Supporting Information

Hierarchical mesoporous yolk-shell structured carbonaceous nanospheres for high performance electrochemical capacitive energy storage

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Section S1. Chemicals and reagents

Chemicals: Hexadecyltrimethylammonium bromide (CTAB, 99%), Pluronic F127, tetraethylorthosilicate (TEOS, 99%), resorcinol (99%), 3-aminophenol (98%), ammonium hydroxide solution (25%) and formaldehyde aqueous solution (37%) were purchased from Sigma-Aldrich company. Fluorocarbon surfactant, FC4, was bought from Yick Vic Chemicals (Hong Kong). Water was purified by a Milli Q system and had an electrical resistance of 18 MΩ•cm.

Section S2. Characterization

Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100F microscope (JEOL, Japan) operated at 200 kV. The samples for TEM measurement were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Scanning electron microscopy (SEM) was taken with a JEOL-7800F field emission electron microscopy. The N_2-sorption experiments were performed at 77 K on a Micromeritics Tristar 3000 system with micropore analysis. Prior to the measurement, the samples were out-gassed at 120 °C for at least 6 h. The Brunauer–Emmett–Teller (BET) specific surface areas were calculated using adsorption data at a relative pressure range of $P/P_0 = 0.05$–0.25. The total pore volumes were estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of 0.99. XPS Data was acquired using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer, their atomic concentrations were calculated using the CasaXPS version 2.3.14 software and a Shirley baseline with Kratos library Relative Sensitivity Factors (RSFs). Peak fitting of the high-resolution data was also carried out using the CasaXPS software.

Section S3. Synthesis of Hierarchical Mesoporous Carbon Spheres

Synthesis of YSCN: As-synthesised mesoporous RF resin spheres were prepared via the method reported previously with slightly modification.[1] In a typical synthesis of YSCN, 100 mg as-synthesised mesoporous RF resin spheres were dispersed in 40 mL CTAB aqueous alcoholic solution (5.14 mmol/L, Vwater/Vethanol, 5:3), 200 μL ammonium hydroxide solution was then added and kept stirring for 30 minutes, then different amount of silica precursor tetraethyl orthosilicate (TEOS) was poured into the above solution and kept stirring for another 6 h. After stopping reaction by centrifuge and washing with ethanol and water for several times, the sample of RF@SiO$_2$ is obtained by drying in 100 °C oven. To obtain YSCN@meso-SiO$_2$, the RF@SiO$_2$ is pyrolysed under nitrogen flow in the tube furnace using a heating rate of 1°C/min up to 350 °C, dwelling for 2 h, and resuming heating rate at 1 °C/min up to 700 °C and then dwelling for 4 h. Finally, the YSCN were obtained after HF etching process in 20 mL 10% HF solution. Then the final product YSCNs were washed by water to remove HF acid completely and dried at 100 °C in oven overnight. The resulting powder products were denoted as YSCN-*a-b*, where *a* is a representative of adding amount of TEOS (80, 150, and 200 μL), *b* is indicating the carbonisation temperature (700 and 900 °C).

Synthesis of LP-YSCN: As-synthesised mesoporous RF resin spheres were prepared via the method reported before. 100 mg as-synthesised mesoporous RF resin spheres were dispersed in 10 mL iron acetate solution (0.1M) overnight. Fe^{2+} ions were removed by centrifuge and washed with water and ethanol for several times. Then the RF resin spheres were dispersed in 40 mL CTAB aqueous alcoholic solution (5.14 mmol/L, Vwater/Vethanol, 5:3), after adding

200 µL ammonium hydroxide solution and keep stirring for 30 minutes, different amount of silica precursor TEOS was added and kept stirring for 6 h. After stopping reaction by centrifuge and washing with ethanol and water several times, the sample of RF@SiO$_2$ is obtained by drying in 100 °C oven. To obtain LP-YSCN@meso-SiO$_2$, the RF@SiO$_2$ is pyrolysed under nitrogen flow in the tube furnace using a heating rate of 1°C/min up to 350 °C, dwelling for 2 h, and resuming heating rate at 1 °C/min up to 900 °C and then dwelling for 4 h. Finally, the YSCN were obtained after HF etching process in 20 mL 10% HF solution. Then the final product YSCNs were washed by water to remove HF acid completely and dried at 100 °C in oven overnight, and the product is denoted as LP-YSCS-*a-b*, where *a* is a representative of adding amount of TEOS (200 µL), *b* is indicating the carbonisation temperature (900 °C).

