITEC Raman microscopic system with exciting laser wavelength of 520 nm and the laser spot-size is around 0.5 mm. For the Raman characterization, Si was used as reference for wavenumber calibration.

Preparation of TaS_2 electrode for HER and OER: A piece of the treated Ni foam was wrapped by Teflon tape with exposure area of ≈ 1 cm^2, and immersed into a Teflon-lined stainless steel vessel (Parr Company) containing a previously mixed solution (20 mL) of ethanol and water (volume ratio of 1 : 1), and TaS_2 powder (15 mg) through ultrasound for 30 min. Then, the vessel was sealed for hydrothermal reaction at 170 °C for 6 h with a heating rate of 2 °C min^{-1} from room temperature to grow on the Ni foam. After the vessel was cooled down to room temperature, the samples were rinsed with distilled water and then dried in an oven with argonprotecting environment at 60 °C for 12 h. The obtained sample was further under Ar at 400 °C for 3 h with a heating rate of 2 °C min^{-1}.

Preparation and electrochemical measurements of electrode in supercapacitor: The obtained TaS_2 materials were grinding into fine powder and mixed with PTFE emulsion to form a solid mixture, with the using of commercial carbon as conductive additive. The resulting mixture was rolled into sheet with a thickness around 60 μm, and then heated in muffle furnace at 150 °C for 2 h. After that, the sheet was cut into 1.0 cm × 1.0 cm and pressed onto a nickel foam current collector at 10 MPa to form the working electrode and the mass loading of carbon is 3 mg per square centimeter. The electrochemical tests, including CV (cyclic voltammetry) and GCD (galvanostatic charge/discharge), were carried out in 6 M KOH electrolyte with a CHI760E electrochemical workstation (Chen hua, Shanghai). A nickle wire was used as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. All the potential was presented versus standard hydrogen electrode (SHE).

Calculations of specific capacitance, energy density and power density: The specific capacitance was calculated from the discharge process according to:

$$C = \frac{I \times \Delta t}{m \times \Delta V} \tag{1}$$

Where I is the charge/discharge current (A), m is the mass of active material (g), Δt is the discharge time (s), and ΔV is the potential change (V) during the discharge process.

Hydrogen Evolution Reaction Test: Electrochemical studies were carried out in a three-electrode system and stirred by a magnetic stir bar. The Metro autolab electrochemistry workstation was used to record the tests. Before the test, 0.1 M H_2SO_4 (pH = 0.44) was saturated by bubbling argon for 30 min. TaS_2 was used as the working electrode, coiled platinum wire as the counter electrode, and Ag/AgCl electrode as the reference electrode. The reference was calibrated against and converted to reversible hydrogen electrode (RHE). Linear sweep voltammetry (LSV) was carried out at 10 mV s^{-1} for the polarization curves. The catalyst was cycled about 50 times of CV before the initial test.

Oxygen Evolution Reaction Test: Electrochemical studies were carried out in a three-electrode system and stirred by a magnetic stir bar. The Metro autolab electrochemistry workstation was used to record the tests. Before the test, 1.0 M NaOH (pH = 13.36) was saturated by bubbling oxygen for 30 min. TaS_2 was used as the working electrode, coiled platinum wire as the counter electrode, and Ag/AgCl electrode as the reference electrode. The reference was calibrated against and converted to reversible hydrogen electrode (RHE). Linear sweep voltammetry (LSV) was carried out at 10 mV s^{-1} for the polarization curves. The catalyst was cycled about 30 times of CV in the potential range of 0.98-1.82 V_{RHE} at the sweep rate of 20 mV s^{-1} until a stable CV curve was developed.

Calculations of the electrochemically active surface area: The electrochemically active surface area (ECSA) of the materials was measured by changing CV scans from 0.01 to 0.5 V (the range with no faradaic process) at the different scan rates of 10, 20, 30, 50 and 50 mV s^{-1}. The charging current (Δj) at -0.01 V_{RHE} (HER) and 1.15 V_{RHE} (OER) was equal to the multiplied with the electrochemical double-layer capacitance (C_{dl}). Thus, the ratio of the Δj with various scan rates indicated the C_{dl}. The ECSA was calculated by dividing the C_{dl} by the specific capacitance, C_s.

