

Supplementary Information

Synthesis of one-dimensional hierarchical mesoporous carbon materials for supercapacitors

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Experimental procedures

Materials

The triblock copolymers of poly(ethylene oxide)-block-poly(4-vinylpyridine)-block-polystyrene (PEO-PVP-PS) with different block lengths (PEO113-PVP44-PS97 and PEO113-PVP60-PS200) were prepared by RAFT polymerization. Dopamine hydrochloride (AR) was purchased from Aladdin Co., Ltd. Ammonium hydroxide (AR, 25-28%), anhydrous ethanol (AR, $\geq 99.7\%$), tetraethyl orthosilicate (AR, 37.0-40.0%), hydrofluoric acid (HF, AR, $\geq 40.0\%$), tris(hydroxymethyl)aminomethane (tris-buffer, $\geq 99.9\%$), potassium hydroxide (KOH, AR, $\geq 85.0\%$), anhydrous sodium sulfate (Na_2SO_4 , AR, $\geq 99.0\%$), and cetyltrimethylammonium bromide (AR, $\geq 99.0\%$) were purchased from domestic pharmaceutical companies. None of the drugs used in the experiment was treated with drugs before the experiment. In addition, the water used in the experiment was deionized water, which is an important feature of the scientific rigor of this experiment.

Measurement and Characterization

Transmission electron microscopy (TEM) was performed using a Regulus 7800 instrument to obtain the morphological data of the materials, with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was conducted using a Regulus 8100 instrument to acquire the surface morphological data of the materials. Wide-angle X-ray diffraction (XRD) was carried out using a Rigaku Dmax-3C instrument to obtain the crystal phase information of the materials, with an operating voltage of 40 kV. Nitrogen adsorption-desorption isotherms were measured using a Quantachrome Autosorb-iQ instrument to obtain the pore structure information of the materials, and the test was conducted at 77 K (liquid nitrogen environment). Before the tests, all substances were vacuum degassed at 200 °C for 8 hours. The specific surface area of the materials was calculated using the Brunauer-Emmett-Teller (BET) formula, and the mesopore size distribution curve was calculated using the Barrett-Joyner-Halenda (BJH) formula. X-ray photoelectron spectroscopy (XPS) was performed using

an ESCALABXI+ instrument to obtain the elemental valence state information of the materials. Fourier transform infrared spectroscopy (FTIR) was conducted using a Nicolet iS50R instrument with a resolution of 0.09 cm^{-1} to obtain the surface functional group information of the materials. Raman imaging was performed using a LABRAM HR EVOLUTION instrument.

Preparation of stable triblock single micelles

80 mg of the triblock PS-PVP-PEO copolymer with long PS chains was added to 40 mL of anhydrous ethanol solution ^[1]. Subsequently, the solution was placed at $70\text{ }^{\circ}\text{C}$ to enhance its solubility ^[1]. After 3 hours, a uniform, the ethanol solution of monodisperse single micelle with a concentration of 2.0 mg/mL was formed. Furthermore, the temperature was further cooled down to $25\text{ }^{\circ}\text{C}$, and a stable, monodisperse PS-PVP-PEO single micelle solution was obtained ^[2].

Preparation of one-dimensional silica dioxide rods (m-SiO₂)

We mixed CTAB with deionized water, added ammonia water and TEOS, stirred at $40\text{ }^{\circ}\text{C}$ for 24 hours, and obtained one-dimensional mesoporous silicon dioxide rods (m-SiO₂) via centrifugation and washin.

