

Supplementary Data

A novel strategy to synthesize hierarchical porous carbohydrate-derived carbon with tunable properties

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1. Supporting experimental details

1.1 Experiment and characterization of amphiphilic block copolymer P4VP-PEG

The synthesis of P4VP-PEG was prepared by the usual living anionic polymerization using potassium naphthalene as an initiator in tetrahydrofuran (THF) at -78 °C. 2.0 g dried MePEG-OH was dissolved in 100 mL THF, and added to a 250 mL round-bottomed flask under nitrogen. 4 mL freshly prepared potassium naphthalene in THF was dropped into the above reactor via a nitrogen-washed injector, until the solution color changed to light green. The mixture solution was stirred at room temperature for 0.5 h to form the alcoholate macroinitiator. Known amount of freshly distilled 4VP was then charged to the reactor under nitrogen atmosphere at -78 °C. Polymerization was carried out at this temperature for 24 h. The crude copolymer was dissolved in ethanol at 60 °C and was precipitated at room temperature. Then the copolymer was dissolved in ethanol at 60 °C again and was transferred to a dialysis tube and dialyzed against water for 1 week to remove all low molecular mass molecules.

In the spectrum of P4VP-PEG, the peaks at 3.5 ppm(H_c), 8.3 ppm(H_e) can be used to calculate the number-average molecular weight and the block ratio of the copolymer. We can simply calculate the block ratio using the following equations:

$$\frac{S_c}{S_e} = \frac{N_{H_c}}{N_{H_e}} = \frac{4n_{PEG}}{2n_{4VP}} = \frac{4 \times 2000/44}{2 \times n_{4VP}}$$

$$M_{\text{copolymer}} = 2000 + n_{4VP} \times M_{4VP}$$

Where S is the intensity of peaks in the 1H NMR spectrum; the n_{PEG} and n_{4VP} are the number of monomer repeat units along one copolymer backbone; the $M_{\text{copolymer}}$ and M_{4VP} are the number-molecular weights for the copolymer and 4VP respectively.

From the calculation of the NMR spectrum, we found that one P4VP-PEG chain has 45 EO units and 141 4VP units.

Table S1. The characterization of P4VP-PEG

Copolymer	EG ^a	4-VP ^a	M _n ^a	M _n ^b	M _w /M _n ^b
P4VP-PEG	45	141	16664	17935	2.59

^aThe calculated monomer repeat units and molecular weights obtained by ¹H NMR spectra.

^bThe molecular weights and distributions from GPC traces.

1.2 The preparation parameters of different samples

Table S2. The preparation parameters of diverse carbon materials

Sample Name	Water/Ethanol (mL/mL)	P4VP-PEG (g mL⁻¹)	Fructose (g mL⁻¹)	pH
Contrast	9/6	0	0.27	7
HPC-1.5@0.025-7	9/6	0.01	0.40	7
HPC-1.5@0.037-7	9/6	0.01	0.27	7
HPC-1.5@0.074-7	9/6	0.02	0.27	7
HPC-1.5@0.111-7	9/6	0.03	0.27	7
HPC-1.5@0.037-3	9/6	0.01	0.27	3
HPC-1.5@0.037-2	9/6	0.01	0.27	2
HPC-4@0.037-2	12/3	0.01	0.27	2
HPC-0.67@0.037-2	6/9	0.01	0.27	2
HPC-1.5@0.077-2	9/6	0.01	0.13	2
HPC-4@0.037-7	12/3	0.01	0.27	7
HPC-0.67@0.037-7	6/9	0.01	0.27	7