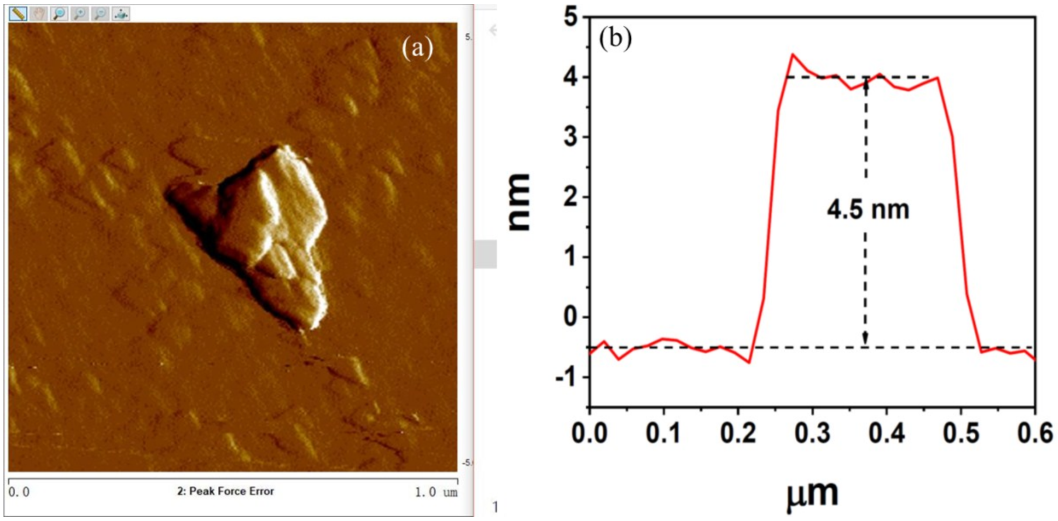


Fig. S1 AFM images and the height profiles of the as-prepared TaS_2.

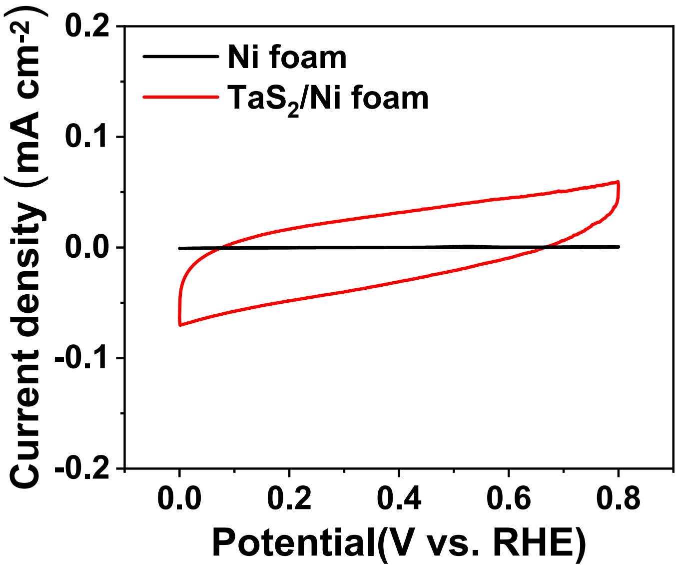
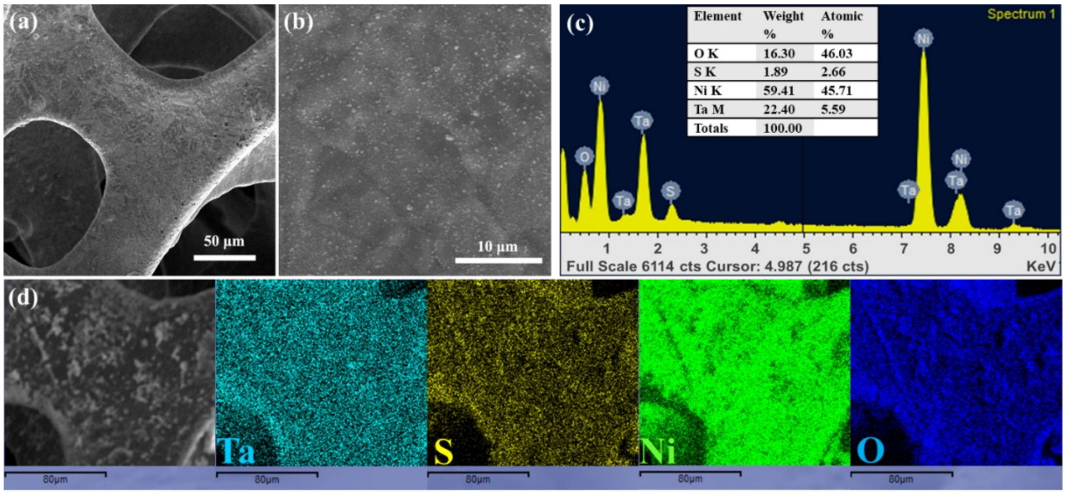


