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The design and construction of 3D rose petal-shape MoS_2 hierarchical nanostructures with structure-sensitive properties

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Experimental Section

Materials and methods

Synthesis of the eletrospun polyacrylonitrile nanofibers (PANF)

Based on our recent work11, the PANFs were synthesized by a common electrospinning method. In brief, 3 g PAN powder was dissolved in 22 mL dimethyl formamide (DMF, 99.5 %) under magnetic stirring at 65 °C to get a homogeneous solution. The mass fraction of PAN in the DMF solution was 10 wt % and the as-prepared solution was used to prepare a nanofibrous mats via electrospinning technique. The solution was transferred into a syringe with a stainless copper needle at the tip. The needle was connected to a high voltage power supply. The applied voltage was 12 kV, the needle to collector distance was 12 cm and the flow rate of the solution was 0.01 mL/min. The electrospun PANFs were collected onto a piece of aluminum foil. All experiments were performed at room temperature.

Preparation of the carbon nanofibers (CNFs)

The as-prepared PANFs fibrous mats were placed to the ceramic boats in a horizontal tube furnace for heat treatment. The PANFs nanofibrous mats was firstly heated to 280 °C in air at a rate of 5 °C/min and maintained for 6 h for the pre-oxidation. Then, the samples were heated up to 1000 °C at a rate of 5 °C/min under Ar protecting environment for the carbonization of PANFs. The desired graphitization temperature was held constant for 8 h and then the as-prepared CNFs nanofibrous mats were cooled to room temperature under Ar atmosphere.

Synthesis of the hierarchical MoS_2/CNFs hybrid fibrous mats

The direct growth of MoS_2 nanocrystals on the surfaces of CNFs was carried out in a home-built CVD furnace. The MnO_2 power, MoO_3 power and CNFs fibrous mats were placed in three ceramic boats, respectively, which are close to the center of heating zone of the furnace. Another ceramic boat with S powder (99.99 %, 0.5 g) was placed upstream relative to the gas flow direction. The MoO_3 boat was placed close to the CNFs boat while the distance between the S and MoO_3 is 20 cm. MnO_2

power was added to react with extra S at the initial stage of MoO_3 reduction to allow MoO_2 grow up to shells along the CNFs before the growth was terminated by sulfurization caused by too much S. At the beginning of the growth, the CVD furnace was firstly purged with Ar for 30 min. Then, the furnace was heated up to 700 °C at a rate of 20 °C/min with 120 sccm Ar. When the temperature reached 700 °C, the S boat was heated by a heating belt with an individual temperature controller at ~150 °C. After 30 min, the furnace was heated up to 900 °C with a rate of 10 °C/min and the temperature was held constant for 6 h. The temperature of S was maintained at 150 °C throughout the synthesis. After the heat treatment, the heating belt for S was removed immediately and the furnace was cooled to room temperature.

Characterization

TEM images and SAED patterns of all the samples were obtained with a JSM-2100 transmission electron micros-copy (JEOL, Japan) at an acceleration voltage of 200 kV. The morphology evolutions of all the MoS_2-CNFs were observed by a JSM-6700F FE-SEM (JEOL, Japan) at an acceleration voltage of 3 kV. XRD patterns of the CNFs and MoS_2-CNFs were characterized with a SIEMENS Diffraktometer D5000 X-ray diffractometer using Cu K_α radiation source at 35 kV, with a scan rate of 0.02^o 2θ s^{-1} in the 2θ range of $10\text{-}80^o$. X-ray photoelectron spectra of CNFs and MoS_2-CNFs were recorded using an X-ray Photoelectron Spectrometer (Kratos Axis Ultra DLD) with an aluminum (mono) K_α source (1486.6 eV). The aluminum K_α source was operated at 15 kV and 10 mA. Raman spectra of all the samples were recorded by a Renishaw inVia Raman microscope using a 532 nm laser excitation source. The excitation light intensity in front of the objective was 10 mW with a spectral collection time of 1s. The integration time for our measurements was set to 10 s. The HAADF-STEM mages, STEM mapping mages, and EELS spectra were recorded by a STEM (Tecnai G2 F30 S-Twin, Philips-FEI) at an acceleration voltage of 300 kV.