2. Supporting figures

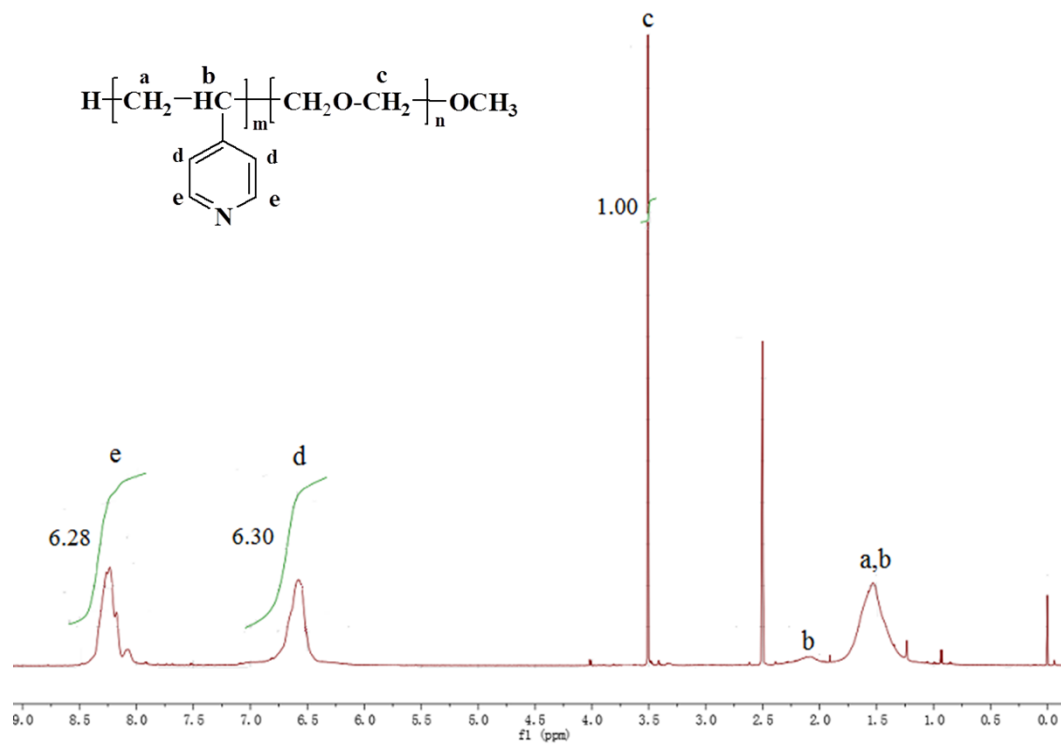
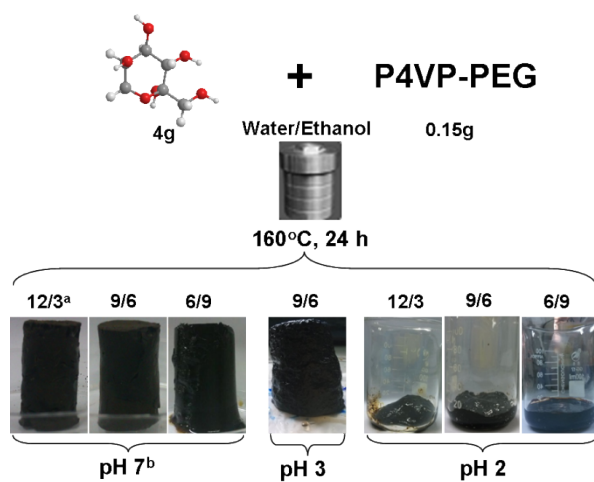


Fig. S1 ^1H NMR spectrum of the synthesized P4VP-PEG block copolymer in $\text{DMSO-}d_6$.



^a the volume ratio of water/ ethanol

^b the pH value of the reaction solutions.

Fig. S2 The photos of hydrothermal carbon prepared at various parameters.