Fig. S2 CV curves of the as-prepared TaS_2 and Ni foam at 50 mV s^{-1}.



Element	Weight %	Atomic %
O K	16.30	46.03
S K	1.89	2.66
Ni K	59.41	45.71
Ta M	22.40	5.59
Totals	100.00	

Fig. S3 SEM images of TaS_2 on Ni foam (a, b). EDX (c) and elements mapping patterns (d) of TaS_2 on Ni foam.

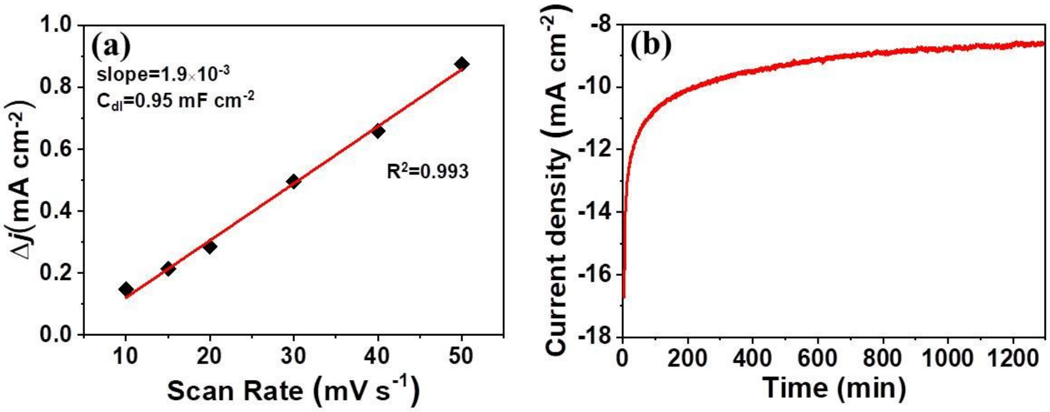


Fig. S4 TaS_2 nanoflakes in HER (a) The ratio of the discharge current at -0.01 V vs. RHE with various scan rates; (b) Chromonoampemetry test (CA) in Ar-saturated 0.1 M H_2SO_4**.** The ECSA for TaS_2 nanoflakes was calculated as 23.75 cm^2.

