Structure-Mediated Fluid-Involved Behaviors Promote Performances of Carbon-based supercapacitor

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Experimental methods

1.Experimental preparation process of carbon nanotubes sponges

The carbon nanotubes sponge used in this study was prepared by chemical vapor deposition (CVD). Carbon nanotubes sponge was prepared by using ferrocene/dichlorobenzene composite solution system, in which dichlorobenzene was used as carbon source and ferrocene as catalyst, and was synthesized by chemical vapor deposition (CVD). The specific methods are as follows: Firstly, use an electronic tray balance to weigh 2.4g ferrocene powder drug dissolved in 40 mL 1, 2-o-dichlorobenzene, and stir it fully on a magnetic stirring platform for 10 minutes (set speed: 200 r/min temperature: 15 °C) to obtain a precursor solution with a concentration of 60 mg/mL. Next, 20ul thiophene solution was added to the precursor; Then put the appropriate size of quartz plate (L× W, 3 cm×4 cm) into the quartz tube with a diameter of 5 cm, connect the air supply system and the flow inlet device, and determine good sealing to ensure the safety of the experiment; Set the heating program: firstly, the quartz tube is heated from room temperature to 550 °C at a heating rate of 20 °C/min, and then to the reaction temperature of 860 °C at a heating rate of 5 °C/min. Before heating up, the air in the system is removed through Ar, and then the flow rates of Ar and H_2 are set at 2000 SCCM and 300 SCCM respectively, and the air is passed through the quartz tube in the CVD tubular furnace through the gas supply pipeline. Turn on the precision flow injection pump and set the flow rate of liquid inlet to 0.125 mL /min. The mixture of gas will carry the precursor droplet into the reaction temperature region of 860 °C, and grow CNTS on the flat quartz plate. The growth process lasts for 2-3h. Carbon nanotubes sponge prepared by CVD method is mainly affected by catalyst concentration, gas load, reaction temperature and roughness of substrate surface. The carbon nanotubes sponge obtained can be peeled from quartz sheet.

2.TiO_2@CNTS composite structure was prepared by hydro-thermal method

The different morphologies of TiO_2@CNTS composite structures were prepared by hydrothermal method. Compared with physical vapor deposition and electrooxidation, hydrothermal synthesis is low-cost, simple to operate and easy to mass production. In addition, the hydrothermal method in this paper is also based on the following two points :(1) the load of titanium dioxide can be accurately controlled by controlling the amount of titanium source. (2) Due to the super-hydrophobic properties of carbon nanotubes sponges, hydrophilic reagents are difficult to penetrate into the sponge at room temperature. If the sponge is chemically modified, the surface properties of carbon nanotubes may be changed, and then the structure and aggregation state of carbon nanotubes may be destroyed. High temperature and high pressure can reduce the surface tension of water and enhance its wetting ability. Hydrolysis of titanium source under high temperature and high pressure can make the solution fully infiltrate the sponge without damaging the CNTS structure.

The specific process of hydrothermal method is as follows: (1) 16mL mixed solution of tetrabutyl titanate ($Ti(OBu)_4$)/ ethanol (C_2H_5OH)/ hydrochloric acid/deionized water with different volume ratios is prepared first (volume ratios of the four components are: 0.05-0.3:2:2:12, 0.05-0.3:2:4: 10, 0.05-0.3:2:6:8, 0.05-0.3:2:8:6); (2) Mix 16 mL titanium dioxide precursor mixture solution with CNTS and transfer it to a stainless steel high-pressure reaction kettle with volume of 25 mL in a vacuum oven for hydrothermal reaction at 170°C and reaction time of 5h. After the reaction, the autoclave was allowed to naturally cool down to room temperature inside the furnace; (3) At the end of the test, the TiO_2@CNTS composite material obtained was taken out after the container was fully cooled, then washed repeatedly with ethanol and deionized water, and finally dried in vacuum for later use. The key of hydrothermal synthesis of different titanium dioxide nanostructures is to regulate the concentration ratio of hydrochloric acid and tetrabutyltitanate ($Ti(OBu)_4$). In addition, reaction temperature and time also have certain effects.