Synthesis of CSCNs: As-synthesised mesoporous RF resin spheres were prepared via the method reported before.[1] The APF coating process is conducted based on our previous study.[1] Firstly, 0.13 g CTAB, 0.1 g F127 and 0.2 g cysteine was dissolved in 28 mL aqueous alcoholic solution (Vwater/ Vethanol. 5:2). Secondly, 100 mg as-synthesised mesoporous RF resin spheres were dispersed in above solution. Different amount of 3-aminophenol and formaldehyde solution were added in every 30 minutes. After reaction for 24 h, the above solution were transferred to autoclave and heated in 100 °C oven for another 24 h. The sample of RF@APF is obtained after washing in ethanol and water several times then dried in 100 °C oven. The CSCN products were obtained after pyrolysing RF@APF resin spheres in the tube furnace using a heating rate of 1°C/min up to 350 °C, dwelling for 2 h, and resuming heating rate at 1 °C/min up to 700 °C and then dwelling for 4 h.

Synthesis of N-YSCNs: The as-synthesised RF@APF was prepared by above procedure. To obtain RF@APF@SiO$_2$ nanoparticles, 100 mg as-synthesised core-shell RF@APF resin spheres were dispersed in 40 mL CTAB aqueous alcoholic solution (5.14 mmol/L, Vwater/Vethanol, 5:3), after addition of 200 µL ammonium hydroxide solution and keep stirring for 30 minutes, different amount of silica precursor TEOS was added and kept stirring for 6 h. After stopping reaction by centrifuge and washing with ethanol and water several times, the sample of RF@APF@SiO$_2$ is obtained by drying in 100 °C oven. To obtain N-YSCN@meso-SiO$_2$, the RF@APF@SiO$_2$ is pyrolysed under nitrogen flow in the tube furnace using a heating rate of 1°C/min up to 350 °C, dwelling for 2 h, and resuming heating rate at 1 °C/min up to 700 °C and then dwelling for 4 h. Finally, the N-YSCNs were obtained after HF etching process in 20 mL 10% HF solution. Then final product N-YSCNs were washed by water to remove HF acid completely and dried at 100 °C in oven over night, and the product is denoted as N-*m*-YSCS-*a-b*, where *a* is a representative of adding amount of TEOS (200 µL), *b* is indicating the carbonisation temperature (700 and 900 °C), and *m* (20, 50, and 200 mg) is the addition amount of aminophenol.

Section S4. Electrochemical measurement

In a typical electrochemical measurement, 2 mg carbon powder was dispersed in 1 ml 0.2 % Nafion aqueous solution by ultrasonication. 10 µL of the dispersion was dipped onto a the glassy carbon electrode (5 mm in diameter) and dried under ambient condition. About 0.1 mg cm-2 catalyst was loaded on the electrode. The electrode was then used as the working electrode in a 3-electrode electrochemistry system. In the system, a Ag/AgCl electrode (in 4 M KCl) and a Pt wire were used as the reference electrode and the counter electrode respectively. Nitrogen saturated 1 M KOH aqueous solution was used as the electrolyte. Cyclic voltammetry (CV) was applied to the working electrode between 0.3 V and -1.1 V at

scanning rate between 10 mV s^{-1} and 500 mV s^{-1}. The charging/discharging is measured from -1.1 V to 0.2 V and then back to -1.1 V. The current densities range from 1 A g^{-1} to 100 A g^{-1}.

Reference:

1. J. Liu, T. Yang, D.-W. Wang, G. Q. Lu, D. Zhao and S. Z. Qiao, *Nature Commun*, 2013, **4,** 2798

Table S1 Physical and chemical properties of hierarchical YSCNs and N-YSCNs

Sample	Particle size (nm)	Yolk diamerter (nm)	Shell thickness (nm)	BET surface area (m²/g)	Pore volume (cm³/g)	C 1s	O 1s	N 1s
YSCN-80-700	187	93	27	1236	1.1	94.2	5.8	
YSCN-100-700	184	67	25	1010	0.91	94.6	5.4	
YSCN-150-700	188	64	23	810	0.7	94.5	5.5	
YSCN-200-700	190	61	21	1068	0.97	94.8	5.2	
YSCN-200-900	168	62	7	1623	1.53	92.4	7.6	
N-20-YSCN-200-700	184	80	22	1035	0.86	93.4	5.7	0.9
N-50-YSCN-200-700	196	81	24	807	0.73	92	5.1	2.9
N-150-YSCN-200-700	316	49	45	725	0.53	90	5.9	4.1
N-200-YSCN-200-700	359	40	55	646	0.48	90.1	5.9	4

