

Electronic Supplementary Information for:

**Synthesis of hierarchically porous carbon spheres by an emulsification-
crosslinking method and its application in supercapacitor**

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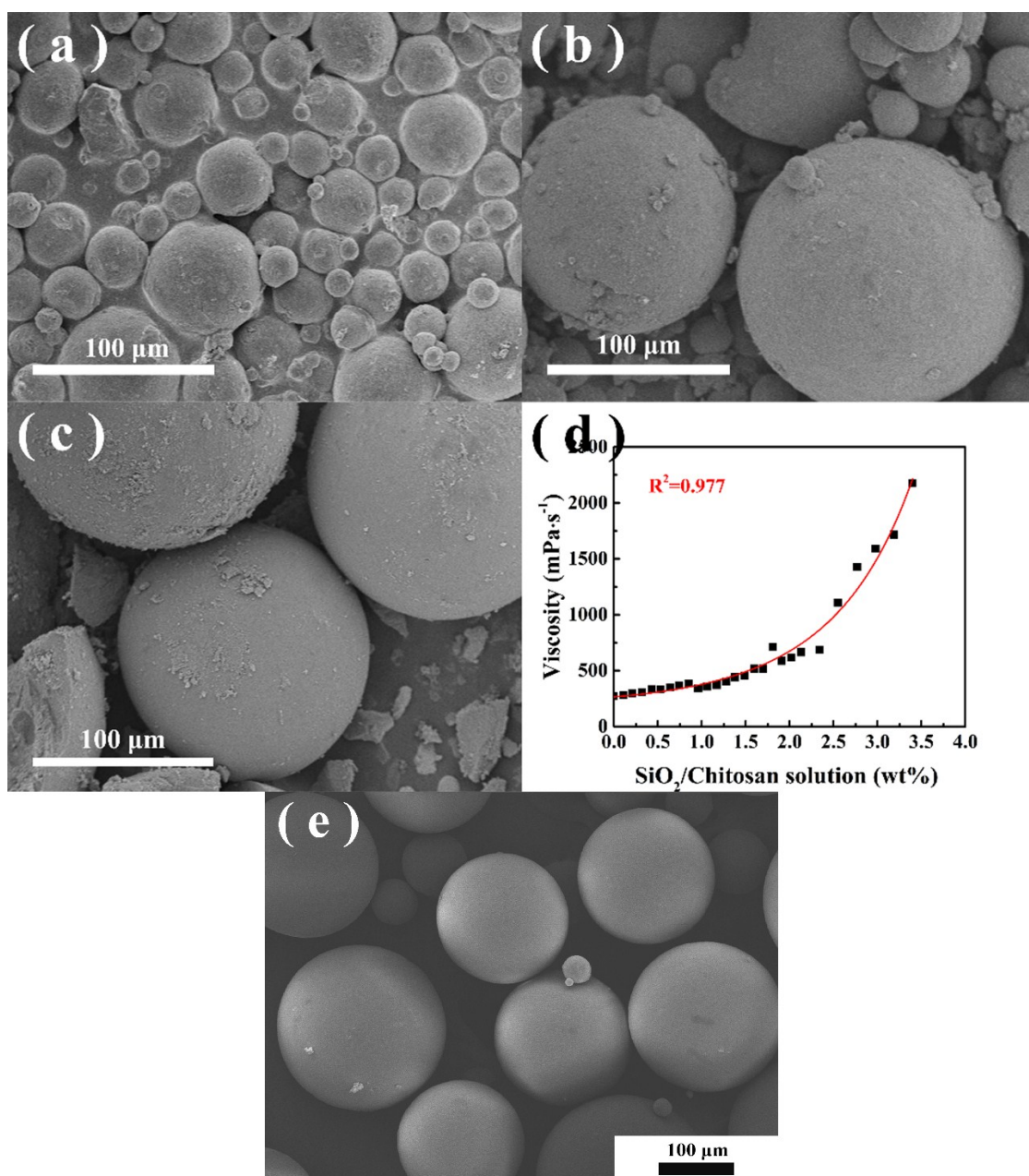


Fig. S1 SEM images of CSi spheres morphology prepared in different conditions: (a) 0.2 g, 600 rpm; (b) 0.2 g, 700 rpm; (c) 0.5 g, 600 rpm; (d) relationship between the viscosity and weight ratio of SiO₂ to chitosan aqueous solution, (e) SEM image of the CCSs.