Electrocatalytic measurement

The HER activity of the MoS_2-CNFs nanomaterials was assessed using a typical three-electrode system in which a MoS_2-CNFs fibrous mats electrode, Pt foil and saturated Ag/AgCl electrode served as the working, counter and reference electrodes, respectively. Linear sweep voltammetry were conducted with Autolab potentiostat/ galvanostat (Model PGSTAT302N) workstation with scan rate of 2 mVs^{-1}. AC impedance measurements were carried out in the same configuration at $\eta = 0.12$ V from 10^6-0.02 Hz with an AC voltage of 5 mV. In all measurements, we used saturated Ag/AgCl electrode as the reference and all the potentials were converted to values with reference to reversible hydrogen electrode (RHE). In 0.5 M H_2SO_4, E (RHE) = E (SCE) + 0.2224 V. All the potentials reported in our manuscript are against RHE and the current density was normalized to the geometrical area. As a control experiment, the HER activity of the pure CNFs mats, MoS_2 powder and mixture of MoS_2 powder and CNFs are also tested. The MoS_2 powder is obtained through the directly vulcanize by S vapor.

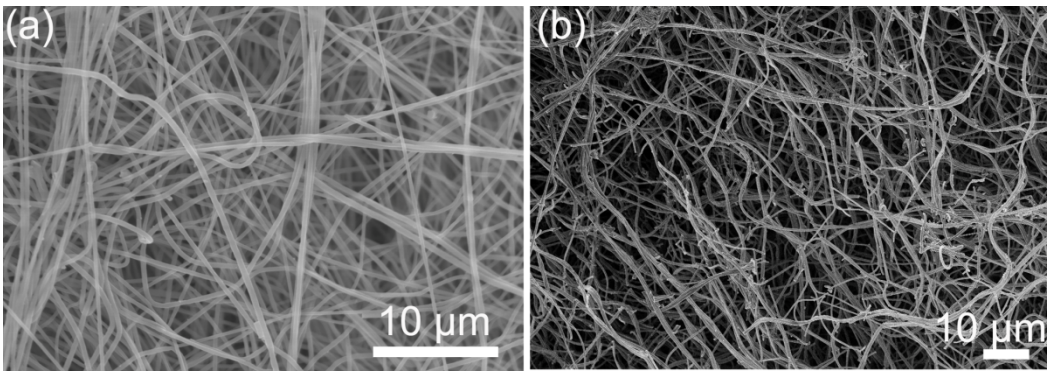

Figure S1 FE-SEM images of the (a) electrospun PAN nanofibers mats and (b) carbon nanofibers mats after carbonization treatment.

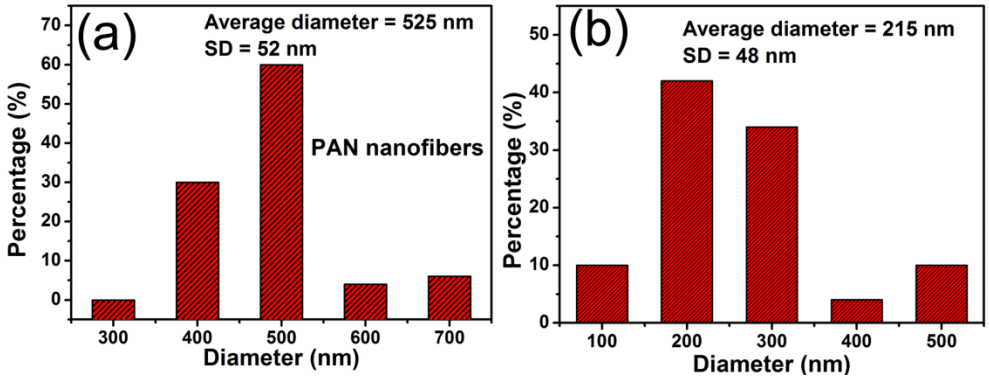

Figure S2 The diameter distributions of the (a) PANFs and (b) CNFs.