Table S2 Capacitances of hierarchical YSCNs and N-YSCNs with different nanostructures and compositions

Samples	10mV/s	20mM/s	50mV/s	100mV/s	200mV/s	500mV/s
YSCN-200-700	107	99	85	74	63	50
YSCN-200-900	139	135	126	117	107	87
LP-YSCN-200-900	133	131	129	127	124	121
N-20-YSCN-200-700	108	94	79	70	63	54
N-50-YSCN-200-700	145	136	120	110	102	94
N-50-YSCN-200-900	146	144	137	131	122	103
N-150-YSCN-200-700	148	142	132	125	119	110
N-200-YSCN-200-700	159	151	140	133	125	114
N-20-CSCN-200-700	53	52	49	45	40	32
N-50-CSCN-200-700	58	57	54	48	44	36
N-200-CSCN-200-700	105	99	91	84	80	77
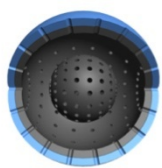
YSCN@meso-SiO$_2$
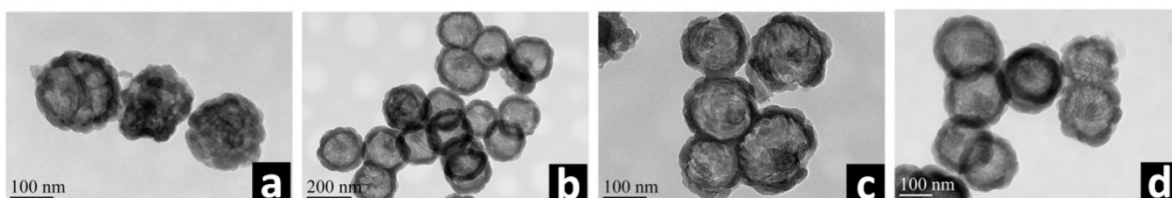
