Electronic Supplementary Information

Distinct Correlation Between $(CN_2)_x$ Units and Pores: A Low-cost Universal Way for Predesigned Wide Range Control of Micropore Size of Porous Carbon

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Experimental Section

Synthesis of p-(CN₂)_x (x \approx 5, 13 and 26): To prepare p-(CN₂)_x (x \approx 5,13 and 26), 1.00 g of melamine was placed into an open alumina crucible and heated in a tube furnace at 450 °C for 2 h in the flow of Ar gas, the white product of melem (p-(CN₂)₅) was obtained.^{1,2} Similarly, the light yellow product of melon (p-(CN₂)₁₃) was obtained at 550 °C for 2 h by the pyrolysis of melamine with other conditions maintained the same.³ The deep yellow product of g-C₃N₄ networks (p-(CN₂)₂₆) was prepared at 650 °C for 2 h using melamine.⁴ The TEM images are shown in Fig. S1.

The size of $p-(CN_2)_x$ was evaluated using Gaussian 09 platform, and the conformation of $p-(CN_2)_x$ was first optimized, then the size of the decomposable portion (indicated with red circles in Fig. 2c) of each $p-(CN_2)_x$ was measured directly.

*Synthesis of PC*_{(CN2)x}: 0.20 g of p-(CN₂)_x was grinded with 1.00 g of potassium carbonate and 1 ml of furfural to make sure the uniform mixing, then the mixture was transferred into a 100 mL autoclave, heated to 180 °C for 6 h. The solid products were heated at 250 °C for 1h, then raised to 750 °C at a rate of 3 °C/min and kept for 2 h under Ar atomosphere in a tube furnace. The carbonized products were grinded and washed with HCl (1 mol L⁻¹) and deionized water alternatively, then dried at 60 °C for 12 h. The carbonized products were named as $PC_{(CN2)x}$. To prepare $PC_{(CN2)0}$, only potassium carbonate and furfural were grinded and follow the same procedure described above. Carbonization temperatures of 600, 650, 700, 750, 775, and 800 °C were tested using p $(CN_2)_3$ and the products were named as $PC_{(CN2)3}$ -T $(PC_{(CN2)3}$ -600, $PC_{(CN2)3}$ -650, $PC_{(CN2)3}$ -700, $PC_{(CN2)3}$ -750, $PC_{(CN2)3}$ -775 and $PC_{(CN2)3}$ -800, respectively).

*Synthesis of PC*_{(CN2)3}-*prepolymerized*: Melamine-terephthalaldehyde nanoparticles were prepared following the literature method,⁵ melamine (0.38 g) and terephthalaldehyde (0.10 g) were mixed and dissolved in 20 mL of dimethylsulfoxide, then transferred into a 100 mL Teflon-lined autoclave, heated at 180 °C for 3 h. After reaction, 20 mL of the bright yellow solution was precipitated by addition of 60 mL of acetone, then centrifuged (10000 rpm) for 10 min. The solid precipitate was washed by dichloromethane and tetrahydrofuran orderly, then dried in a vacuum oven at 100 °C for 6 h. The product was grinded with potassium carbonate and furfural, and carbonized following the same procedure described above.

*Synthesis of PC*_{(CN2)26+(CN2)3}: p-(CN₂)₂₆ and p-(CN₂)₃ were mixed with a mass ratio of 3:1, then grinded with potassium carbonate and furfural, and carbonized at 750 °C with a rate of 3 °C/min for 2 h as described above.

Characterization

Thermogravimetric analysis (TGA) curves were recorded on a Linseis-STA PT1600 thermobalance. Infrared spectra were recorded on a Thermo Nicolet NEXUS 670 Fourier-transform infrared spectrometer using KBr pellets. Raman spectra were acquired on a Nicolet Raman 950 Fourier-transform Raman spectrometer. X-ray diffraction (XRD) data were obtained from a PANalytical X'Pert Pro X-ray diffractometer at 40 kV and 150 mA. A JEOL JEM-2010 transmission electron microscope (TEM) was used to observe the morphologies of prepared materials. N₂ adsorption – desorption (77 K) isotherms were measured by ASAP 2020 instrument. The nitrogen sorption isotherms were calculated based on the Brunauer-Emmet-Teller (BET) model. The pore size distributions were calculated by Horvath-Kawazoe method and 2D-NLDFT method. X-ray photoelectron spectroscopy (XPS) was carried out on a VG (ESCALAB210) multifunctional X-ray photoelectron spectrometer. Elemental analysis was measured by vario EL cube elemental analyzer.

