

**Electronic Supplementary Information for**  
**The Synergistic Effect Achieved by Combining Different Nitrogen-doped Carbon Shells**  
**for High performance Capacitance**

Jiangtao Hu, Jie Yang, Yandong Duan, Chaokun Liu, Hanting Tang, Lingpiao Lin, Yuan Lin,  
Haibiao Chen, Feng Pan\*

School of Advanced Materials, Peking University, Peking University Shenzhen Graduate  
School, Shenzhen 518055, China

\* Corresponding author: [panfeng@pkusz.edu.cn](mailto:panfeng@pkusz.edu.cn)

**Materials and methods**

**Preparation of nano-hollow  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@Graphene:** Prussian Blue (PB), glucose and vitriol (H<sub>2</sub>SO<sub>4</sub>, 85%) were purchased from Sinopharm Chemical Reagent Co., Ltd. The synthesis process can be referred to our previous work.<sup>1</sup>

**Preparation of CS-650, CS-850, CS-1050, CS-650+850 and CS-650+1050:** The nano-hollow  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@Graphene was leached in excess concentrated H<sub>2</sub>SO<sub>4</sub> solution at 80 °C for 12h, and the product was designated as CS-650. CS-650 was calcined at 850 or 1050 °C for 6 h at a heating rate of 2 °C min<sup>-1</sup> under Ar atmosphere, followed by centrifuge, rinsed with deionized water and dried at 80 °C, and the final products were designated as CS-850 and CS-1050, respectively. We blended CS-650 and CS-850, CS-1050 or carbon black with the proportion of 1:1, and labeled the mixture as CS-650+850, CS-650+1050 or CS-650+Carbon black.

**Structure and Morphology Characterization**

The crystal structures of the final examples (CS-650, CS-850, CS-1050) were characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer using Cu K $\alpha$ ,  $\lambda$ =1.5405 Å). The

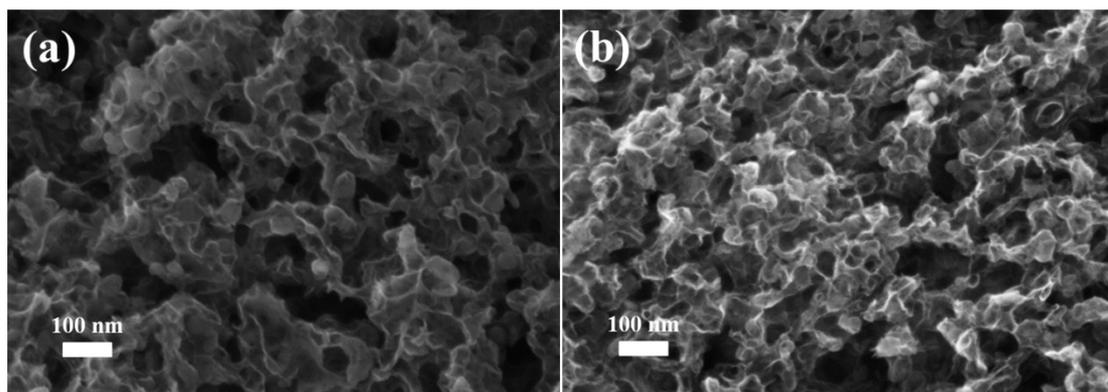
morphology was observed by scanning electron microscopy (SEM, ZEISS Supra 55) and transmission electron microscopy (JEM-3200FS). The Raman spectra of the three materials were recorded by iHR 320 Raman spectroscopy (Horiba). The surface area was measured by nitrogen adsorption/desorption using the Brunauer-Emmett-Teller method (BET, Micromeritics ASAP 2020 HD88) and the pore size distribution was derived using the Barrett-Joyner-Halenda (BJH) model. The X-ray photoelectron spectra (XPS) analysis was performed on ESCALAB 250XL.