Figure S1 a-d) TEM image of YSCN@meso-SiO$_2$-80-700, YSCN@meso-SiO$_2$-100-700, YSCN@meso-Si O$_2$-150-700, YSCN@meso-SiO$_2$-200-700.
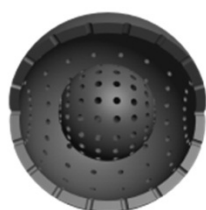
YSCN
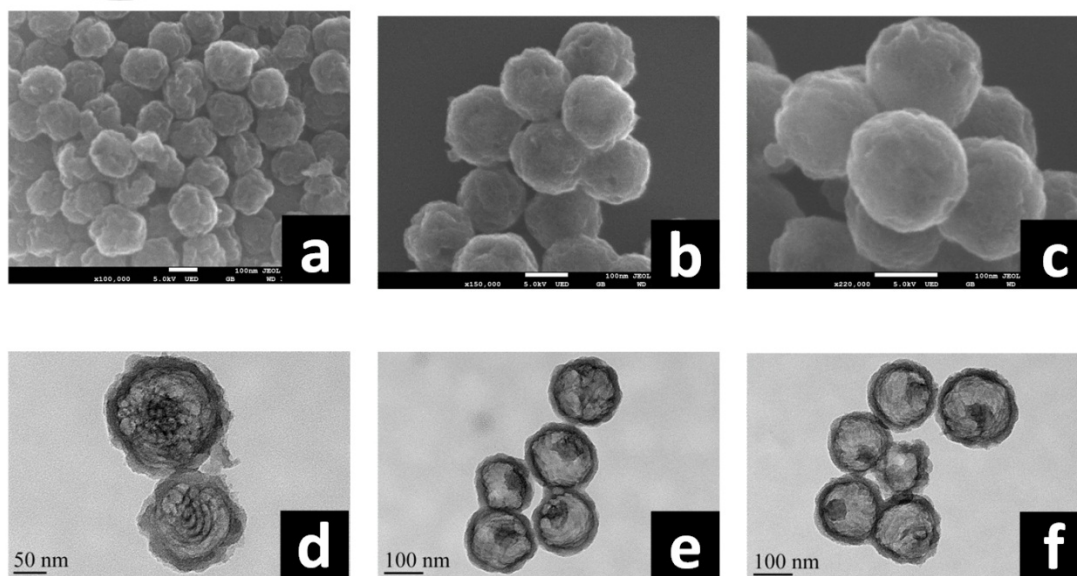
Figure S2 a-c) SEM images of YSCN-80-700, YSCN-100-700 and YSCN-150-700; d-f) TEM images of YSCN-80-700, YSCN-100-700 and YSCN-150-700.
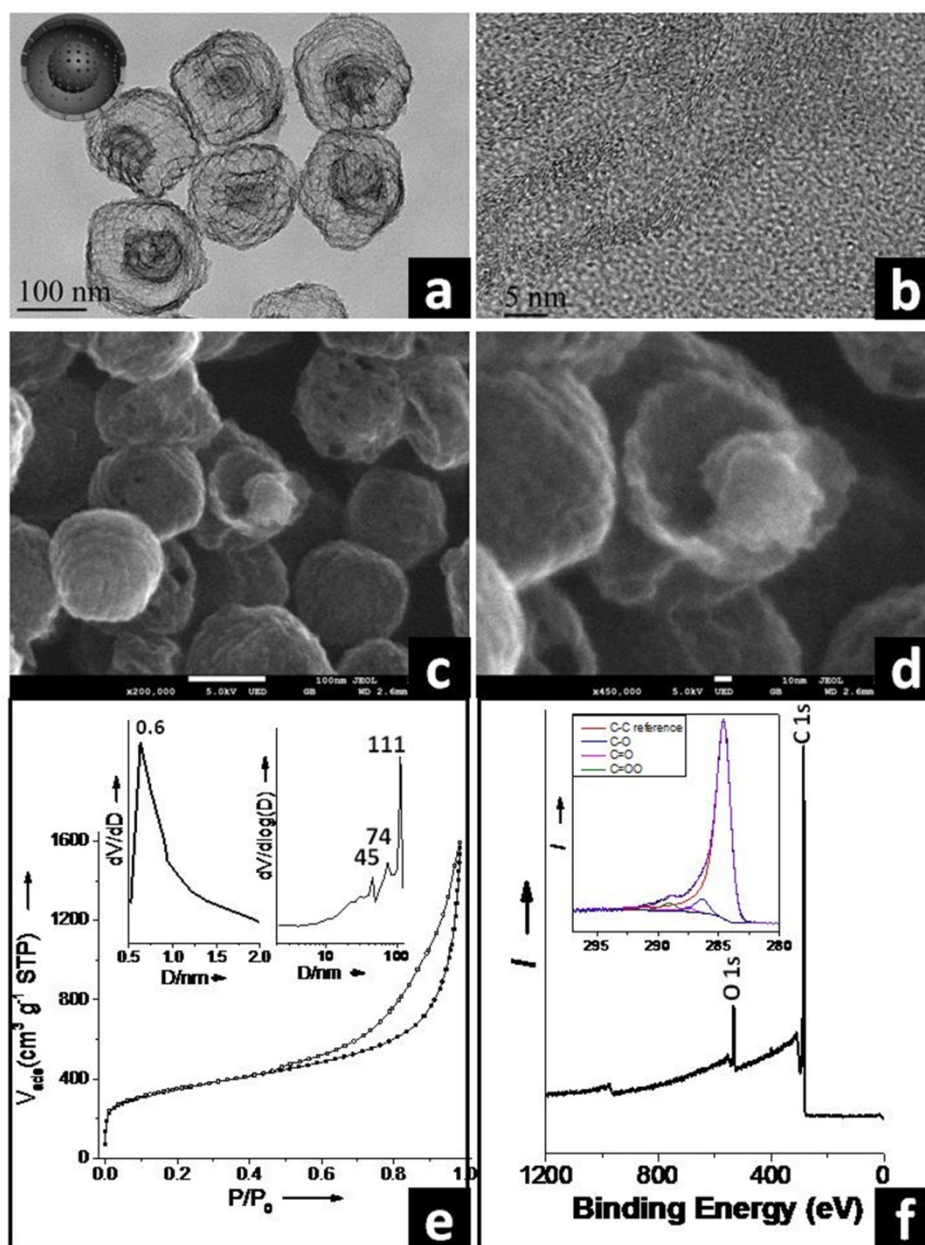
Figure S3 a) TEM image of LP-YSCN-200-900; b) HRTEM of shell in LP-YSCN-200-900; c) SEM image of LP-YSCN-200-900; d) HRSEM image of broken LP-YSCN-200-900; e) N2 sorption isotherm of LP-YSCN-200-900 and inserted BJH pore size distribution of LP-YSCN-200-900.