Electrochemical measurements

All the electrochemical tests were characterized using a three-electrode electrochemical cell in 6.0 mol L⁻¹ KOH solution on a CHI660D electrochemical workstation (CHIstruments, Shanghai, China) with the platinum foil as a counter electrode and a Hg/HgO reference electrode. For the test, the $PC_{(CN2)x}$ (90 wt %), acetylene black (5 wt %) and polytetrafluoroethylene (5 wt %) were mixed sufficiently, and pressed to a nickel foam. It was then dried at 60 °C for 6 h in a vacuum oven before use. The mass loading of active materials was about 5.0 mg cm⁻².

In the three-electrode system, the specific capacitance (C) was calculated as

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

where C (F g⁻¹) is the specific capacitance, I (A) is the discharge current, Δt (s) is the discharge time, m (g) is the mass of the active substances on the working electrode, and ΔV (V) is the change of voltage during the discharging process.

Fabrication of supercapacitors based on $PC_{(CN2)26+(CN2)3}$: 5.0 mg of $PC_{(CN2)26+(CN2)3}$ was mixed with acetylene black and PTFE with a mass ratio of 90:5:5, then dispersed in ethanol under ultrasonication. The slurry was then casted onto a nickel foam and dried at 100 °C for 6 h. Two pieces of electrodes were assembled in CR2032 stainless steel coin cells using 6.0 mol L⁻¹ KOH as the electrolyte and PP/PE film (thickness: 130 µm) as the separator.

For these supercapacitors, the gravimetric energy density E (Wh kg⁻¹) and power density P (W kg⁻¹) of device were calculated using the following formulas:

$$C_s = \frac{4I\Delta t}{m\Delta V} \tag{2}$$

$$E = \frac{1}{2 \times 4 \times 3.6} C_s V^2 \tag{3}$$

$$P = \frac{E}{\Delta t} \tag{4}$$

where C_s (F g⁻¹) is the capacitance of single electrode capacitance, m (g) represents for the total mass of the active materials in two-electrode cell, V (V) is the operating voltage and Δt (s) is the discharge time.

Figures



Fig. S1. TEM images of $p-(CN_2)_x$ prepared at (a) 550 °C and (b) 650 °C.



Fig. S2. Thermogravimetric analysis curves.



Fig. S3. FTIR spectra of $PC_{(CN2)3}$ obtained at various temperature.



Fig. S4. (a) Nitrogen adsorption–desorption isotherms and (b) Pore size distributions deduced by means of DFT method for $PC_{(CN2)3}$ -T; (c) Nitrogen adsorption–desorption isotherms for $PC_{(CN2)x}$.



Fig. S5. (a) XRD patterns and (b) Raman spectra of $PC_{(CN2)3}$ -T.



Fig. S6. Mapping images of $PC_{(CN2)3}$.

(CN ₂)0	(CN ₂)1	(CN ₂)3			
(CN ₂)5	(CN ₂)13	(CN2)26			

Fig. S7. The cyclohexane contact angles of $PC_{(CN2)x}$.



Fig. S8. (a) CV curves of $PC_{(CN2)3}$ -T at 5 mV s⁻¹; (b) Galvanostatic charge–discharge (GCD) curves of $PC_{(CN2)3}$ -T (0.5 A g⁻¹); (c) CV curves of $PC_{(CN2)3}$ -750 at different scan rates; (d) GCD curves of $PC_{(CN2)3}$ -750 at different current densities.



Fig. S9. (a) CV curves of $PC_{(CN2)26+(CN2)3}$ at different scan rates; (b) GCD curves of $PC_{(CN2)26+(CN2)3}$ at different current densities.



Fig. S10. The Ragone plots of $PC_{(CN2)26+(CN2)3}$ symmetrical supercapacitor.

Sample	$\begin{array}{c} S_{BET} \\ (m^2 \ g^{\text{-1}})^{a)} \end{array}$	S _{micro} (m ² g ⁻¹) ^{b)}	V _{total} (cm ³ g ⁻¹)	V_{micro} (cm ³ g ⁻¹) -	Elemental analysis (wt%)		
					Ν	С	0
PC _{(CN2)3} -precursor	-	-	-	-	9.28	63.44	23.83
PC _{(CN2)3} -600	814	721	0.43	0.38	7.72	75.22	14.62
PC _{(CN2)3} -650	1023	858	0.55	0.45	5.78	60.12	31.30
PC _{(CN2)3} -700	1423	1134	0.76	0.60	4.20	82.91	11.59
PC _{(CN2)3} -750	1782	1235	0.95	0.65	3.95	87.36	8.24
PC _{(CN2)3} -775	1720	1078	0.92	0.57	3.17	72.60	23.61
PC _{(CN2)3} -800	1483	896	0.79	0.48	3.34	88.92	7.20

Table S1. Textural properties and elemental analysis for PC(CN2)3-T and PC(CN2)3-precursor

^{a)}Calculated by the BET model, ^{b)}Calculated by the t-plot method.

References

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