3. Electrochemical performance characterization of

TiO_2@CNTS integrated electrode and three electrode system

The electrochemical properties of all samples were tested in 0.5 M Na_2SO_4 solution with TiO_2@CNTS as working electrode, inert Pt plate as counter electrode and Ag/AgCl as reference electrode. Using 0.5 M Na_2SO_4 as the supporting gel electrolyte, the electrochemical performance of the sample was tested using a three-electrode system at room temperature (approximately 25 °C) under static conditions. Cyclic Voltammetry (CV) was tested with a scanning rate range of 1 to 50 mV/s, and the potential window was set to 0 to -1.2 V. Galvanostatic Charge/Discharge (GCD) test is performed between 0 and -1.2 V, and the current density ranges from 10 to 100 mA/cm2. Electrochemical Impedance Spectroscopy (EIS) was measured at a scanning frequency of 0.01 Hz to 100 kHz with an amplitude of 0.007 V.

The mass specific capacitance (C_m) of electrode material based on CV test is calculated by equation (1-1):

$$C_m = \frac{\int IdU}{2 \times m \times \Delta U \times v}$$ (Equation 1-1)

The mass ratio capacitance of electrode material based on GCD test is calculated by equation (2-2) :

$$C_m = \frac{2 \times I_m \times \int Vdt}{m \times V^2 |_{V_i}^{V_f}}$$ (Equation1 -2)

The energy density Em and power density Pm based on Cm are calculated by equation (2-3, 2-4) :

$$E_m = \frac{1}{2} C_m \Delta V^2$$ (Equation 1-3)

$$P_m = \frac{E_m}{t}$$ (Equation 1-4)

In the above equations, IdU is the integral area of CV curve, m(g) is electrode mass, U (V) is voltage window, V (mV/s) is the scanning rate of CV, Im(mMA/cm2) is the current density of charge-discharge test, ∫Vdt is the integral area of discharge area, $V^2|_{V_i}^{V_f}$ is the voltage window squared. In the equation, U(V) is the voltage changing with time, I(A) is the corresponding current, t(s) is the discharge time, U(V) is the measurement scanning voltage window, m(g) is the mass of the single electrode of the device, and v(mV/ s) is the voltage scanning speed

4. Simulation of fluid behavior of TiO_2@CNTS

The finite element calculation operations we performed using COMSOL are mainly divided into five steps:

(1) Preprocessing and modelling: the electrodes are scanned by SEM, images with appropriate brightness are obtained through ImageJ (Fig. S7a-c), and the structural profile of the nano-TiO_2 is extracted using MATLAB to obtain a two-dimensional structural line (Fig. S7d-f). The data format is .dxf, which is imported into the view to establish the model.

(2) Set different material domains for the nano-TiO_2 and Na_2SO_4 solution, and define the relevant material parameters, where the initial conditions include The water flow inlet is from (0,0) to (0,H), initial flow rate $[m{\cdot}s^{-1}]$: 3.33×10^{-6}, modulus [GPa] of nano-TiO_2: 15, poisson ratio of nano-TiO_2: 0.2 , diffusion coefficient of nano-TiO_2: 1.2 and the viscosity [Pa.s] of the Na_2SO_4 solution: 1.2×10^{-3} .