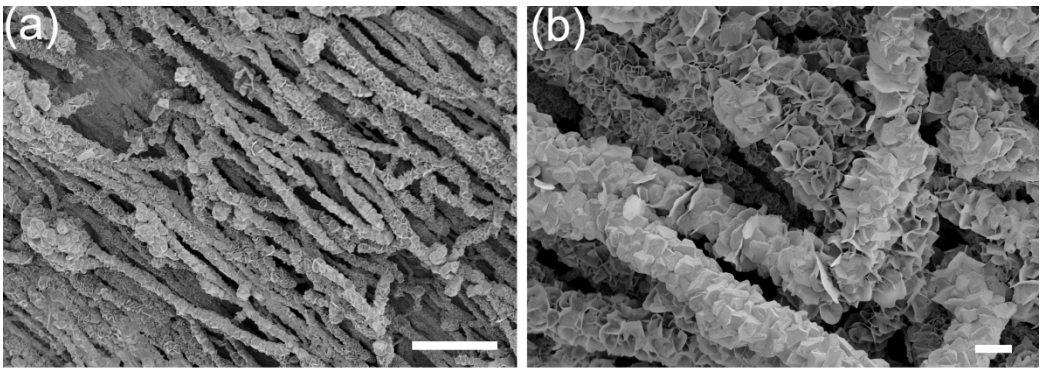

Figure S3 Low resolution FE-SEM images of the MoS_2/CNFs hierarchical nanosctructure.

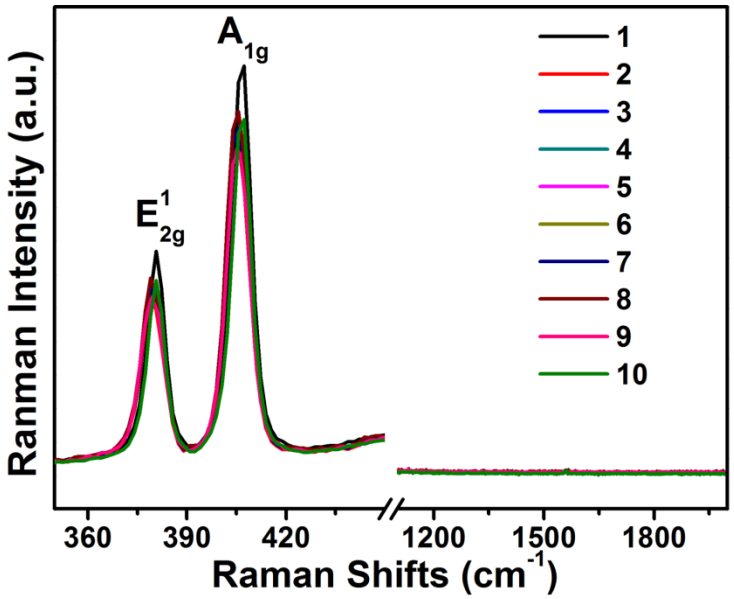

Figure S4 Typical Raman spectra of ten samples of MoS_2/CNFs hierarchical nanostructures mats.

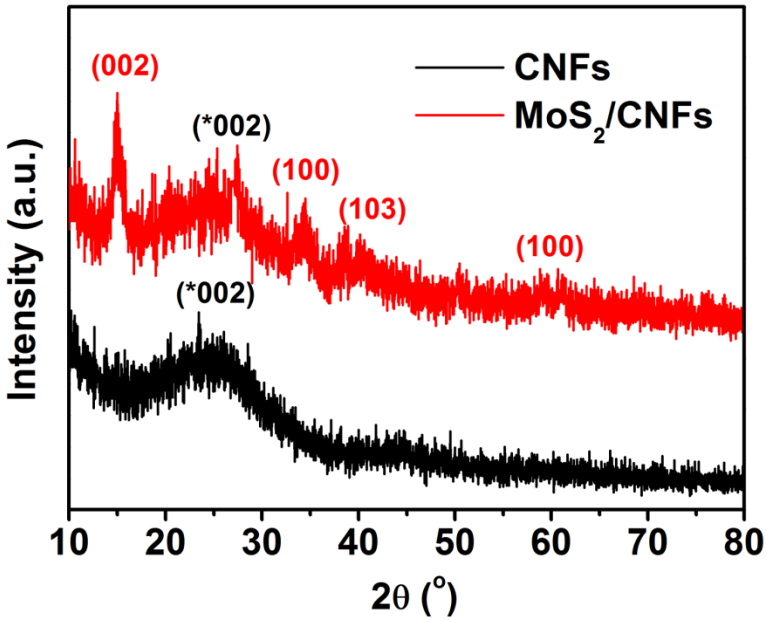

Figure S5 XRD patterns of the CNFs and the flowerer-like MoS_2 ultra nanosheets grown on CNFs.