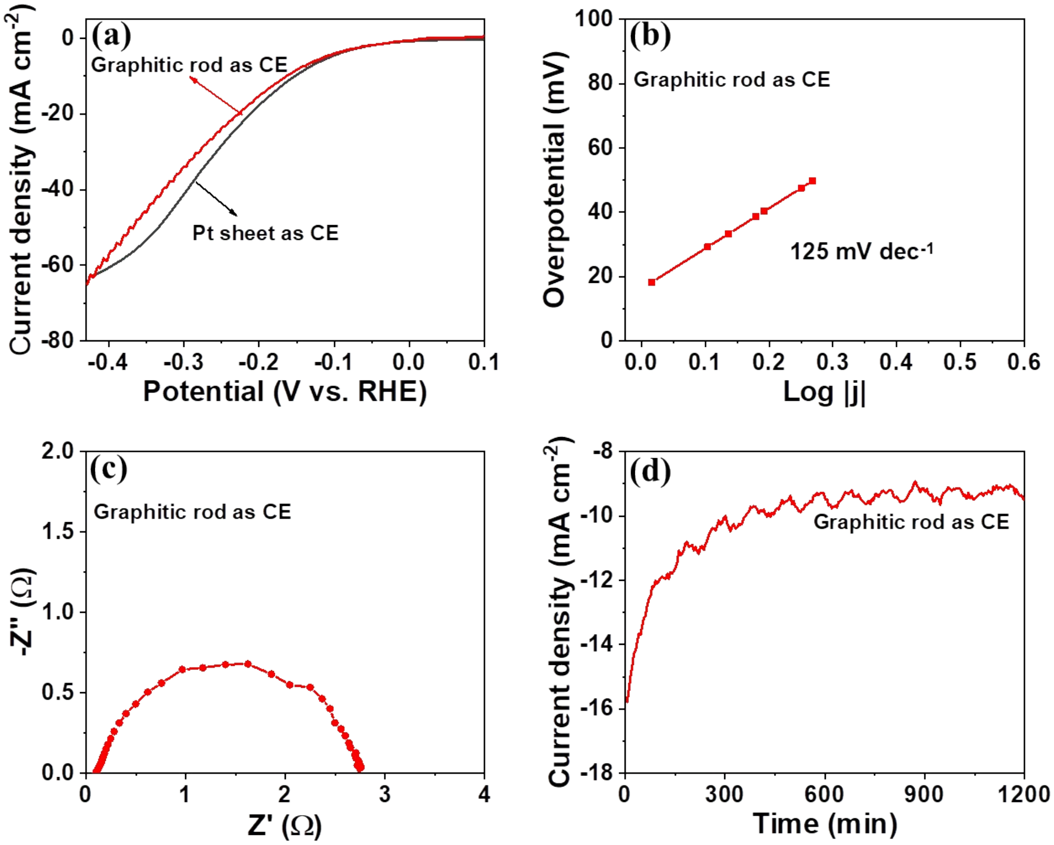


Fig. S5 HER performance: (a) LSV curves of TaS_2 with Pt sheet as counter electrode (CE) and TaS_2 with graphitic rod as CE at 10 mV s^{-1}; Tafel plot (b), EIS spectra (c), Chromonoampemetry test (d) of TaS_2 with graphitic rod as counter electrode.

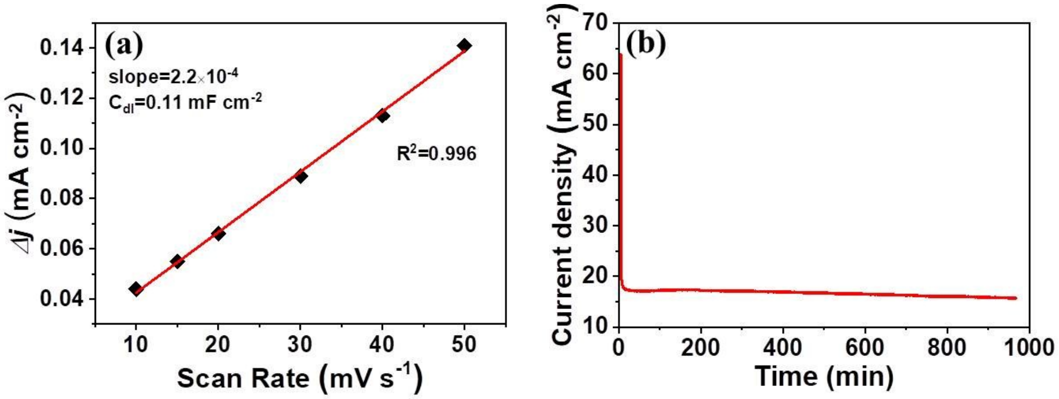


Fig. S6 TaS_2 nanoflakes in OER (a) The ratio of the discharge current at 1.15 V vs. RHE with various scan rates; (b) Chromonoampemetry test (CA) in oxygen-saturated 1.0 M NaOH**.** The ECSA for TaS_2 nanoflakes was calculated as 2.75 cm^2.