### **Electrochemical measurements**

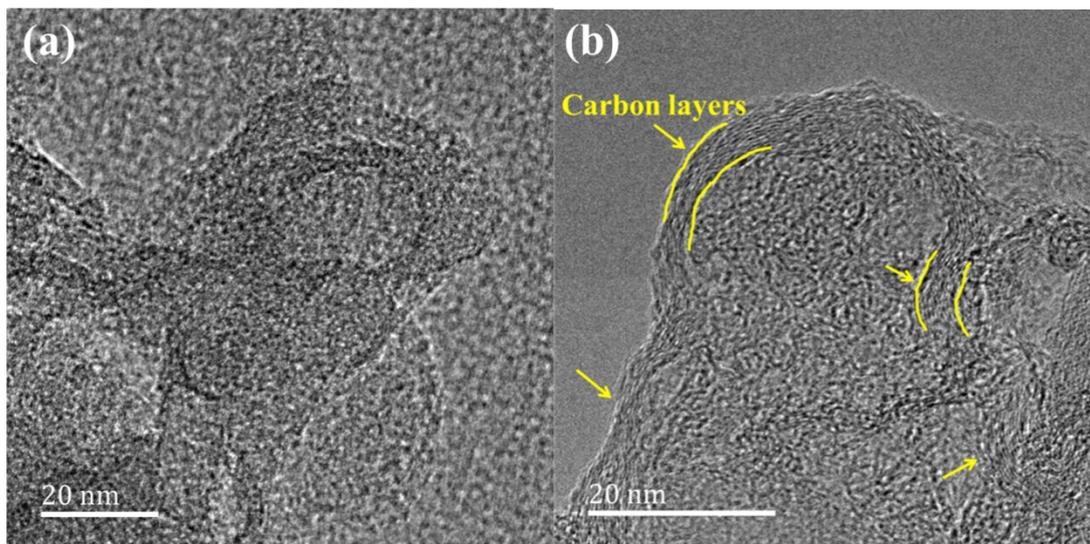
The final carbon materials were mixed with carbon black and polytetrafluoroethylene (PTFE) with a weight ratio of 80:10:10. The mixture was rolled into a thin film which was punched into small disks. The average masses of CS-650, CS-850, CS-1050, CS-650+850, CS-650+1050 and CS-650+Carbon black are about 1.13, 1.30, 0.9, 1.06, 1.03 and 1.12 mg, respectively. After dried at 110 °C for 8 hours, the small disks were rolling onto a titanium mesh to fabricate the working electrode. The electrochemical performance was tested in a three-electrode system in 6 M KOH electrolyte with Pt and Hg/HgO as counter electrode and reference electrode, respectively. The cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge curves were collected by electrochemical testing station (CHI604E, Maccor) with a potential window from 0 V to 1 V.

Combining our previous work, we can control the content of nitrogen dopant in our final carbon materials, which is our main reason for choosing carbon shells. Moreover, the contact form between different carbon shells (or carbon shell and carbon black) is surface contact other

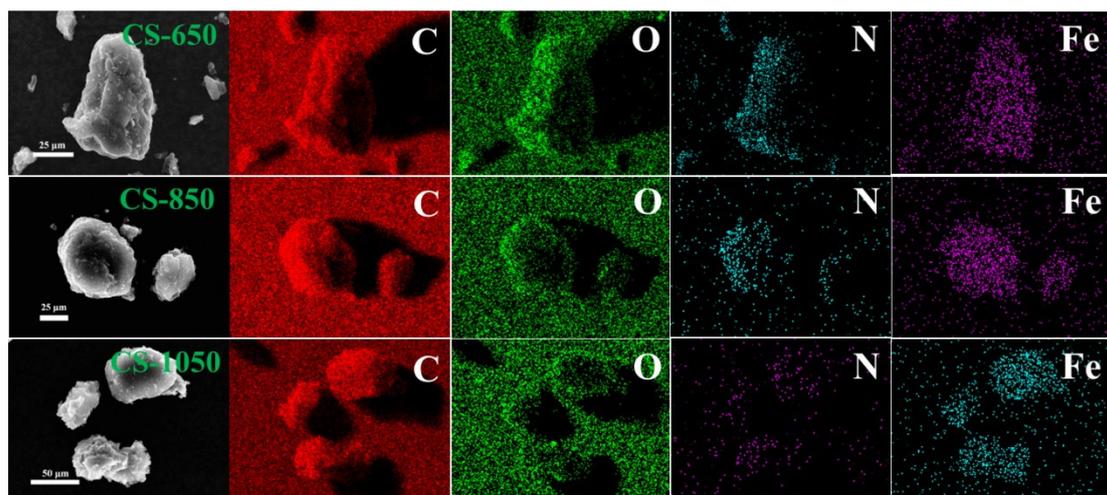
than point contact like carbon spheres or nanotubes, which helps to improve the conductivity of the electrode and improve the electrochemical performance. We believed that the materials were mixed homogeneously. In order to illustrate the reproducibility of this physical blending method, we summarized CV data with different electrodes of CS-650+850 and CS-650+1050 as shown in **Figure S15**. Obviously, the difference between different batches of CS-650+850 or CS-650+1050 is very small as shown in **Figure S15a** and **S15b**. According to the CV data, we can get the specific capacitances of different electrodes: 158.8 F g<sup>-1</sup> and 151.9 F g<sup>-1</sup> for the two batches of CS-650+850, 110.6 F g<sup>-1</sup> and 105.8 F g<sup>-1</sup> for the two batches of CS-650+1050. The CV and the specific capacitance results of different batches can be reproduced within an acceptable error.