(3) We used the CFD module in COMSOL Multiphysics to establish a laminar flow model. The laminar flow model is based on the Navier-Stokes equations, which describe the kinematics of fluid motion. The specific formula is as follows:

$$\rho\left[\frac{\partial V_x}{\partial \tau}+V_x\frac{\partial V_x}{\partial x}+V_y\frac{\partial V_x}{\partial y}+V_z\frac{\partial V_x}{\partial z}\right]=\mu\left[\frac{\partial^2 V_x}{\partial x^2}+\frac{\partial^2 V_x}{\partial y^2}+\frac{\partial^2 V_x}{\partial z^2}\right]-\frac{\partial P}{\partial x}+\rho g_x \quad \text{(Equation 2-1)}$$

Where ρ and μ are the fluid density and viscosity respectively, $\frac{\partial V_x}{\partial \tau}$ represents the momentum accumulation, $V_x\frac{\partial V_x}{\partial x}+V_y\frac{\partial V_x}{\partial y}+V_z\frac{\partial V_x}{\partial z}$ represents convective momentum,

$\frac{\partial^2 V_x}{\partial x^2} + \frac{\partial^2 V_x}{\partial y^2} + \frac{\partial^2 V_x}{\partial z^2}$ represents viscous momentum, $\frac{\partial P}{\partial x}$ is the pressure variation, and ρg_x represents the gravitational contribution.

(4) Solving it by setting an appropriate physical field model and boundary conditions, and we use a triangular mesh and set the minimum 0.1um cell size to mesh the model.

(5) Finally, we can calculate the relationship between the flow velocity and time.

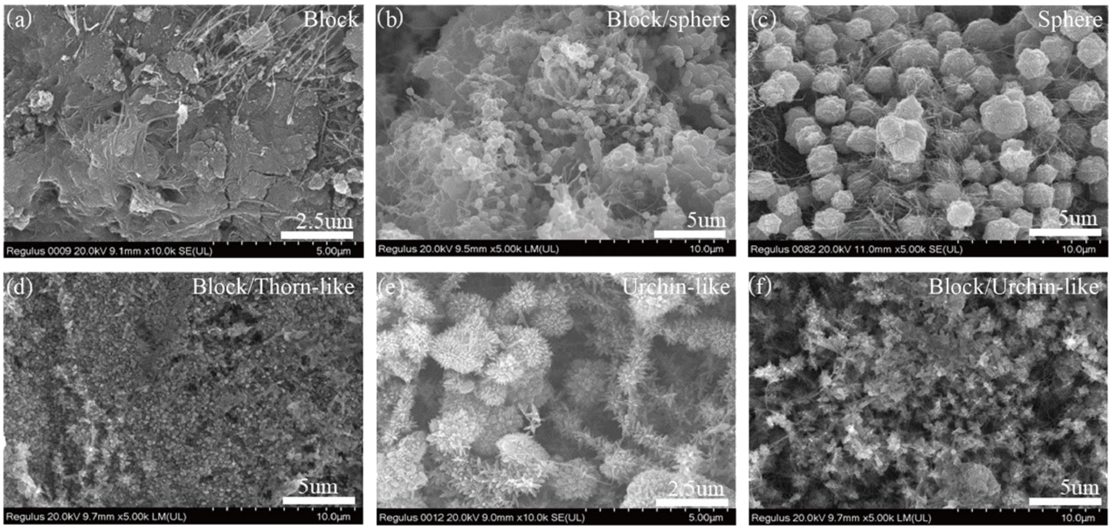


Figure S1 SEM images of TiO_2@CNTS composite structure with different characteristic morphologies, samples corresponding phase diagram (Figure 1 h)