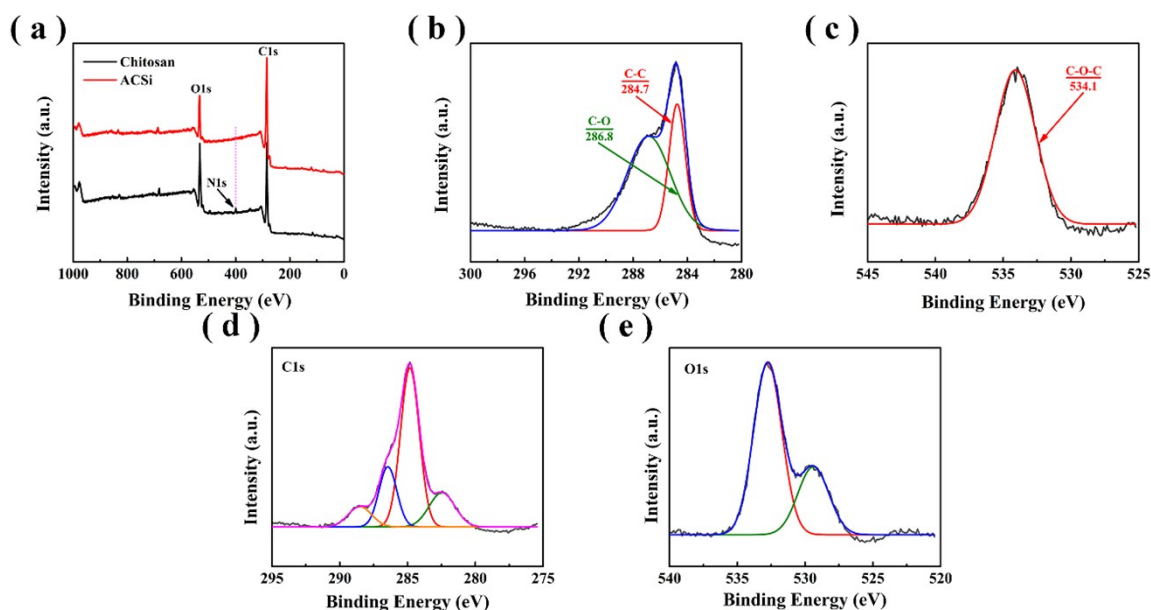


Fig. S2 (a) XPS survey spectrums of the chitosan and ACSi sample, (b) C 1s spectrum and (c) O 1s spectrum of the ACSi sample, (d) C 1s spectrum and (e) O 1s spectrum of the chitosan sample.

Table S1 Element contents of the chitosan powder and ACSi sample.

Sample	Element content (atomic %)			
	C1s	O1s	N1s	Others
Chitosan	69.9	25.4	2.0	2.7
ACSi	84.9	12.9	0.1	2.1

The XPS survey spectrums of the ACSi sample with binding energies of 0-1000 eV are presented in Fig. S2a. The peak assignable to N 1s in ACSi disappears, accompanying with weakening of the O 1s peak intensity and the increase of C 1s peak intensity. As shown in Fig.S2b of the C 1s spectrum of ACSi, the peak at 288.5eV attributed to O-C-O carbon^{1, 2} existed in chitosan (Fig. S2d) is gone, while the intensity of the peak identified as C-O carbon increases due to the aldolization reaction. Compared with the peaks of O

1s spectrum of chitosan (Fig. S2e), the peak attributed to C-OH at 529.4 eV^{1, 2} disappears in the ACSi sample (Fig. S2c) owing to the acetal reaction between aldehyde and hydroxyl, and the peak at 532.4eV identified as the C-O-C oxygen shifts to 534.1eV. Table. S1 shows the change of the elemental contents of chitosan and ACSi characterized by the elemental analysis of XPS. As expected, the content of nitrogen has diminished after crosslinking and carbonizing. Furthermore, the elemental mappings of C, O and N reveal the change of the content and distribution of these elements (Fig. S3b, Fig. S3c and Fig. S3d). Compared with the distribution of C, the distribution of O and N are sparse, especially N, proving the change of these elements during the crosslinking and carbonization in another aspect.