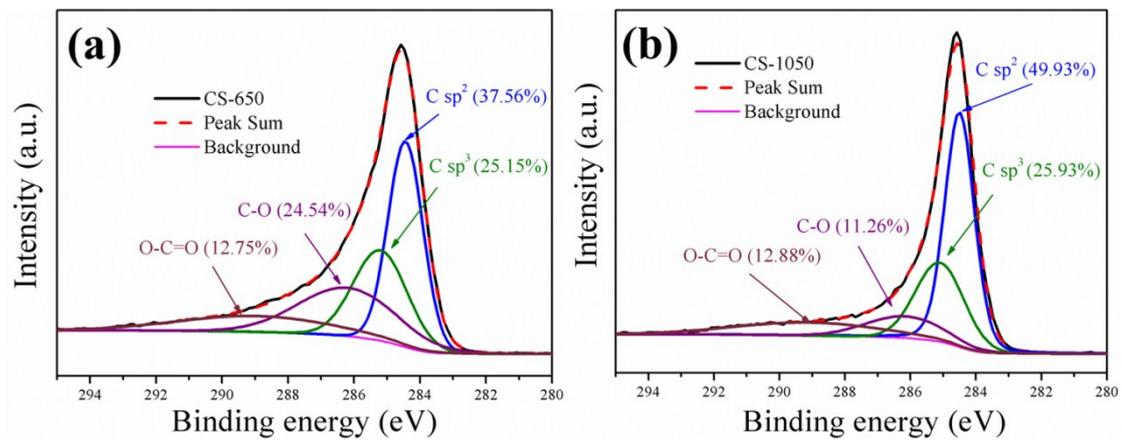
**Figure S1.** SEM images of (a) CS-650 and (b) CS-1050.



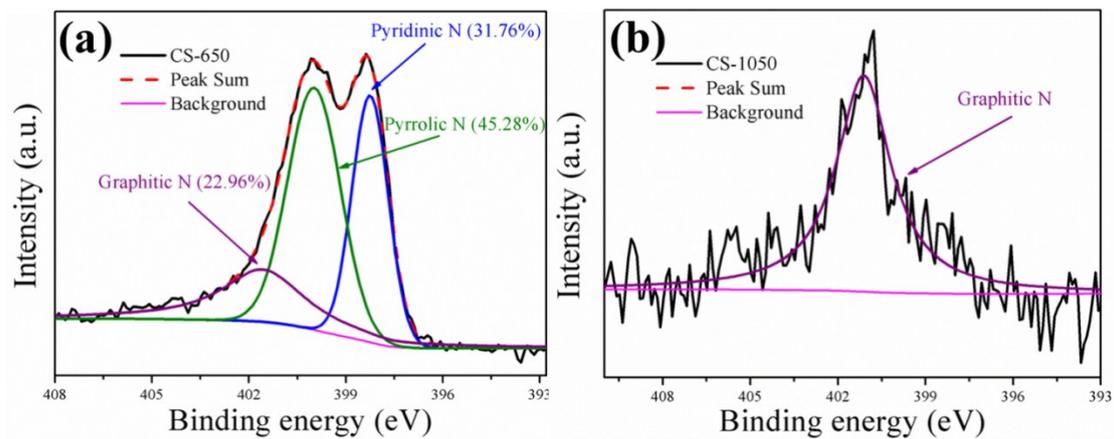
**Figure S2.** TEM images of (a) CS-650 and (b) CS-1050.