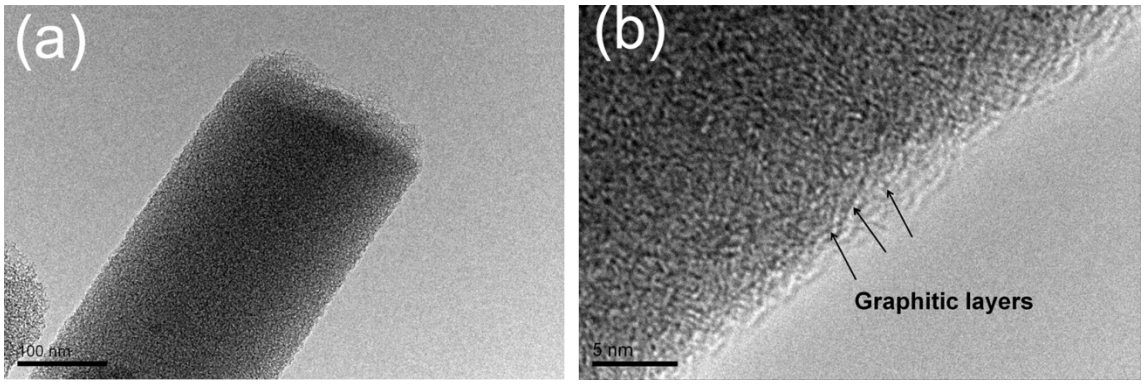

Figure S6 (a) TEM and (b) HRTEM images of the CNFs.

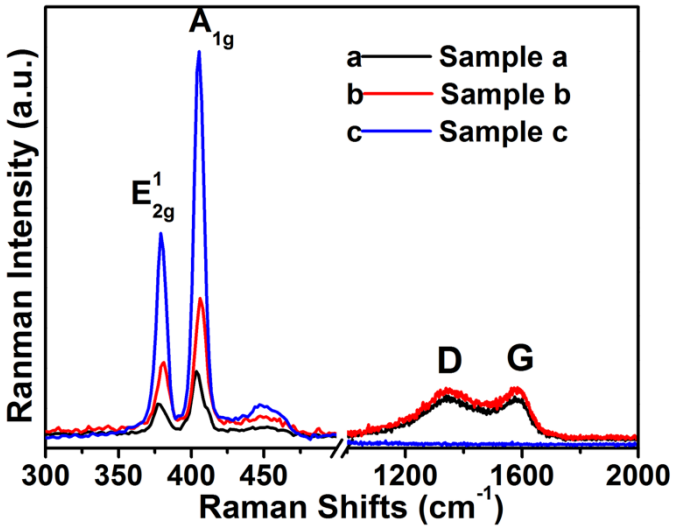

Figure S7 Raman spectra of the hierarchical MoS_2-CNFs nanomaterials with morphology evolutions: (sample a) scrolled MoS_2-CNFs, (sample b) small 2D MoS_2 nanosheets grown on the scrolled MoS_2-CNFs and (sample c) 3D MoS_2-CNF nanostructures.