In Figure S3a, the TEM image indicates that the LP-YSCN-200-900 with a uniformly ordered large mesopores were produced on the ultrathin 7 nm carbon shells. The HRTEM of carbon shell reveals a partially graphitic structure of the mesoporous carbon shell (Figure S3b). The SEM image reveals the ordered structure with abundant large pores on the carbon shell surface (Figure S3c), while the HRSEM image of the broken LP-YSCN-200-900 further confirms that the mesopores were located on the yolk and the inside of carbon shell (Figure S3d). LP-YSCN-200-900 shows a type of I and IV mixed N_2 sorption isotherm with three condensation steps at relative pressures P/P_0 of 0.2-0.45, 0.7-0.8, 0.85-0.95, respectively (Figure S3e), which is a characteristic feature of hierarchical porous architectures with high BET surface area (1222 m²/g) and ultra-large pore volume (1.78 cm³/g, Table 1). The pore size distribution shows that the primary, secondary, tertiary and quaternary pore diameters are centred at 0.6, 45, 74 and 111 nm, respectively (Figure S3e insert). This can be attributed to micropores on the yolk and shell, large mesopores on the shell and void size and particle-particle interspace, respectively. The XPS survey spectra of LP-YSCN-200-900 shows only carbon and oxygen elements with no Fe catalyst remaining. The high resolution C1s spectrum indicates that the carbon shell is dominate with C-C bonding (284.6 eV), along with C-O (286.4 eV), C=O (287.5 eV) and O-C=O (289.1 eV), consistent with the O1s spectrum.
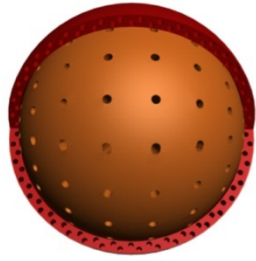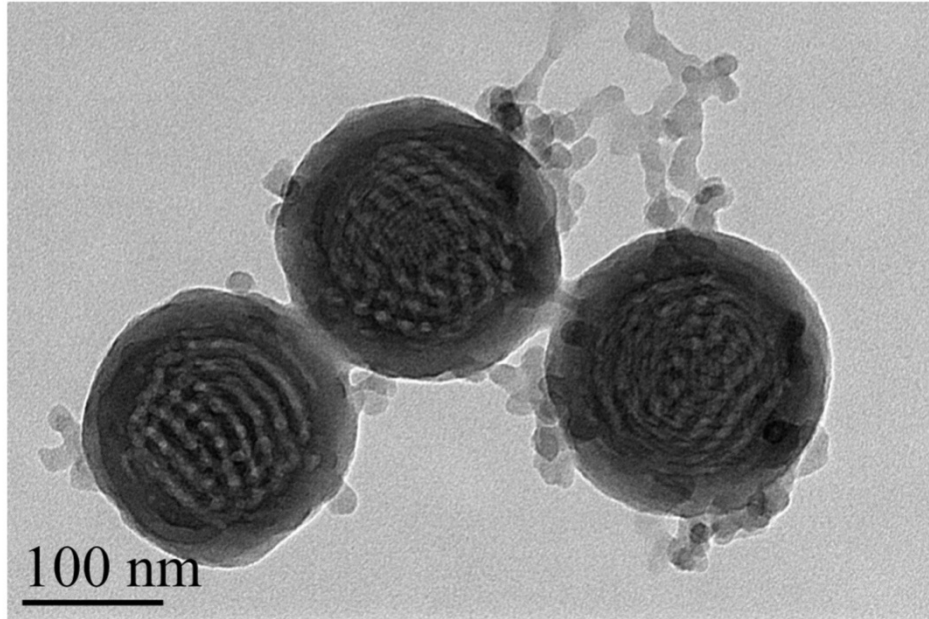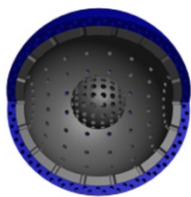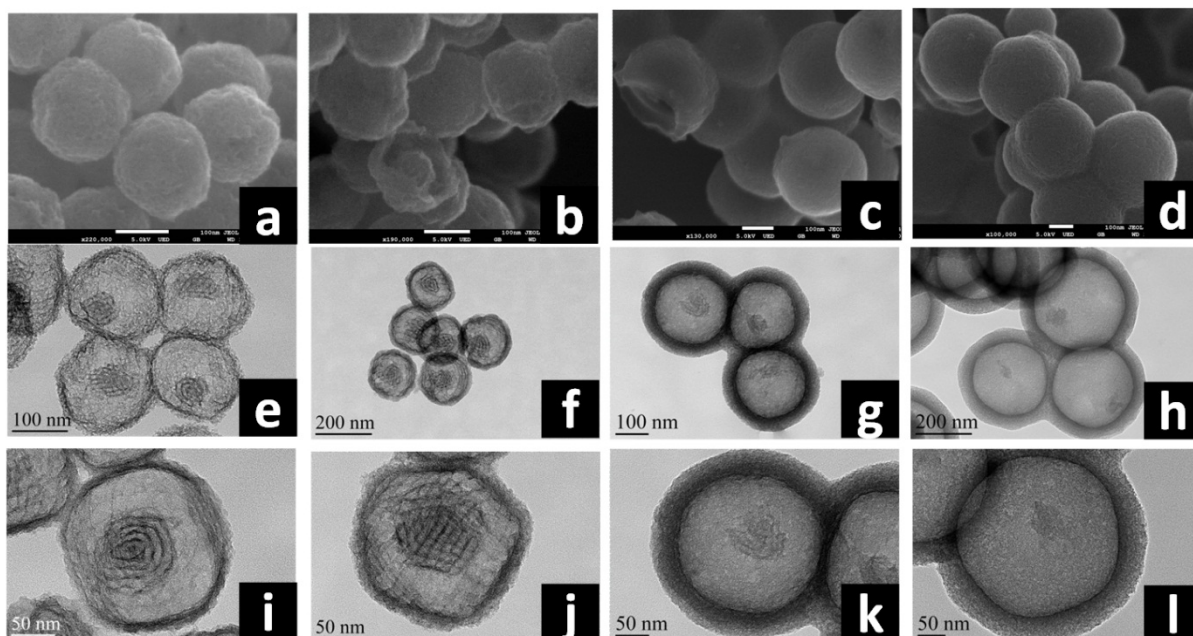
RF@APF