Preparation of one-dimensional porous nitrogen-doped material (1D N-mC)

The ethanol dispersion of m-SiO₂ was added to the aqueous solution of PEO-PVP-PS micelles, and the mixture was stirred at room temperature for 6 hours. After washing, m-SiO₂@micelle was obtained. Subsequently, m-SiO₂@micelle was mixed with deionized water at a 1:1 ratio, the pH of the mixture was adjusted to 8, and dopamine hydrochloride was added. The resulting mixture was stirred at room temperature for 24 hours and then dried at $60\text{ }^{\circ}\text{C}$ to obtain m-SiO₂@micelle@PDA. This material was subjected to calcination by programmed temperature in a nitrogen atmosphere (heated at a rate of $1\text{ }^{\circ}\text{C}/\text{min}$ to $350\text{ }^{\circ}\text{C}$ and held for 3 hours, then further heated to $800\text{ }^{\circ}\text{C}$ and held for 2 hours). After cooling down, it was etched with a $2\text{ wt}\%$ hydrofluoric acid aqueous solution at room temperature for 5 hours, followed by washing and drying. Finally, the one-dimensional hierarchical porous nitrogen-doped carbon material (1D N-mC) was obtained.

Morphology control of SiO₂

The concentration of CTAB can regulate the morphology and dimensions of SiO₂ rods. Specifically, an excessively high concentration leads to an increase in their diameter, while an excessively low concentration tends to result in the formation of spherical particles.

Control of the size of 1D N-mC mesopores

By changing the molecular weight of the PS-PVP-PEO triblock copolymer, the precise regulation of the size of 1D N-mC mesopores can be achieved: when the copolymer molecular weight is PS₆₉-PVP₄₂-PEO₁₁₃, the diameter of the spherical monolayer micelles is approximately 10 nm, and the final material mesopore size is 10 nm; when the molecular weight is increased to PS₁₀₆-PVP₄₇-PEO₁₁₃, the diameter of the monolayer micelles expands to 35 nm, and the corresponding material mesopore size is also 35 nm, indicating that the molecular weight of the copolymer is the key regulatory factor for the mesopore size.

Electrochemical Supercapacitor Experiment

1. Three-electrode system, using an electrochemical analyzer (CHI 760 E) in 6 M KOH electrolyte, conduct electrochemical measurements using a three-electrode electrochemical cell. The Hg/HgO electrode and platinum wire serve as their reference and counter electrodes respectively. The one-dimensional multi-level porous nitrogen-doped carbon material (80 wt%), acetylene black (10 wt%), and polytetrafluoroethylene (10 wt%) were fully mixed and stirred. Then, the mixture is pressed onto foam nickel as the working electrode. The mass of the porous carbon loaded on the working electrode is 2 mg. The electrochemical performance of the capacitor was tested using cyclic voltammetry, constant current charge-discharge, and AC impedance methods. The results show that the working potential window of CV and GCD is selected in the range of (-1-0 V). The scan rate of CV is 10-200 mV/s, and the current density of GCD is 1-10 A/g.

$$C = I\Delta t / \Delta V m$$

Where I (A), Δt (s), ΔV (V), and m (g) are the discharge current, discharge time, voltage window, and total mass of the active material respectively.

2. Two-electrode system, using an electrochemical analyzer (CHI 760 E) in 1 M Na₂SO₄ electrolyte, conduct electrochemical measurements using a symmetric working electrode. The working potential window is selected in the range of 0-1.2 V, and other measurement conditions are the same. The mass of carbon loaded on each working electrode is 1 mg. The specific capacitance (C_t , F/g⁻¹), energy density (E, W h kg⁻¹), and power density (P, W kg⁻¹) are calculated using the following formulas:

$$C_t = I\Delta t/\Delta Vm$$

$$E = 3.6/2C_t(\Delta V)^2$$

$$P = 3600 E/\Delta t$$

Where I , t , V , and m are the discharge current (A), discharge time (s), voltage window during discharge (V), and the total mass of the active material on both electrodes (g).