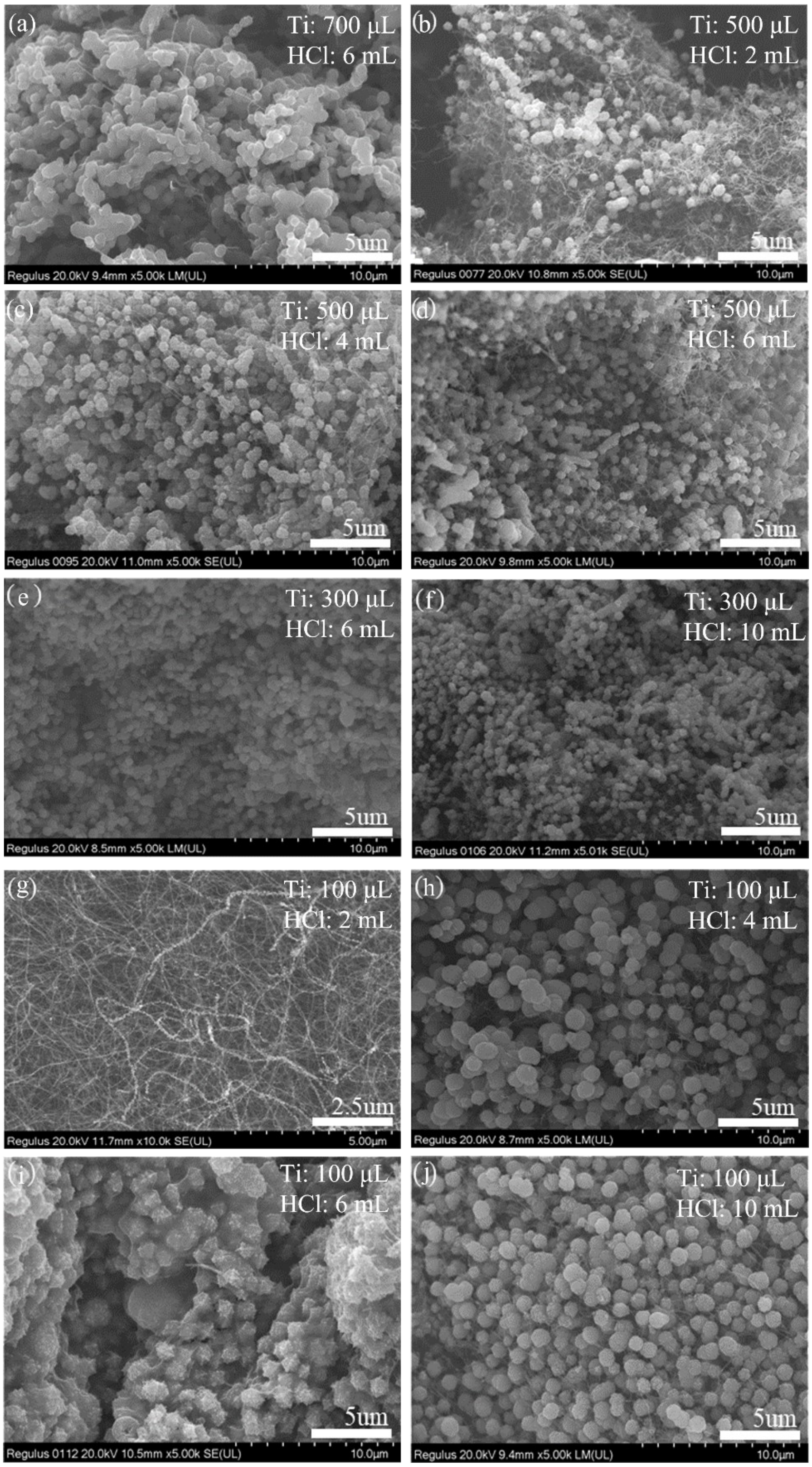


Figure S2 SEM images of TiO2@CNTS composite structures with different morphologies synthesized under different solution conditions.