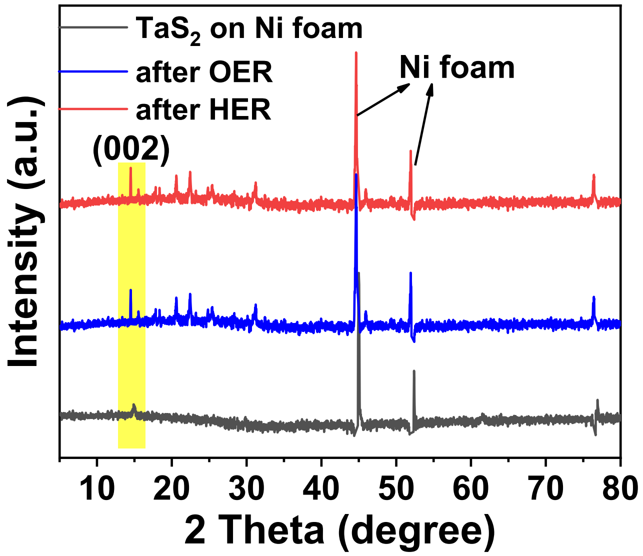


Fig. S7 XRD of the as-synthesized TaS_2 on Ni foam and TaS_2 after HER or OER process.

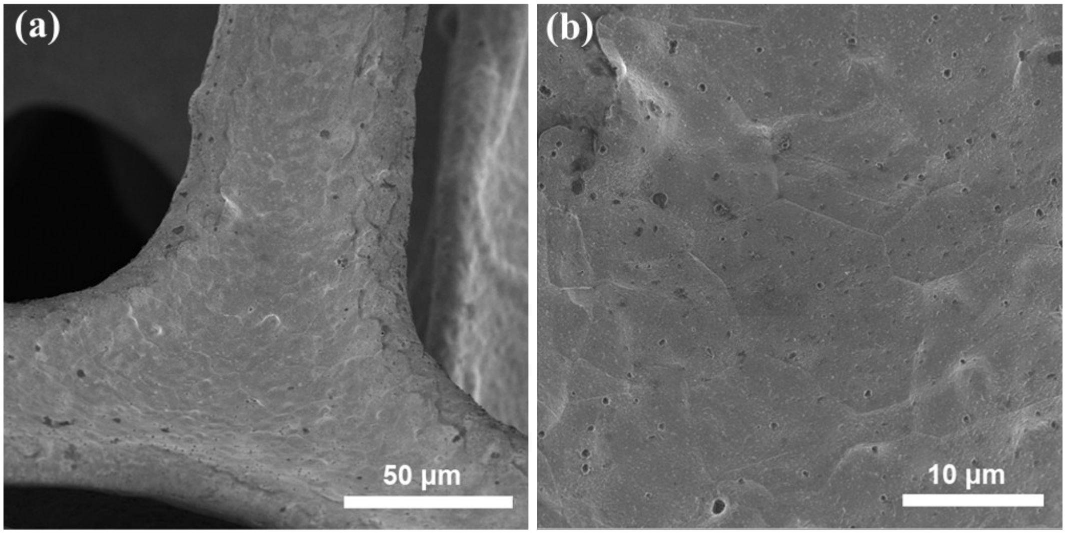


Fig. S8 SEM images of the TaS_2 on Ni foam after electrochemical reaction.