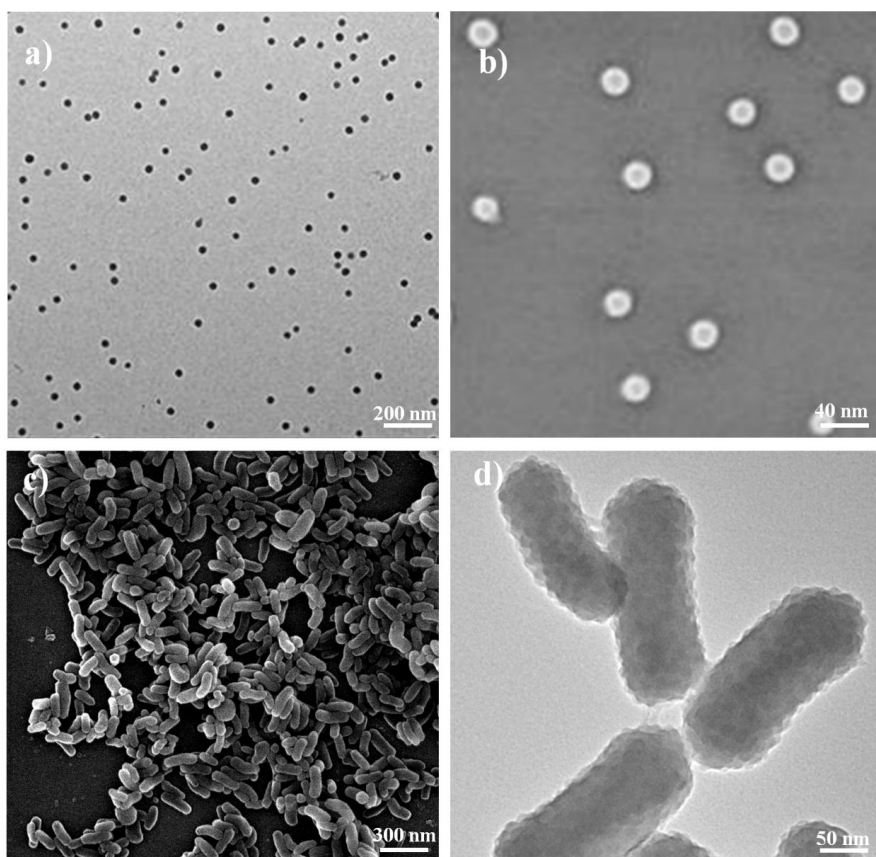


Figure S1. a) TEM and b) SEM image of a single PS-PVP-PEO micelle; c) SEM image of m-SiO₂; d) TEM image of m-SiO₂@monomicelle composites.

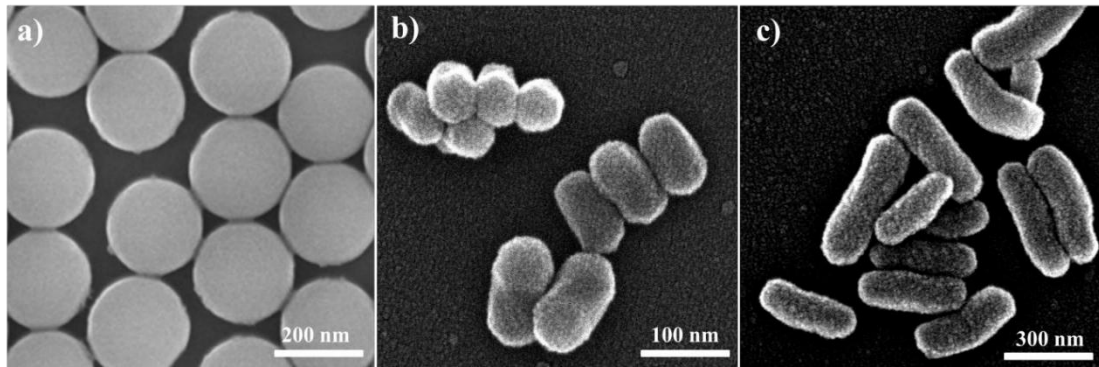


Figure S2 SEM images of SiO₂ with increasing CTAB content. a) SiO₂ spheres (200 nm); b) SiO₂ rods (100 nm); c) SiO₂ rods (350 nm).