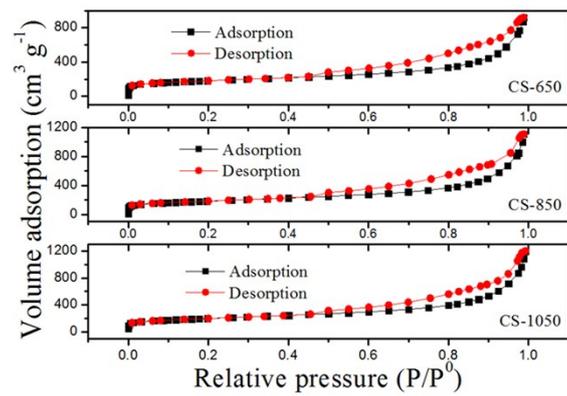
**Figure S3.** EDS images of CS-650, CS-850 and CS-1050.



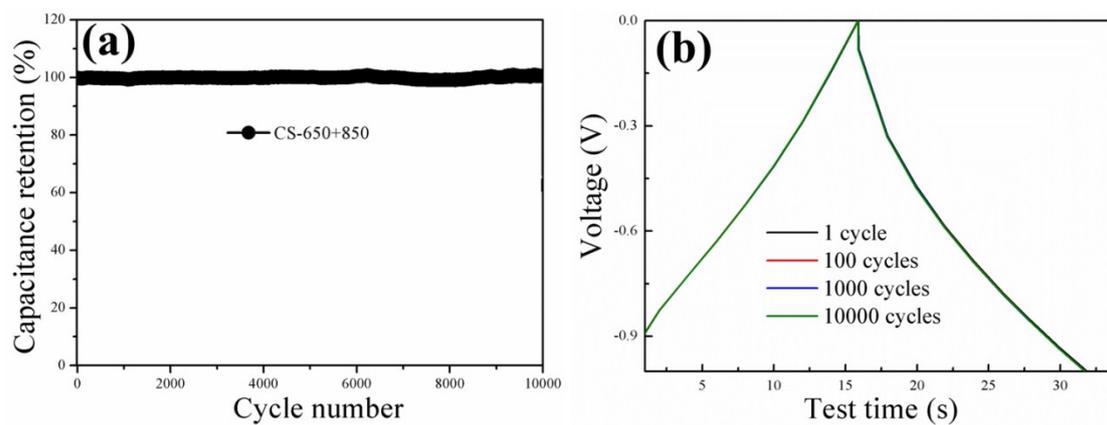
**Figure S4.** The C1s XPS spectra of CS-650 and CS-1050.