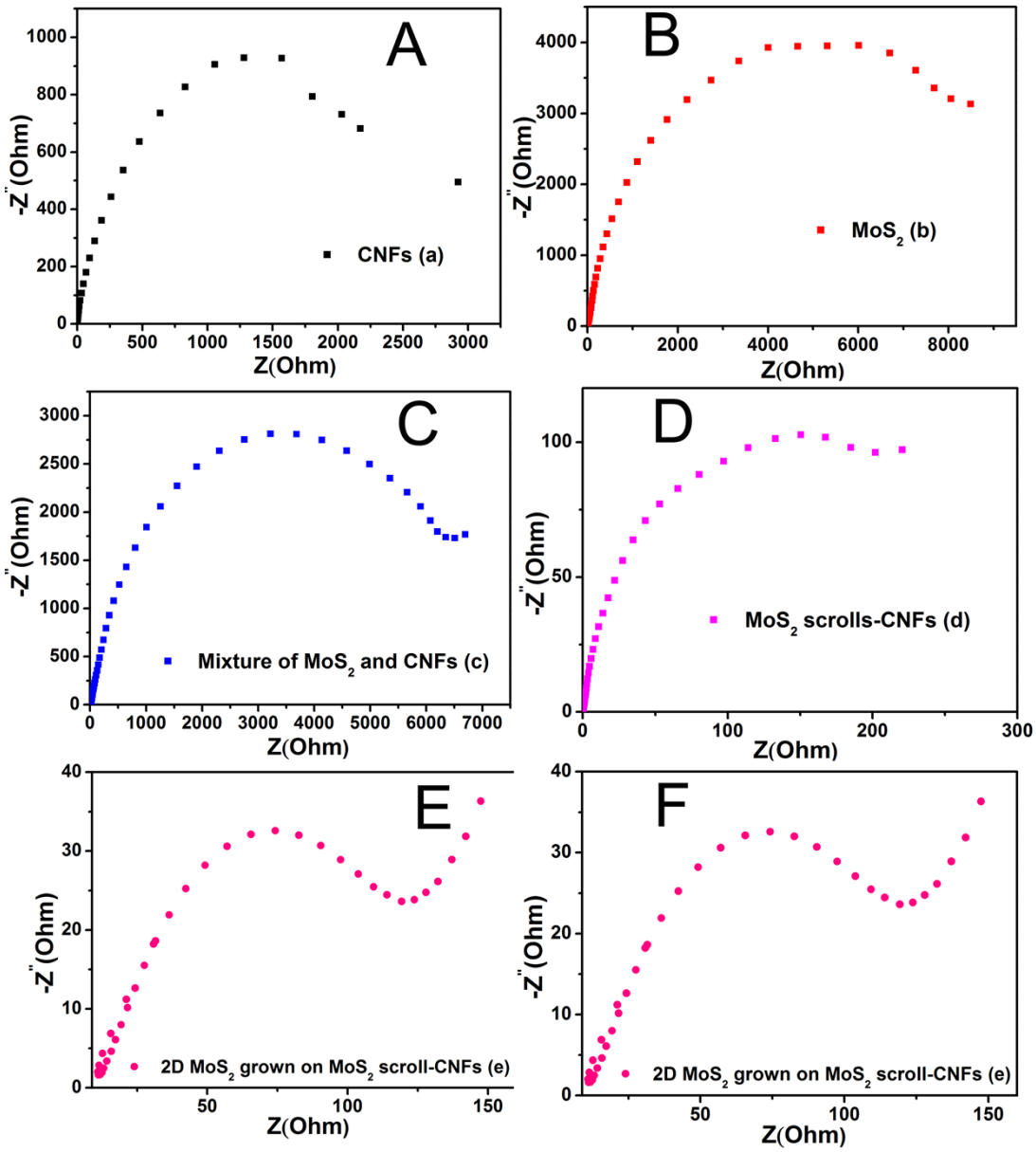

Figure 8 AC impedance spectroscopy of (a) CNFs, (b) MoS_2 powder, (c) mixture MoS_2 powder and CNFs, (d) scrolled MoS_2-CNFs, (e) small 2D MoS_2 nanosheets grown on the scrolled MoS_2-CNFs and (f) 3D MoS_2-CNF nanostructures at $\eta = 0.12$ V.

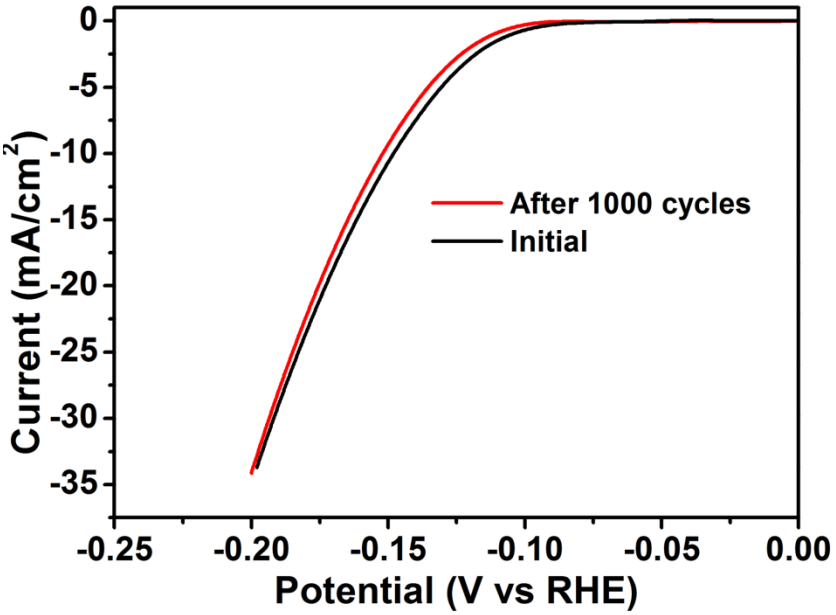

Figure 9 Polarization curves showing that the MoS_2-CNFs (sample c) still exhibited excellent catalytic activity after cycles of continuous operation.