Figure S4 TEM image of RF@APF50.

N-YSCNs

Figure S5 a-d) SEM images of N-20-YSCN-200-700, N-50-YSCN-T200-700, N-150-YSCN-200-700, N-200-YSCN-200-700; **e-h)** TEM images of N-20-YSCN-200-700, N-50-YSCN-T200-700, N-150-YSCN-200-700, N-200-YSCN-200-700; **i-l)** HRTEM images of N-20-YSCN-200-700, N-50-YSCN-T200-700, N-150-YSCN-200-700, N-200-YSCN-200-700.
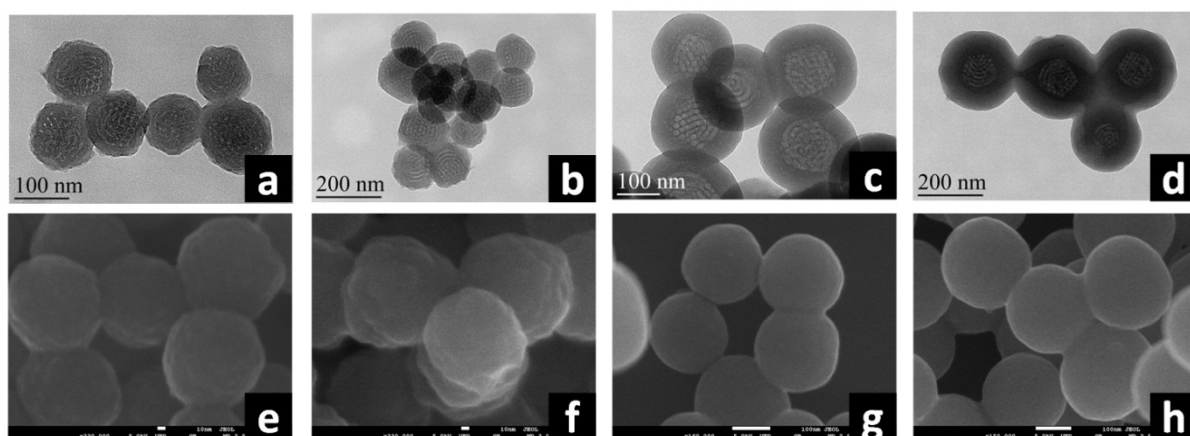
N-CSCNs