**Figure S5.** The N1s XPS spectra of CS-650 and CS-1050.



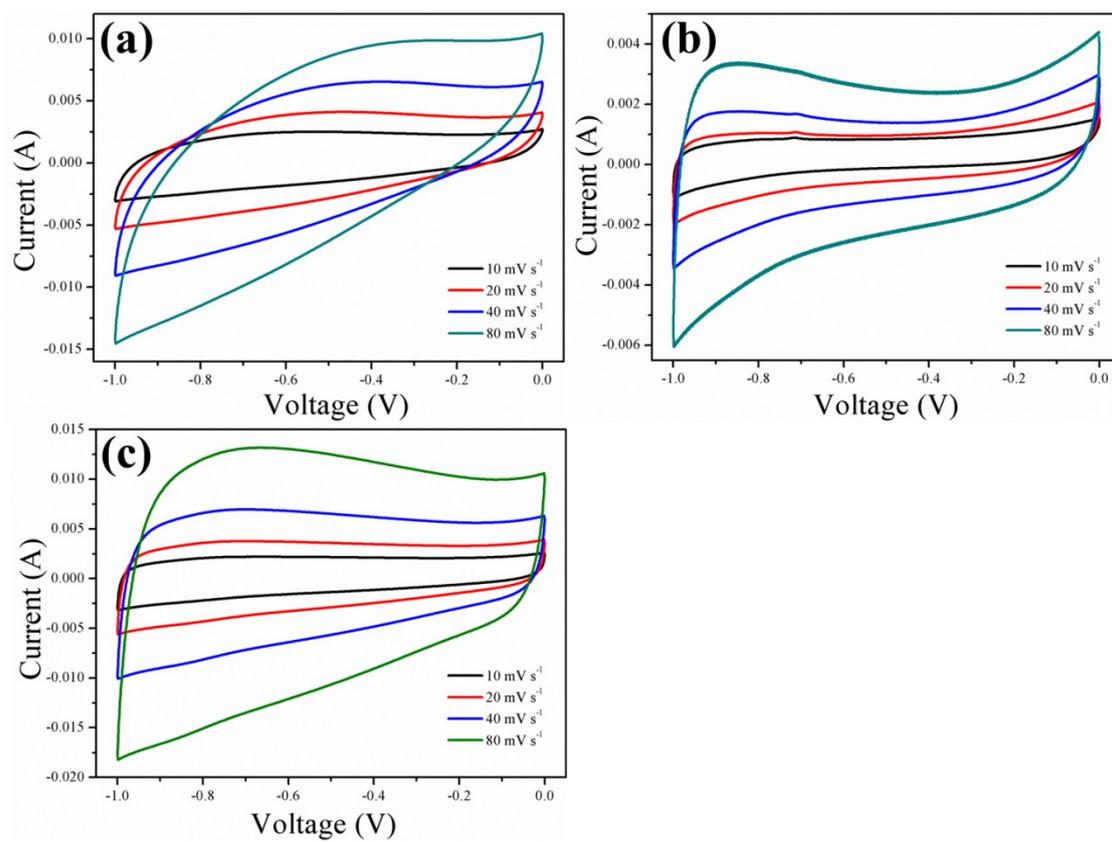
**Figure S6.** N<sub>2</sub> sorption isotherms of CS-650, CS-850 and CS-1050.



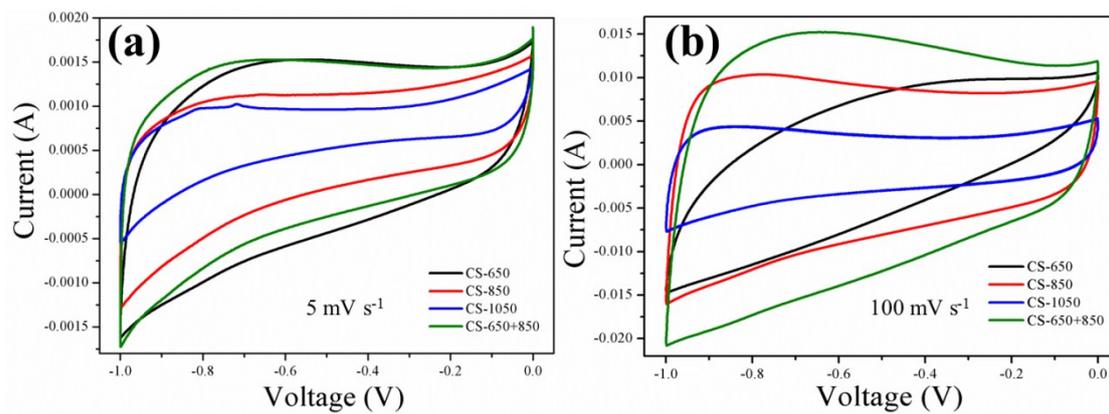
**Figure S7.** (a) Cycle stability of CS-650+850 at 10 A g<sup>-1</sup> for 10000 cycles, (b) the charge-discharge curves at different cycle times.

**Table S1.** The comparison of supercapacitor performance between our carbon composite and other recently reported carbon materials.