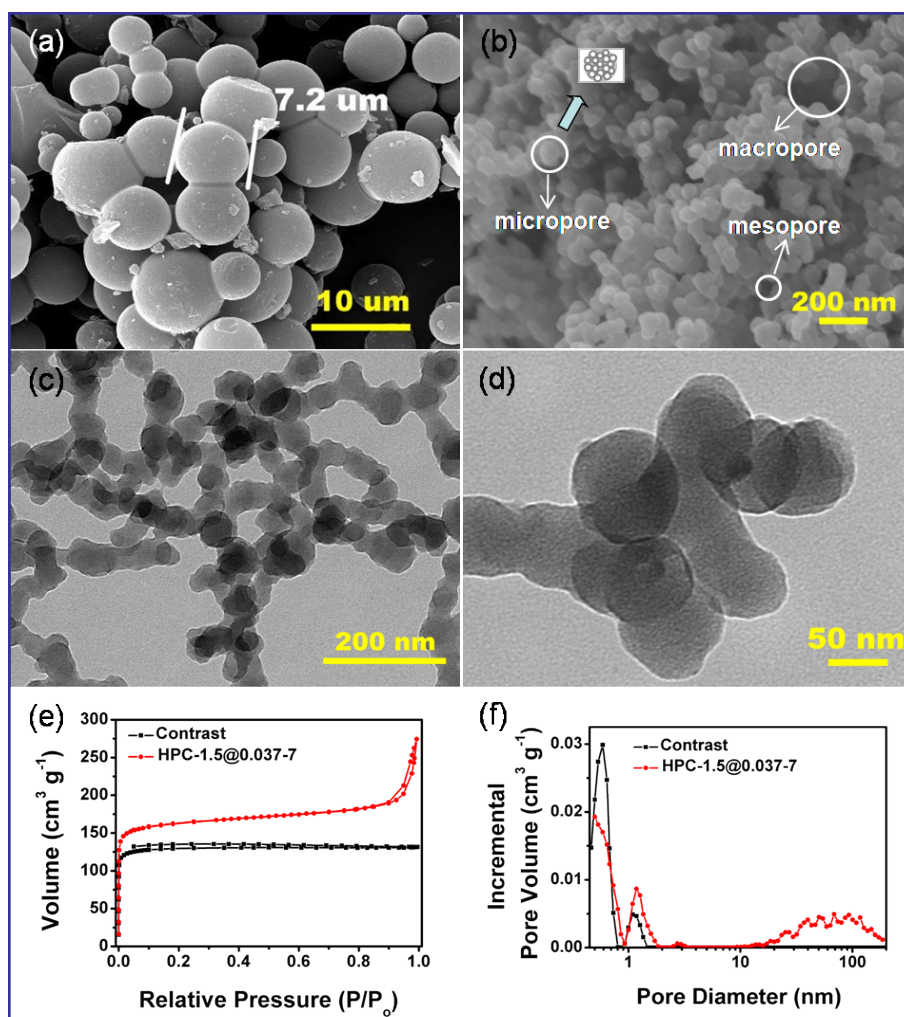


Fig. S3 (a) The SEM image of contrast sample prepared under the same conditions of sample HPC-1.5@0.037-7 but without the addition of P4VP-PEG. (b) The SEM image of sample HPC-1.5@0.037-7, showing the hierarchical porous structures of the obtained carbon materials (inset is a schematic illustration of micropores in the carbon particles). The TEM image (c) and relatively higher magnification TEM (d) of sample HPC-1.5@0.037-7. The N₂ sorption isotherms (e) and the pore diameter distributions (f) of the contrast sample and sample HPC-1.5@0.037-7.

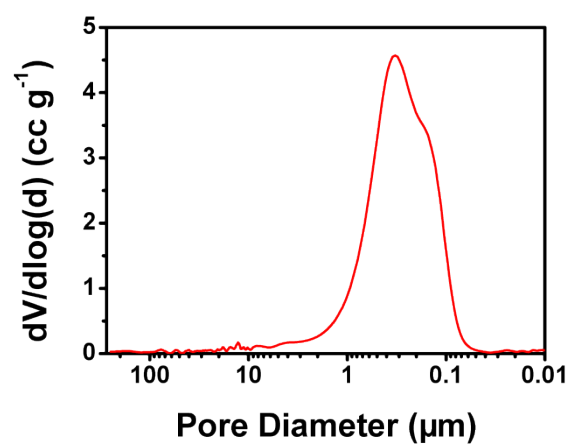


Fig. S4 The macropore diameter distribution of sample HPC-1.5@0.025-7.