Figure S6 a-d) TEM images of N-20-CSCN-700, N-50-CSCN-700, N-150-CSCN-700, N200-CSCN-700; **e-h)** SEM images of N-20-CSCN-700, N-50-CSCN-700, N150-CSCN-700, N-200-CSCN-700.
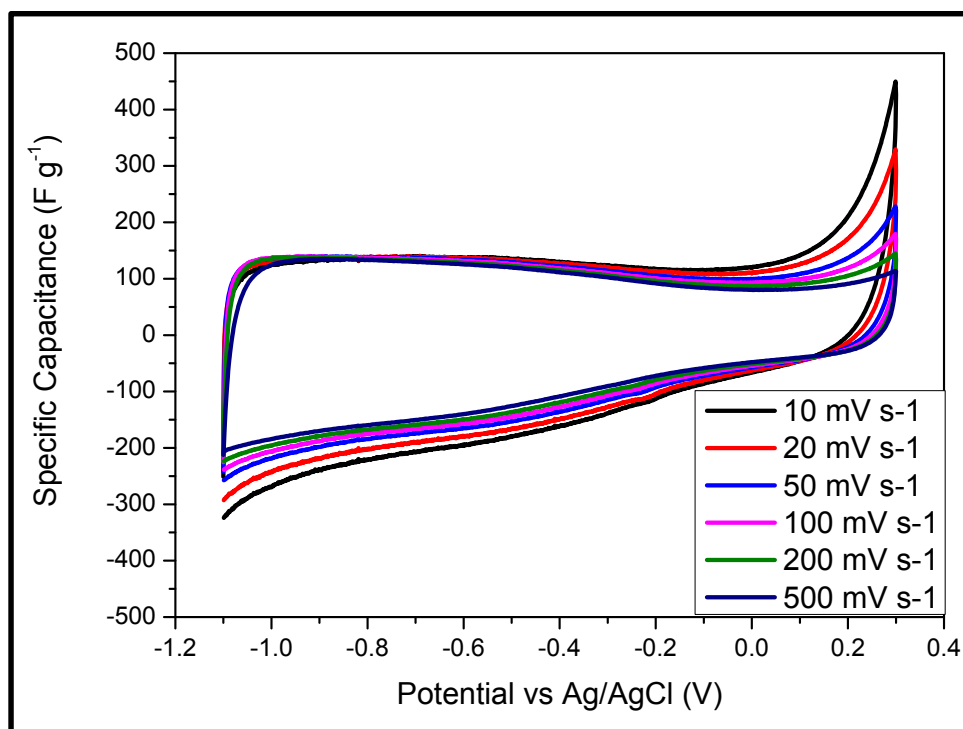
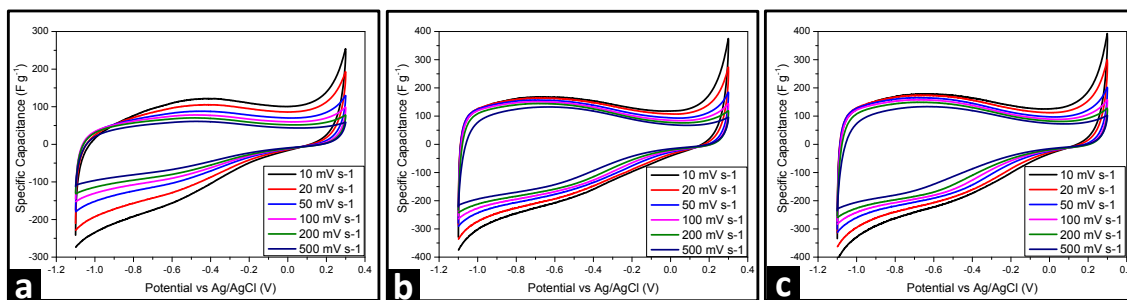**Figure S7 CV curve of LP-YSCN-200-900.**

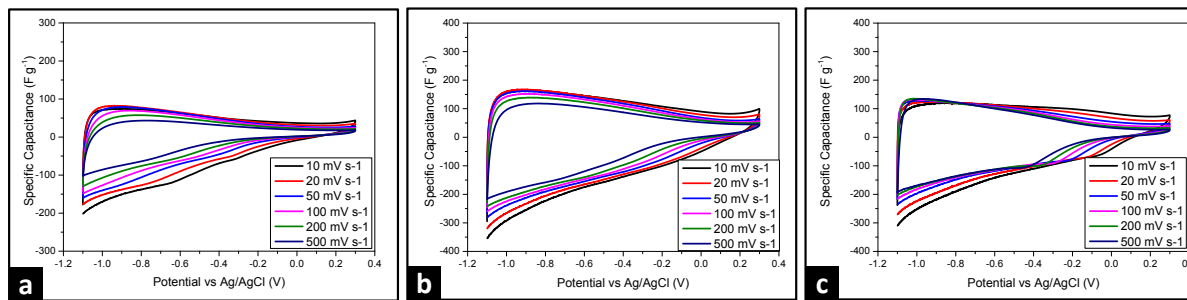**Figure S8 a-d) CV curve of N-20-YSCN-200-700, N-150-YSCN- 200-700, N-200-YSCN-200-700 respectively.**