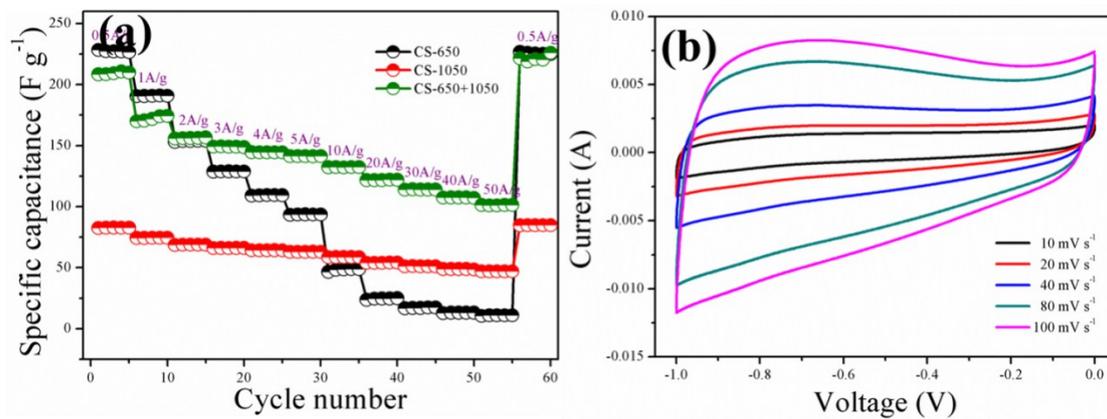
Material	BET (m <sup>2</sup> /g)	Low current density	High current density	Reference
B/N-CSs	/	0.1 A g <sup>-1</sup> / 223 F g <sup>-1</sup>	100 A g <sup>-1</sup> / 140 Fg <sup>-1</sup>	Adv. Funct. Mater.,2016, 26, 111-119.
LRF-700-A	1866	0.25 A g <sup>-1</sup> / 186 F g <sup>-1</sup>	20 A g <sup>-1</sup> / 140 Fg <sup>-1</sup>	J. Power Sources, 2016, 321, 143-154.
NBKBC	171.5	0.2 A g <sup>-1</sup> / 281 F g <sup>-1</sup>	4A g <sup>-1</sup> / 125 Fg <sup>-1</sup>	Electrochim. Acta, 2015, 180, 241-251.
NCC-1h	1085	1.0 A g <sup>-1</sup> / 207 F g <sup>-1</sup>	14A g <sup>-1</sup> / 177 Fg <sup>-1</sup>	Carbon, 2016, 105, 260-267.
OMC/G-K	2109	0.2 A g <sup>-1</sup> / 391g <sup>-1</sup>	10A g <sup>-1</sup> / 194.4g <sup>-1</sup>	Nanoscale, 2016, 8, 15671-15680.
GN/MCS	927	0.2 A g <sup>-1</sup> / 211 F g <sup>-1</sup>	20A g <sup>-1</sup> / 129 Fg <sup>-1</sup>	Mater. Lett.,2016, 178, 304–307.
CS-650+850	/	0.2 A g <sup>-1</sup> / 325.9 F g <sup>-1</sup>	10A g <sup>-1</sup> / 156.9 Fg <sup>-1</sup> 50A g <sup>-1</sup> / 108 Fg <sup>-1</sup>	This work



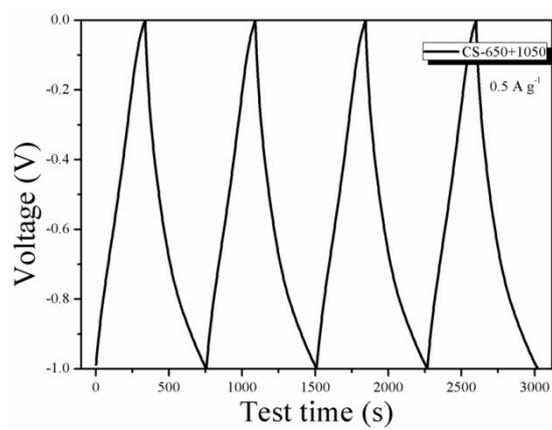
**Figure S8.** CV curves of (a) CS-650, (b) CS-1050 and (c) CS-650+850 at 10, 20 40 and 80 mV s<sup>-1</sup>.