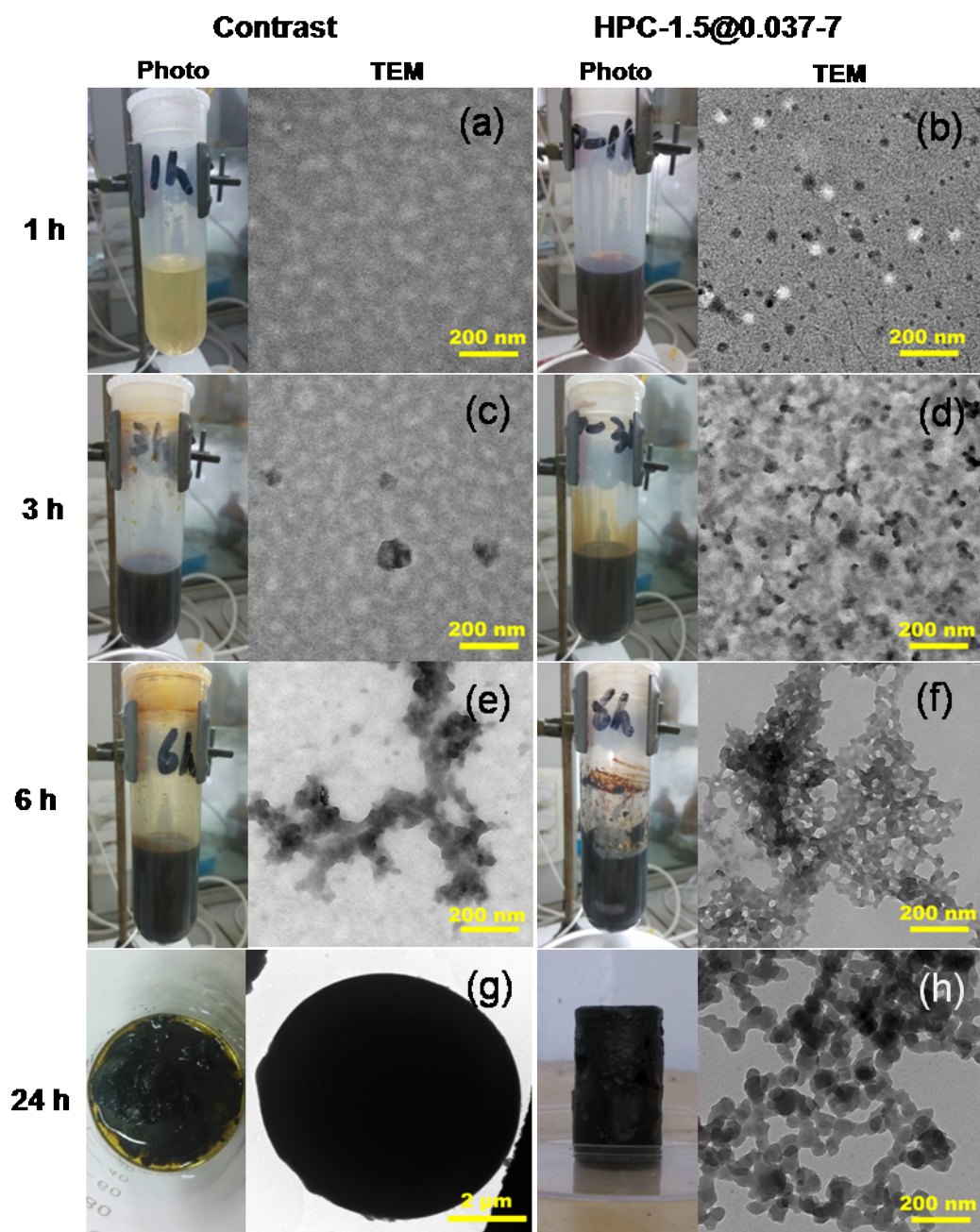


Fig. S5 The photos and TEM images of hydrothermal products prepared with or without the addition of P4VP-PEG for different hydrothermal time under a water/ethanol ratio of 1.5, a fructose concentration of 0.27 g mL^{-1} at pH 7.

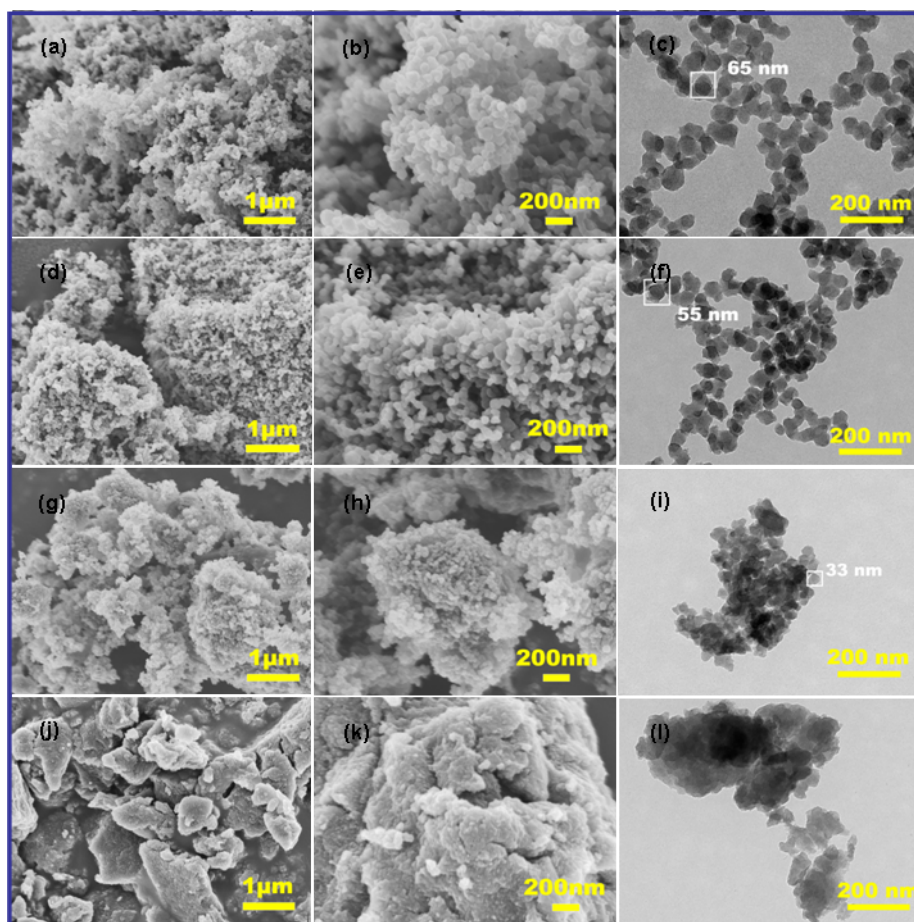


Fig. S6 The SEM and TEM images of samples prepared at different P4VP-PEG concentrations: (a-c) sample HPC-1.5@0.074-7; (d-f) sample HPC-1.5@0.111-7. The SEM and TEM images of samples prepared at different volume ratio of water/ethanol: (g-i) sample HPC-4@0.037-2; (j-l) sample HPC-0.67@0.037-2.