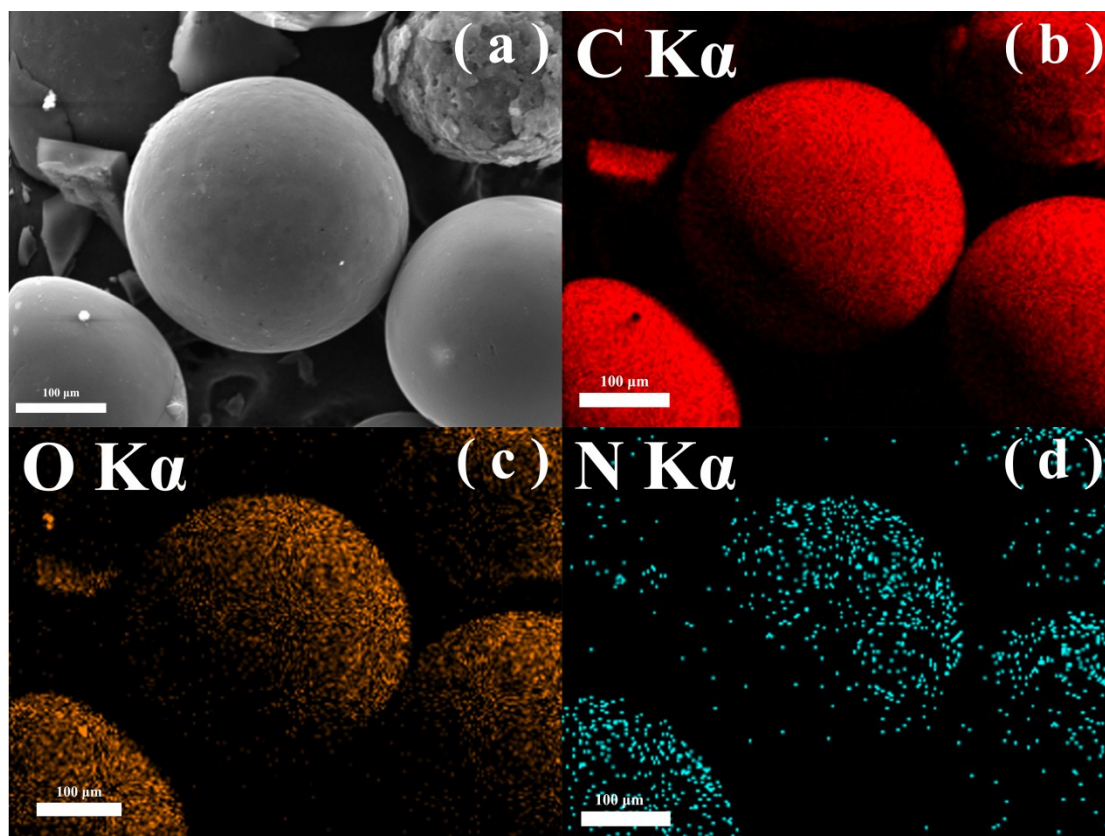


Fig. S3 (a) SEM image of ACSi-800-2 spheres; (b), (c), (d) elemental mapping

images of C, O and N. Scale bar is 100μm.