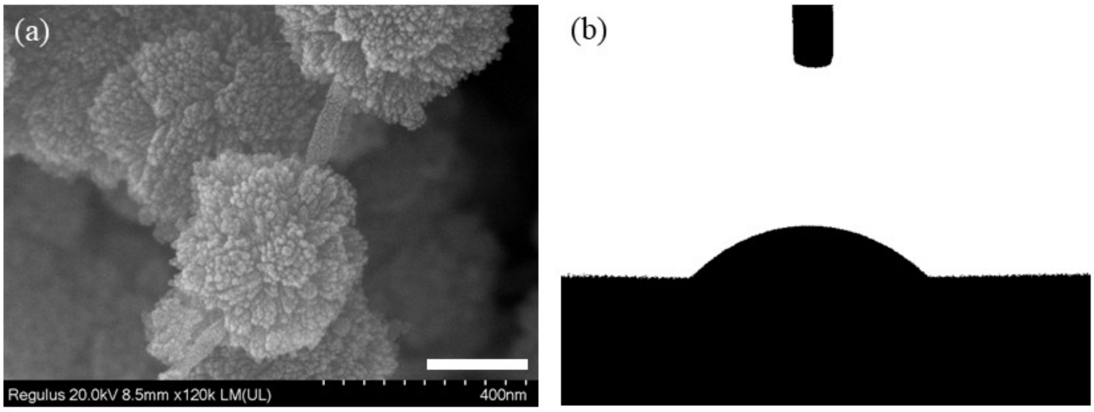


Figure S3. a, SEM image of sphere TiO_2@CNTS. **b**, picture of surface contact Angle of sphere TiO_2@CNTS.

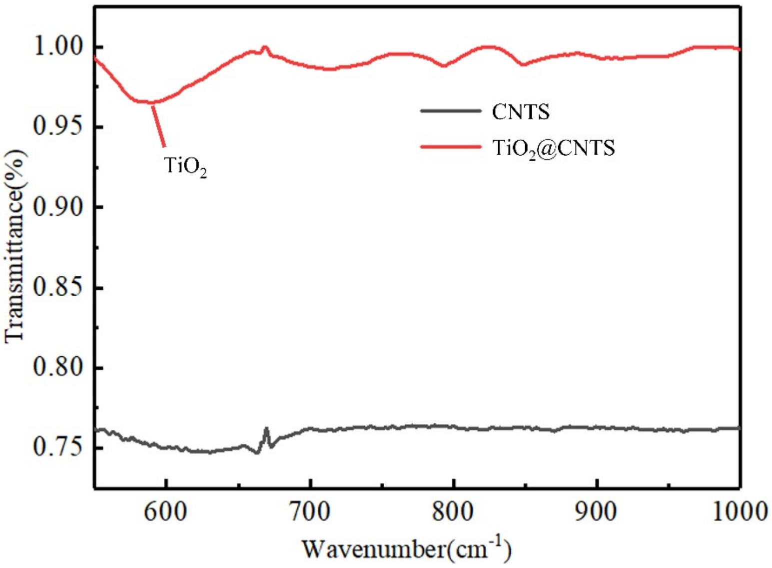


Figure S4 Fourier infrared spectra of TiO_2@CNTS composite materials (red line) and pure CNT-S infrared spectra (black line).

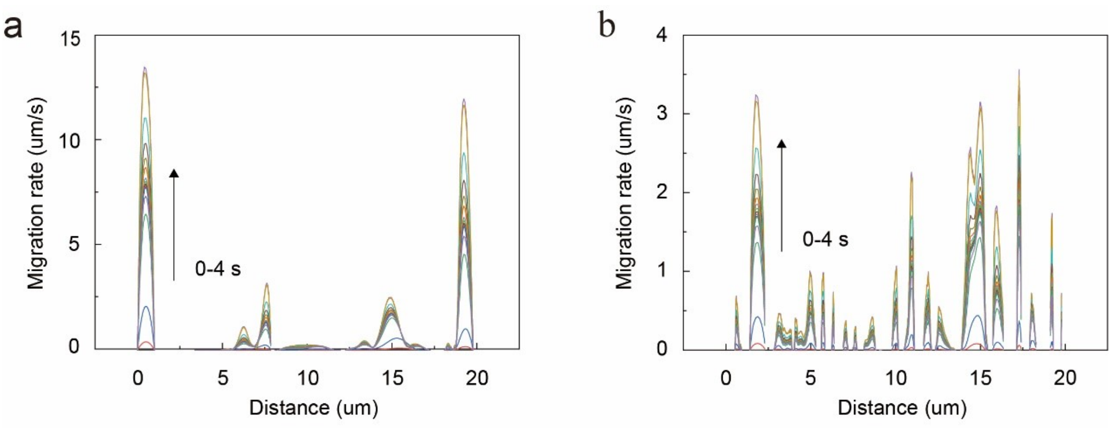


Figure S5. a, Sodium sulfate flow rate diagram of sphere TiO_2. **b**, Sodium sulfate flow rate diagram of thorn-like TiO_2.

