Electronic Supplementary Information (ESI)

Three-dimensional graphene-based hierarchically porous carbon composites prepared by a dual-template strategy for capacitive deionization

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EXPERIMENTAL SECTION

Characterization

The texture properties of prepared samples were characterized by the field emission scanning electron microscopy (SEM, JEOL JMS-700F) as well as transmission electron microscopy (TEM, JEOL JEM-200CX). The X-ray diffraction (XRD) analysis was conducted with a Rigaku D/MAX-RB X-ray diffractometer by using the Cu Kα (40 kV, 20 mA) radiation and a secondary beam graphite monochromator. The Raman spectra were recorded on an in-equipped with an optical microscope at the room temperature. For excitation, the 514.5 nm line from the Ar^+ ion laser (Spectra Physics) was focused on the sample with an analyzing spot of about 1 μm. The nitrogen (N_2) sorption measurement was performed with a Micromeritics ASAP 2020 instrument at 77 K. Prior to the measurements, all the samples were degassed at 493

K in a vacuum line overnight. The specific surface area and pore volume were calculated with the Brunauer-Emmett-Teller (BET) method and the pore size distribution was estimated with desorption branch based on the Barrett-Joyneer-Halenda (BJH) model.

Electrochemical Performance Measurements

The electrochemical behaviors of resultant electrodes were detected by the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge (GC) technologies in a three-electrode cell, where the prepared carbon electrode, graphite sheet and saturated calomel electrode (SCE) serve as the working electrode, counter electrode and reference electrode, respectively. All the electrochemical experiments were conducted in a 1 M NaCl aqueous solution at the room temperature.

The CV measurement with a potential of -0.5-0.5 V at various scan rates from 5 to 40 mV/s and EIS analysis in a frequency of 10 mHz-10 kHz with the alternating voltage amplitude of 5 mV were both performed on the CHI-660D electrochemical workstation. The specific capacitance donated as the *Cm* (F/g) at a given scan rate was calculated according to the obtained CV curve using the following equation[1]:

$$Cm = Q/2m\Delta V \tag{S1}$$

substance, and ΔV (V) is the chosen potential range. Where Q (C) is the integrated area of CV curve, m (g) is the mass of activated

In addition, the GC test at a current load of 100-500 mA/g with a potential of

-0.5-0.5 V were conducted to evaluate the charge/discharge performance of electrodes by using an automatic LAND battery instrument.
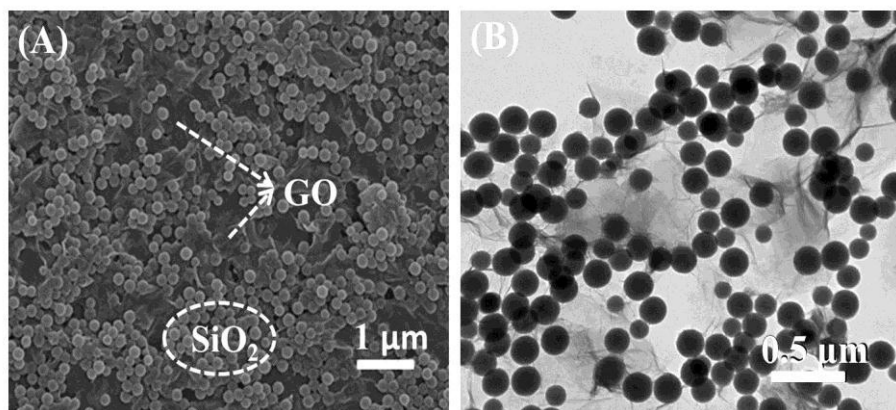
ADDITIONAL DISCUSSIONS

Fig. S1 (A) SEM and (B) TEM images of the GO/SiO$_2$ composite.

The GO/SiO$_2$ composite with a mass concentration ratio of 1:5 (GO:SiO$_2$) was prepared according to a continuous sonication-vacuum filtration-ambient drying step. The texture properties were detected by the SEM and TEM measurements as displayed in Fig. S1A-B. Clearly seen in Fig. S1A, the absence of SiO$_2$ aggregates and individual GO monolithic phase suggests that an efficient combination of the GO and SiO$_2$ spheres can be developed in this way. Moreover, SiO$_2$ spheres are well dispersed on the GO surface without any obvious aggregation, which ensures a highly developed porosity of the resultant GE. In addition, as presented in Fig. S1B, microspheres with a diameter of ca. 170 nm as well as layered structures can be both observed in the composite, further proving the perfect connection between SiO$_2$ spheres and GO. In brief, SiO$_2$ and GO can realize an excellent combination, which