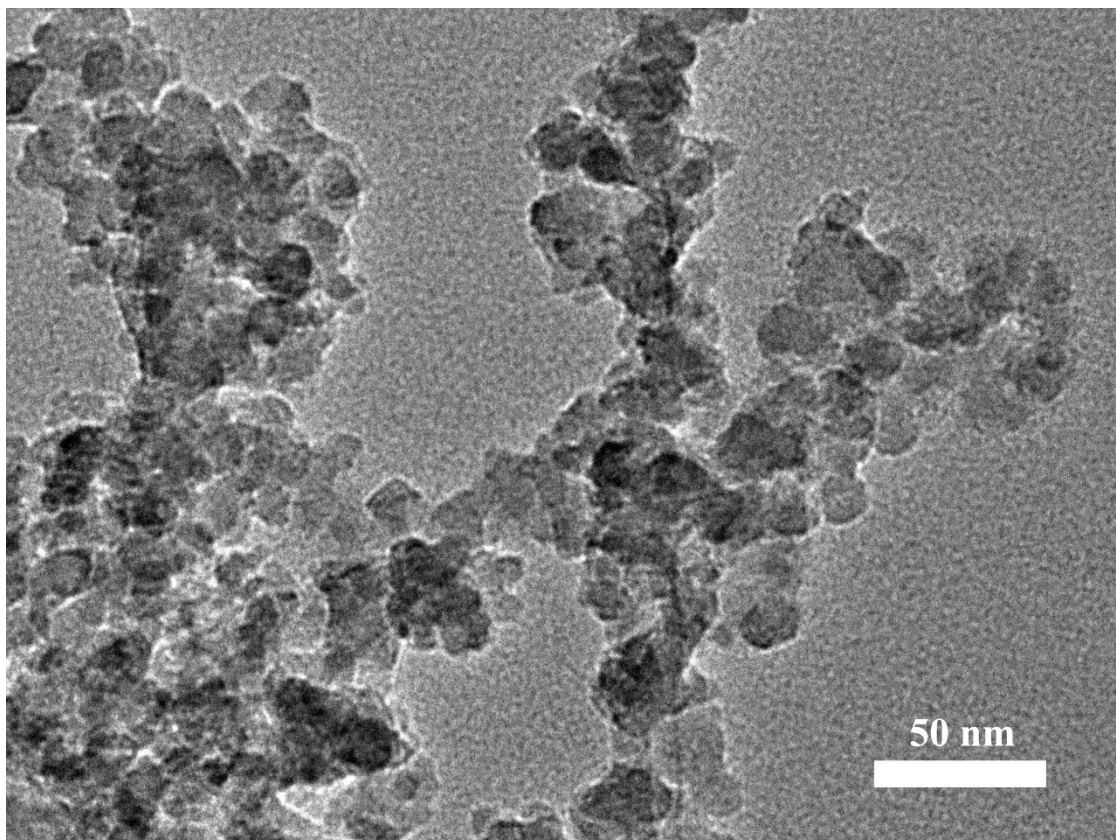


Fig. S4 TEM image of aerol-SiO₂.

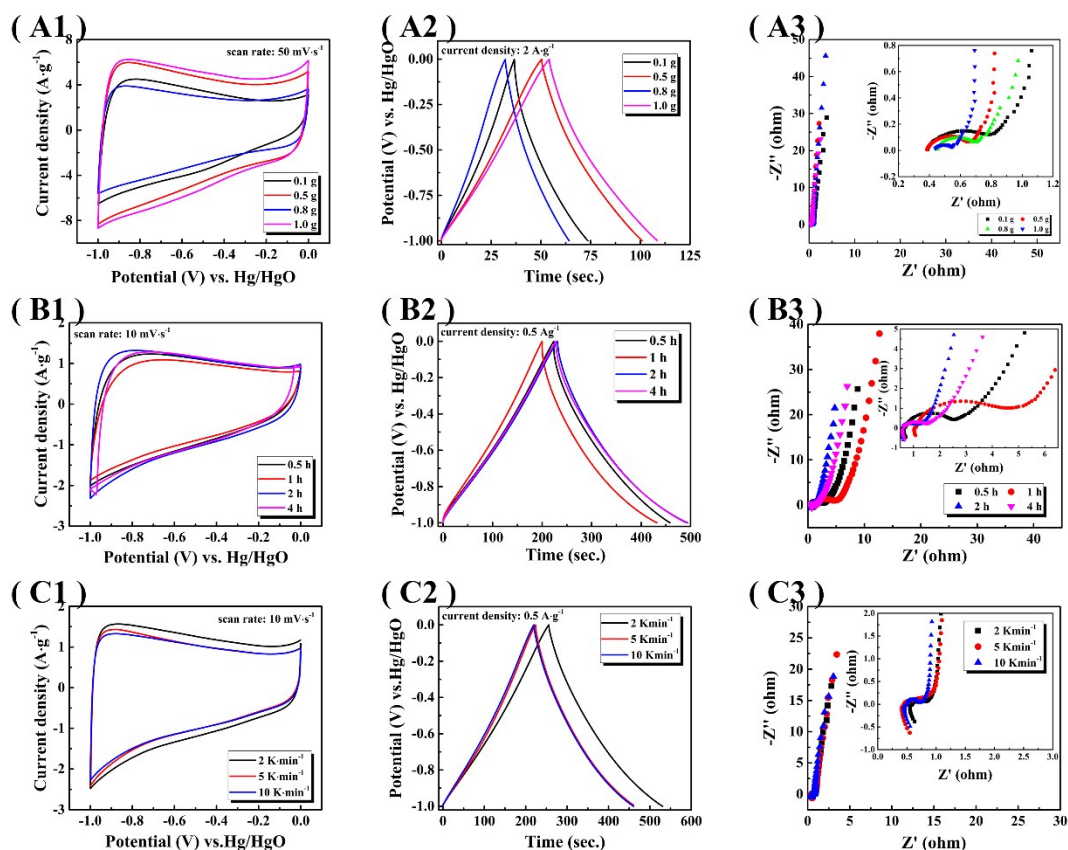


Fig. S5 Electrochemical performance of the CSi samples prepared under different conditions: CV curves, GCD curves and EIS of the CSi samples prepared at different SiO₂ dosage (A1, A2, A3); CV curves, GCD curves and EIS of the CSi samples prepared at different carbonization time (B1, B2, B3); CV curves, GCD curves and EIS of the CSi samples prepared at different heating rate (C1, C2, C3).