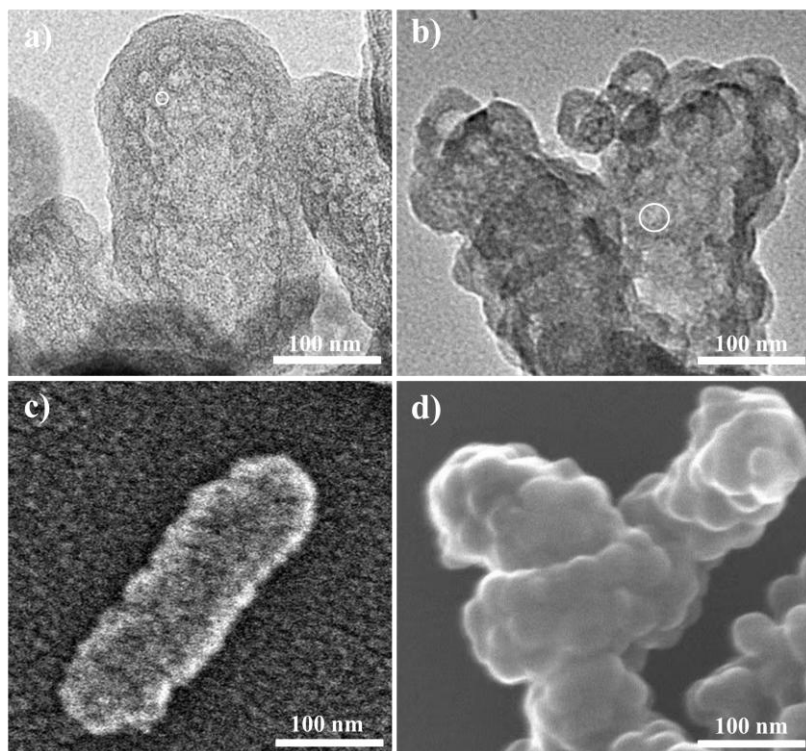


Figure S3 a) TEM image of 1D N-mC; b) TEM image of the material with 35 nm mesopores; c) SEM image of 1D N-mC; d) SEM image of the material with 35 nm mesopores.

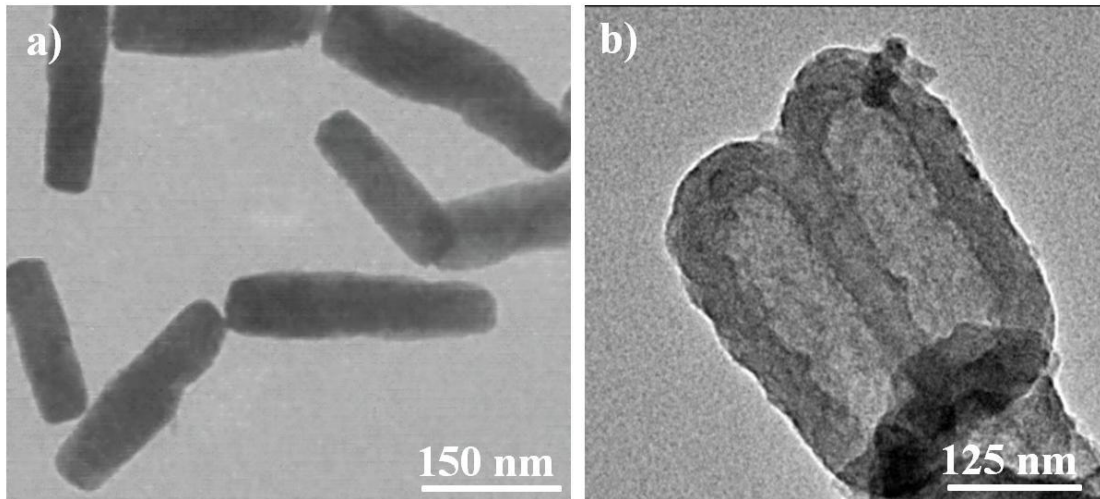


Figure S4 TEM images of control samples. a) TEM image of N-CNR; b) TEM image of 1D N-C.

Reference

- [1] ZHAO Z, WANG X, JING X, et al. General synthesis of ultrafine monodispersed hybrid nanoparticles from highly stable monomicelles. *Advanced Materials*, 2021, 33(23): 2100820.
- [2] ZHAO Z, DUAN L, ZHAO Y, et al. Constructing unique mesoporous carbon superstructures via monomicelle interface confined assembly. *Journal of the American Chemical Society*, 2022, 144(26): 11767-11777.