may ensure an efficient coating of polymers onto the monodisperse SiO_2 of the composite and a well-developed macroporous GE framework.
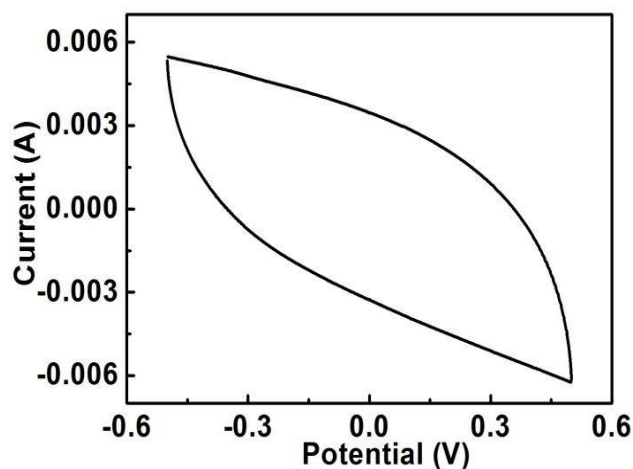

Fig. S2 Typical CV curve of the PC electrode in a 1 M NaCl aqueous solution at a scan rate of 10 mV/s.

For comparison, the PC was also prepared according to a previously reported procedure with some modification[2]. The CV measurement has also been conducted to reveal its electrosorption behavior, and the resultant profile was displayed in Fig. S2. Clearly, the profile exhibits a typically electrical double-layer capacitance characteristic without any humps in the chosen potential range, suggesting that only the electrostatic force between the electrode and salt solution occurs during the adsorption/desorption process[3, 4]. Noteworthy, as compared with the 3DGHPC electrode, the pristine PC one presents an evident decrease in the closed CV area, indicating a reduced specific capacitance[5]. The calculated specific capacitance of PC electrode is 55.44 F/g, which is much lower than that of the 3DGHPC one (80.34 F/g). The poorer electrosorption behavior of the pristine PC electrode is deduced to result from its higher inner resistance as revealed by the EIS measurement in the
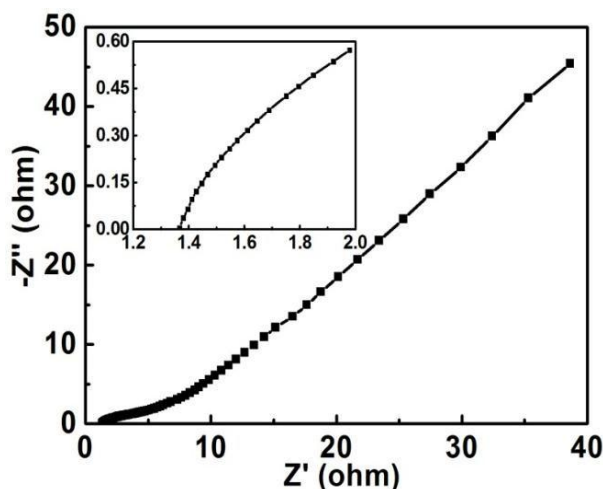
following text.

Fig. S3 Electrochemical impedance spectra presented as Nyquist plot of the PC electrode in a 1 M NaCl aqueous solution. The inset is local enlarged frequency region.

The electric conductivity of pristine PC electrode was revealed by the EIS measurement in a 1 M NaCl aqueous solution, which is an effective method to characterize the conductivity ability of carbon electrode[6]. As displayed in Fig. S3, the resultant profile presents a nearly similar shape to that of the 3HGHPC electrode, including a small quasi-semicircle at the high region of frequency as well as two linear traits at the low one. Firstly, a negligible small quasi-semicircle at the high frequency region reveals that the inner resistance caused by the polarization behavior of electrode can be neglected. Moreover, two linear parts with distinct tilt angles can also be detected, indicating that the pristine PC electrode shows no obvious difference in the Warburg resistance as well as capacitive behavior as compared with the composite electrode. It is worth noting that the pristine PC and 3DGHPC electrodes exhibit the evidently different behaviors in the ESR value, which can be evaluated by

the point of intersection with the real axis at the high region of frequency. Clearly, as depicted in the inset of Fig. S3, the PC electrode presents a much higher ESR than 3DGHPC one, indicating its higher inner resistance. The poorer electric conductivity of the pristine PC electrode can reasonably explain its attenuated specific capacitance regardless of the higher specific surface area. Therefore, it can be concluded that both the higher specific surface area and improved electric conductivity is expected simultaneously for a higher performance electrosorption process.

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