Electrochemical performance of the CSi samples prepared under different conditions are shown in Fig.S5. In Fig.S5A, when the dosage of SiO₂ was up to 1.0g, the prepared-CSi showed the maximal specific capacitance (Fig.S5 A1, A2 and A3). But, considering the viscosity change with the increase of the SiO₂ dosage, the best added amount of SiO₂ is 0.5g. For the carbonization time, the CSi prepared under

carbonization time of 2h showed the highest specific capacitance (Fig.S5 B1, B2 and B3). For the heating rate, the CSi prepared at 2 °C·min⁻¹ showed the highest specific capacitance (Fig.S5 B1, B2 and B3), implying slower heating rate is advantage for the improvement of the specific capacitance.

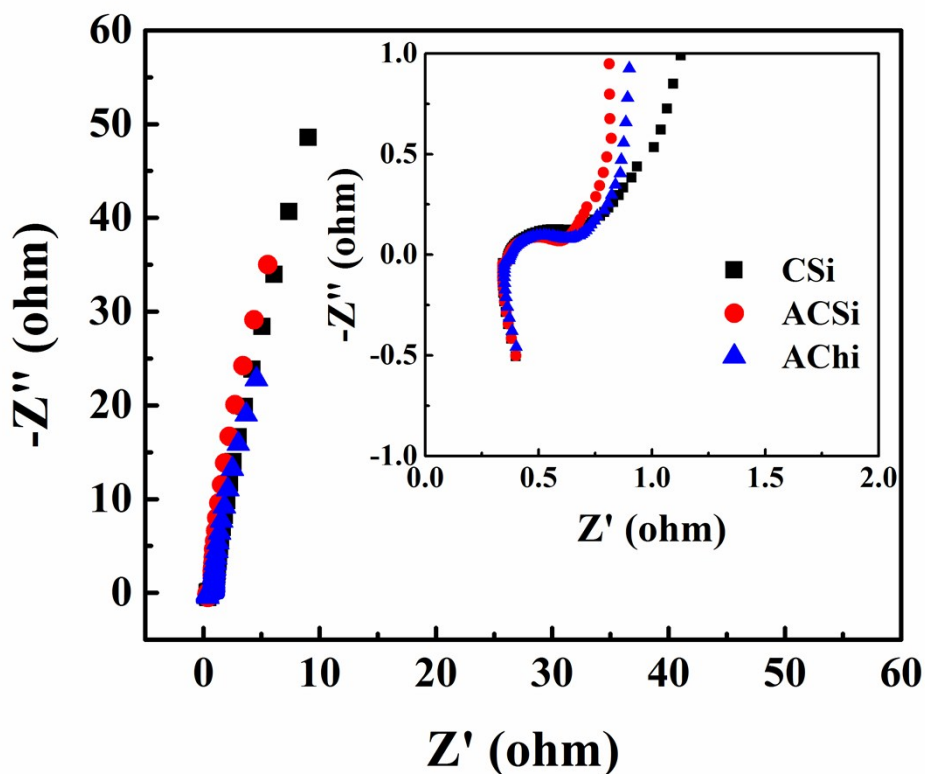


Fig. S6 Nyquist plots of the CSi, ACSi and AChi carbon samples (the inset shows the plots at high frequency region).

EIS, a powerful technique to investigate the capacitive behavior of electrode, was tested in a frequency range of 0.01 to 100 kHz. From the Nyquist plots of ACSi, CSi and AChi shown in Fig. S6, the plots of the three samples are composed with two parts, including a straight line in low frequency region and a semicircle line in high frequency region. The nearly vertical lines exhibited at low frequencies, which stand for the control of EDLC, showing an ideal capacitor behavior³. The semicircles existed in high frequency region are related to the accessible electrode porosity to the electrolyte, indicating the electrolyte solution resistance (the intercept of the

semicircle with the real axis, R_s) and the charge-transfer resistance (the diameter of the semicircle loop in the high frequency range, R_t)^{4,7}. The ACSi has smaller semicircle diameter than the other samples (the inset in Fig.S6), indicating smaller R_t ^{4,7}. But these samples showed the approximately equal intercept of the semicircle with the real axis. Compared with the values of R_t and R_s of the CSi and ACSi, the ACSi possessed smaller resistance than CSi after activation, indicating that the conductivity of ACSi is higher than the CSi, and the activation is beneficial for enhancement of conductivity.

References

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