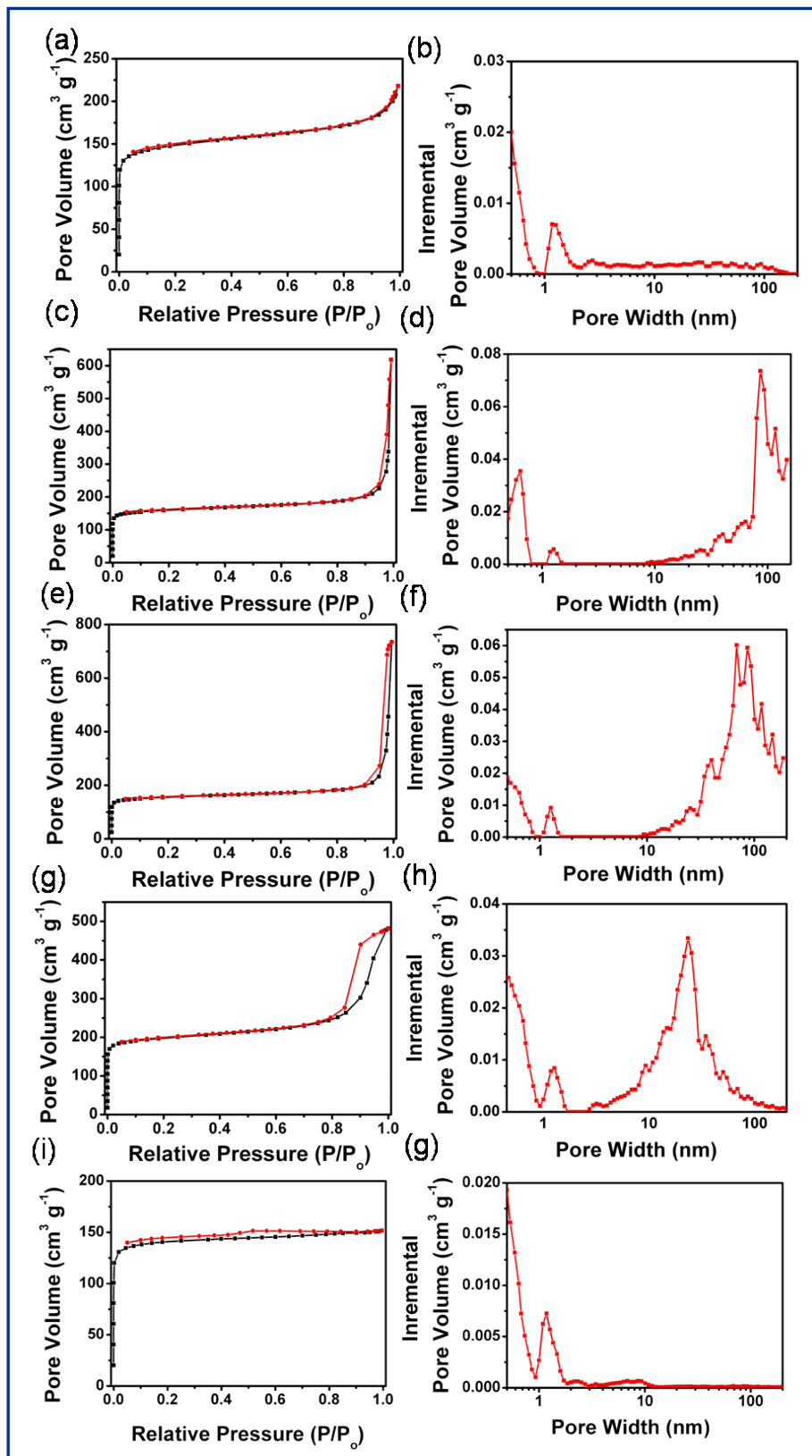


Fig. S7 The N_2 sorption isotherms and pore width distributions of sample HPC-

1.5@0.025-7 (a, b), sample HPC-1.5@0.074-7 (c, d), sample HPC-1.5@0.111-7 (e, f),
sample HPC-4@0.037-2 (g, h) and sample HPC-0.67@0.037-2 (i, j).