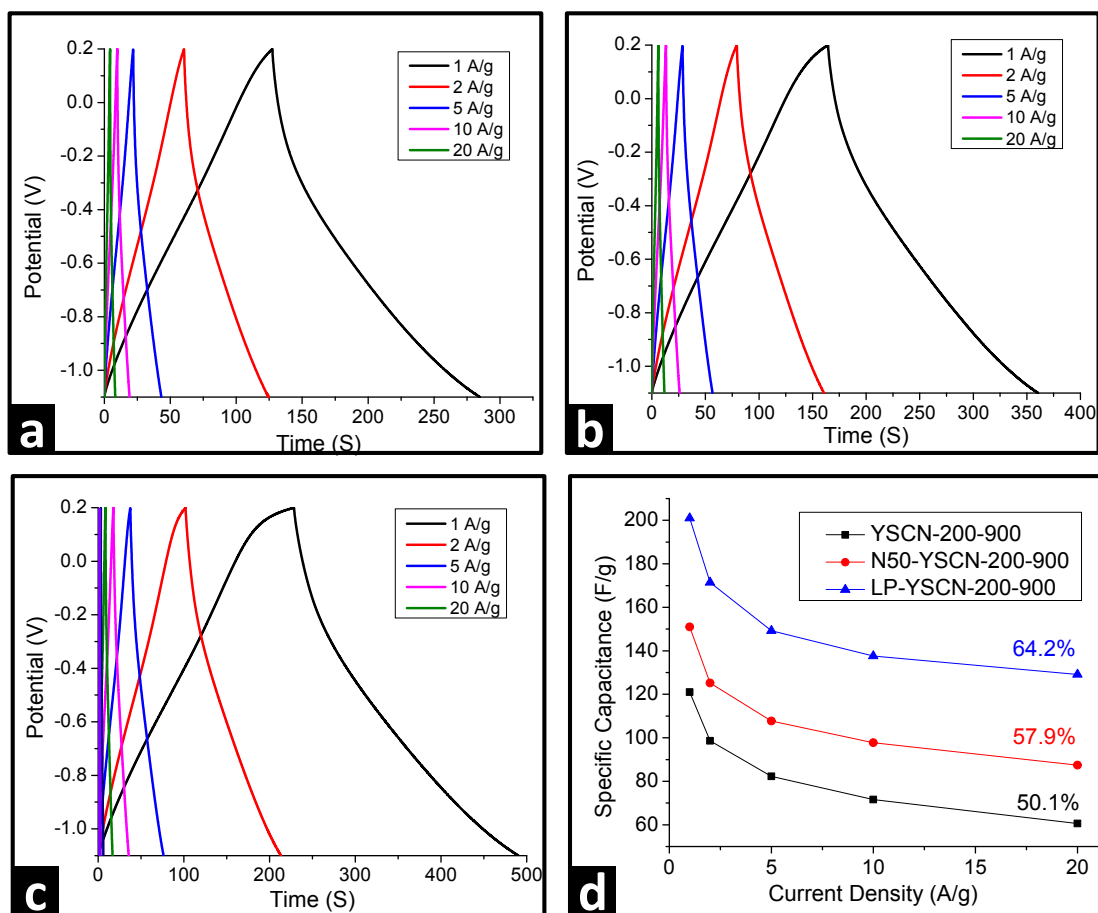**Figure S9 a-d)** CV curve of N-20-CSCN-200-700, N-50-CSCN-200-700 and N-200-CSCN-200-700 respectively.

Figure S10 a-c) Galvanostatic charge/discharge curves of the a) YSCN-200-900, b) N50-YSCN-200-900 and c) LP-YSCN-200-900; d)Specific capacitance plot of the YSCN-200-900, N50-YSCN-200-900 and LP-YSCN-200-900 calculated from the discharge curves versus current density.