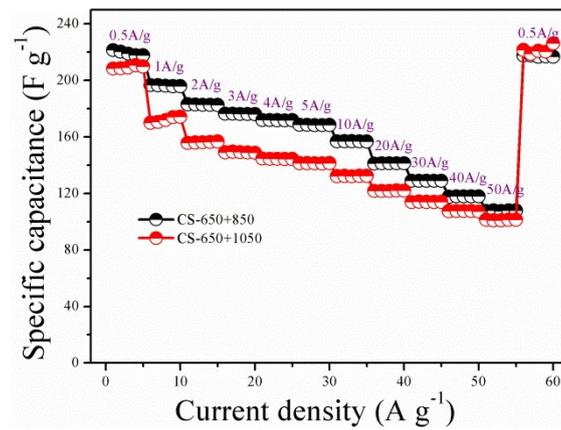
**Figure S9.** CV curves of CS-650, CS-850, CS-1050 and CS-650+850 at (a) 5 mV s<sup>-1</sup> and (b) 100 mV s<sup>-1</sup> (the whole CV data have been normalization).



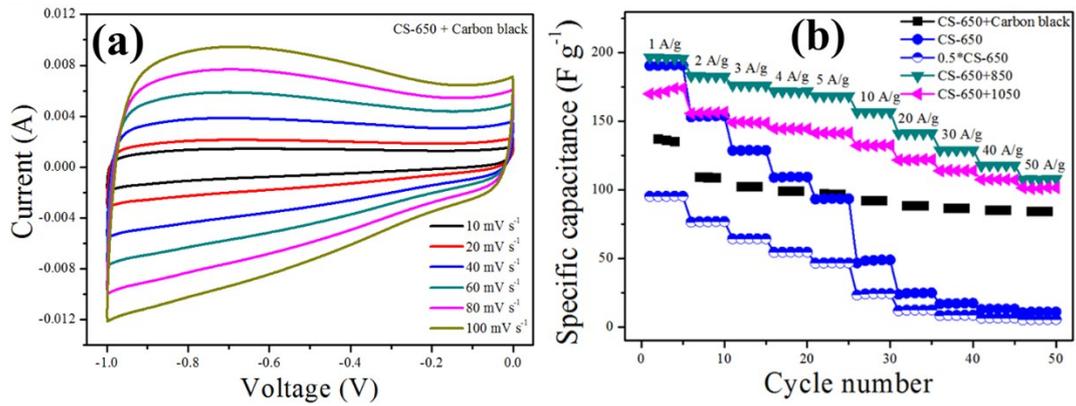
**Figure S10.** (a) Rate performances of CS-650, CS-1050 and CS-650+1050, (b) CV curves of CS-650+1050.