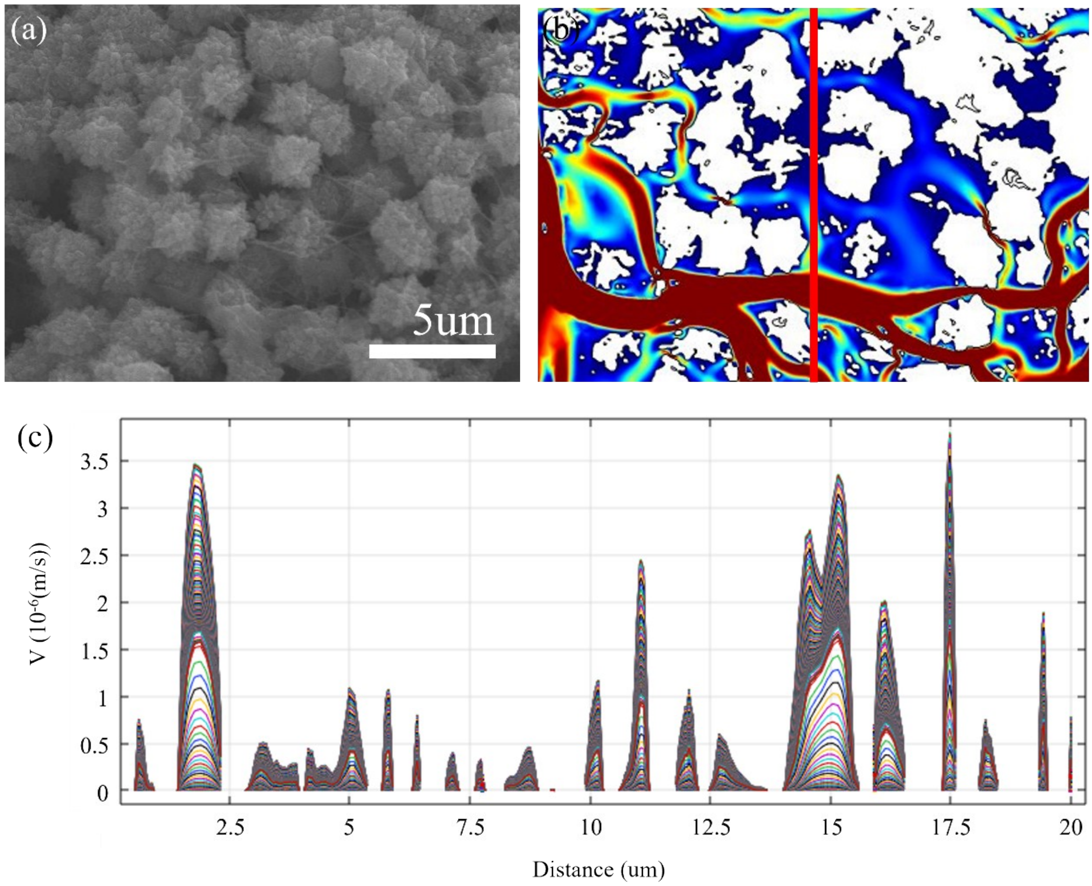
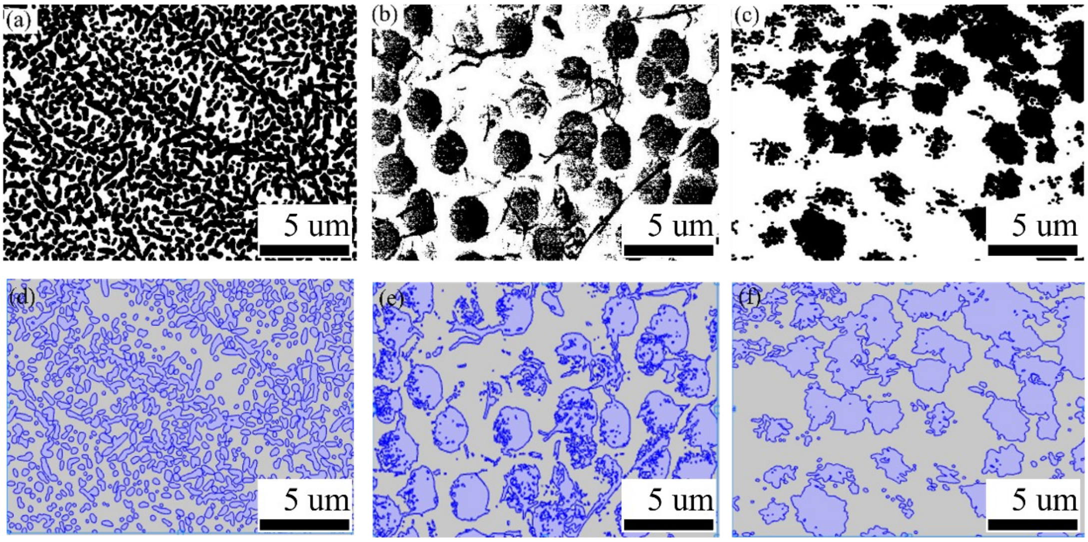