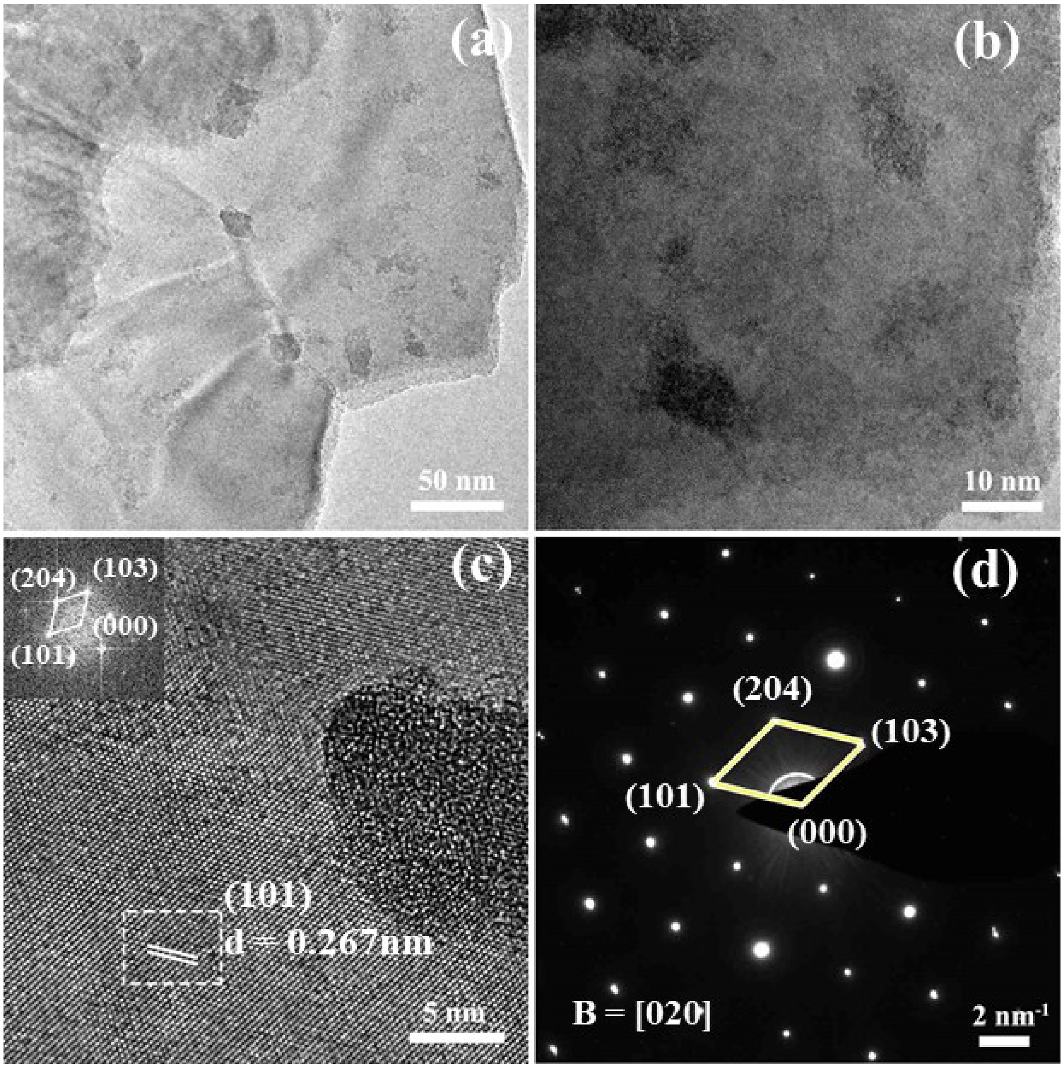


Fig. S9 TEM and HR-TEM images (a-c) of TaS$_2$ nanoflakes form Ni foam after electrochemical reaction and SAED analysis (d).

Table S1 Supercapacitor performance of this work in comparison with previously reported catalysts.

Materials	Current density Or scan rate	Specific capacitance	Capacitance remained (%)	Electrolyte & Test set-up	Refs
Pristine-Ti_2CT_x	1.0 A g^{-1}	234 F g^{-1}	94.7% (5000C)	6 M KOH	1
Ta-Graphene nanocomposite film modified platinum electrode	100 mV s^{-1}	1.42 mF cm^{-2}	67% (1000C)	0.1 M Na_2SO_4	2
1T and 2H Phases in MoS_2 Monolayers	0.5 A g^{-1} 5.0 A g^{-1}	366.9 F g^{-1} 273.76 F g^{-1}	92.2% (1000C)	6 M KOH	3
1T/2H hybrid phases (MoS_2-A)	1.0 A g^{-1} 5.0 A g^{-1}	346 F g^{-1} 282 F g^{-1}	95.4% (2000C)	2 M KOH	4
TiS_2-VACNT	1.11 A g^{-1}	240 F g^{-1}	>95% (10000C)	0.5 M H_2SO_4	5
WS_2	10 mV s^{-1}	18.10 F g^{-1}	80% (20000C)	1 M H_2SO_4	6
TiO_2/boron-doped diamond/Ta multilayer films	5 mV s^{-1}	5.23 mF cm^{-2}	89.3% (500C)	0.1 M Na_2SO_4	7
TaS_2	0.5 A g^{-1} 100 mV s^{-1} 1 A g^{-1}	382.5 F g^{-1} 1100 mF cm^{-2} 168 F cm^{-3}	91% (5000C)	6 M KOH	**This work**

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