**Figure S11.** Galvanostatic charge/discharge curves of CS-650+1050 at the current density of 0.5 A g<sup>-1</sup>.

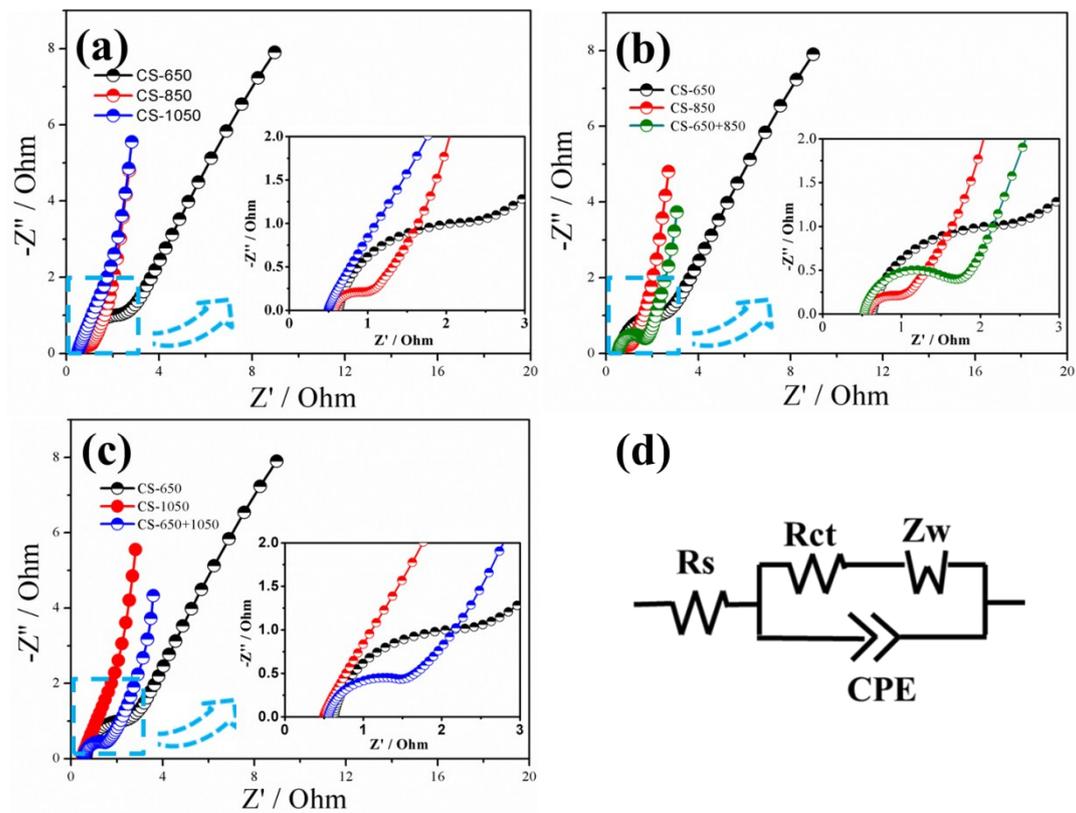


**Figure S12.** Rate performance of CS-650+850 and CS-650+1050.

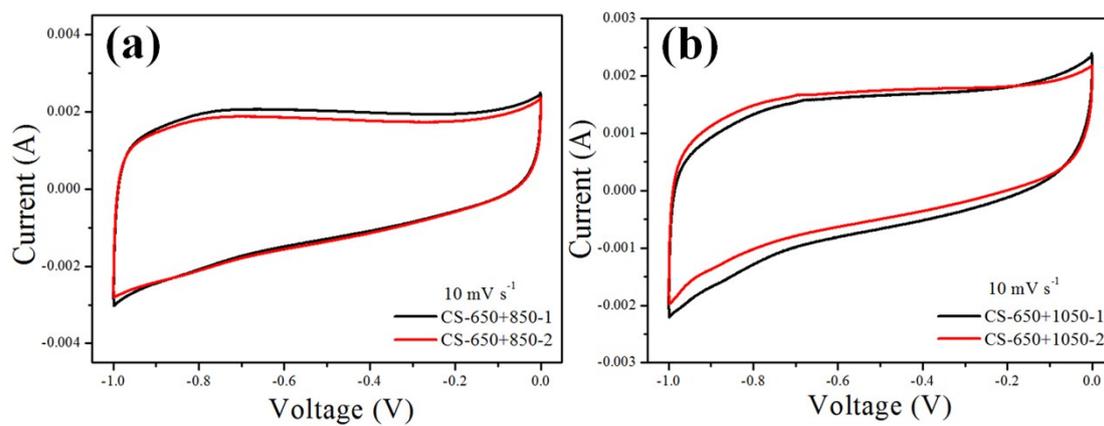


**Figure S13.** (a) CV curves of CS-650+Carbon black at different scan speed, (b) the rate performance of CS-650+Carbon black, CS-650, 0.5\*CS-650, CS-650+850 and CS-650+1050 at different current density, the meaning of 0.5\*CS-650 is half of the rate performance of CS-650.

Please note that in **Figure S13b**, the performance of CS-650+Carbon black is superior to 0.5\*CS-650, while inferior to that of CS-650. The comparison is based on identical weight of “active material”. When carbon black is included in the weight of active material, the specific capacitance is lower compared to CS-650 since carbon black contributes little capacitance. When carbon black is excluded from the weight of active material, the specific capacitance is higher compared to 0.5\*CS-650 since carbon black serves as a highly conductive network.



**Figure S14.** (a, b and c) Nyquist plots of CS-650, CS-850, CS-1050, CS-650+850 and CS-650+1050 with the frequency range from 1 Hz to 100 kHz, (d) the equivalent circuit of the EIS data.



**Figure S15.** CV curves of (a) CS-650+850 and (b) CS-650+1050 with different electrodes at 10 mV s<sup>-1</sup>. (The CV data have been normalized, CS-650+850/1050-1/2 represent different electrodes measured at different times)

- 1 J. Hu, J. Zheng, L. Tian, Y. Duan, L. Lin, S. Cui, H. Peng, T. Liu, H. Guo, X. Wang and F. Pan, *Chem Commun*, 2015, **51**, 7855.