Figure S6 a, SEM image of Urchin-like TiO_2. **b,** CMOSOL visualization diagram of Urchin-like TiO_2. **c,** Sodium sulfate flow rate diagram of Urchin-like TiO_2.



Thorn-like Sphere Urchin-like

Figure S7. a-c, image J processing binarization result graph. **d-f**, MATLAB extract the contour of binary graph.

Table 1

Velocity area integral and solid-liquid interface statistics of COMSOL results.

	Flux [$m^3 \cdot s^{-1}$]	solid-liquid interface [μm]
Sphere TiO_2	2.23×10^{-16}	388.65
Urchin-like TiO_2	4.99×10^{-16}	724.26
Thorn-like TiO_2	1.43×10^{-16}	1588.40

the total interfacial integral length was calculated by accumulating the geometric distances between adjacent edge pixel points using the formula:

$$\text{Length} = \Sigma\sqrt{\triangle x^2 + \triangle y^2}. \qquad \text{(Equation 3-1)}$$

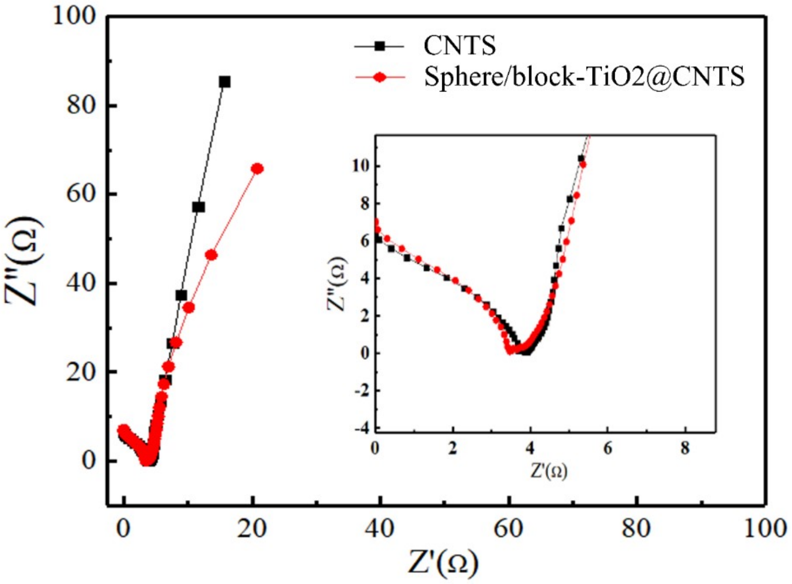


Figure S8 Comparison of EIS between the two electrodes.