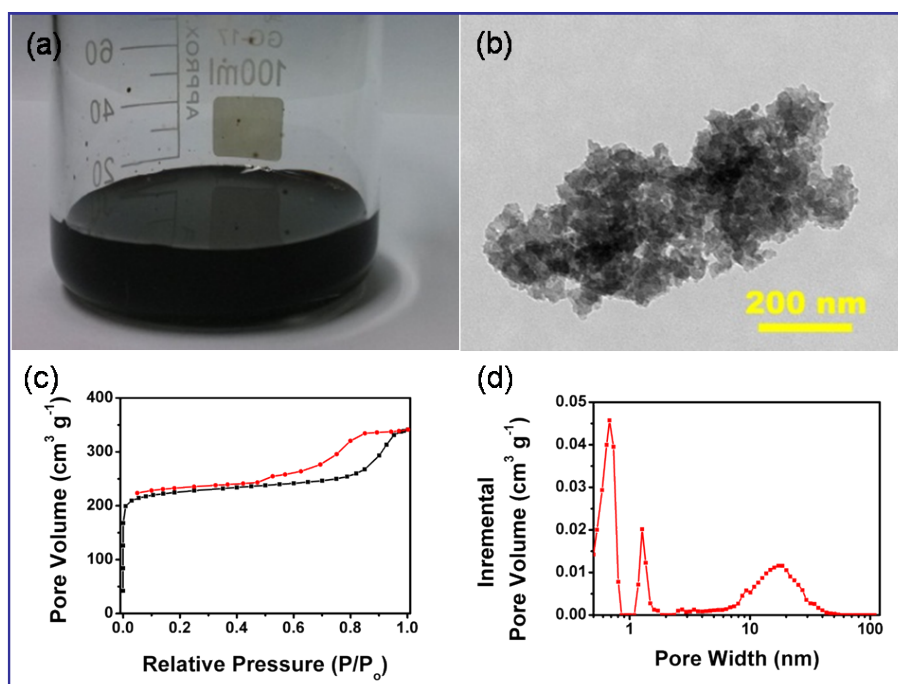


Fig. S8 The characterizations of sample HPC-1.5@0.077-2 prepared under a water/ethanol volume ratio of 1.5, a P4VP-PEG concentration of 0.01 g mL⁻¹ and a fructose concentration of 0.13 g mL⁻¹ at pH 2: (a) the photo of sol-like hydrothermal products; (b) TEM image; (c) N₂ sorption isotherm; (d) the graph of pore diameter distribution.

Fig. S8 a evidenced that sol solution was prepared after hydrothermal treating the solution under a water/ethanol volume ratio of 1.5, a P4VP-PEG concentration of 0.01 g mL⁻¹ and a fructose concentration of 0.13 g mL⁻¹ at pH 2. Then, hierarchical porous carbon materials were obtained by a calcination process (Fig. S7 b, c, d).

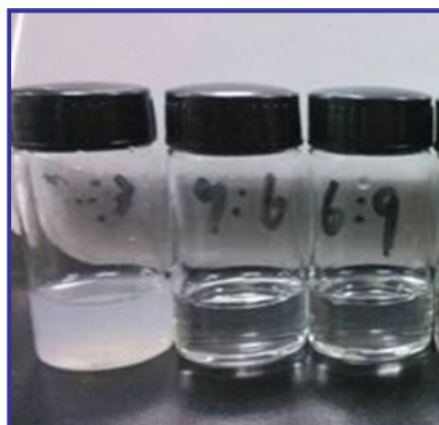


Fig. S9 The mixed solutions prepared with different water/ethanol volume ratios (4, 1.5, 0.67) under a P4VP-PEG concentration of 0.01 g mL^{-1} and a fructose of 0.27 g mL^{-1} at pH 7.

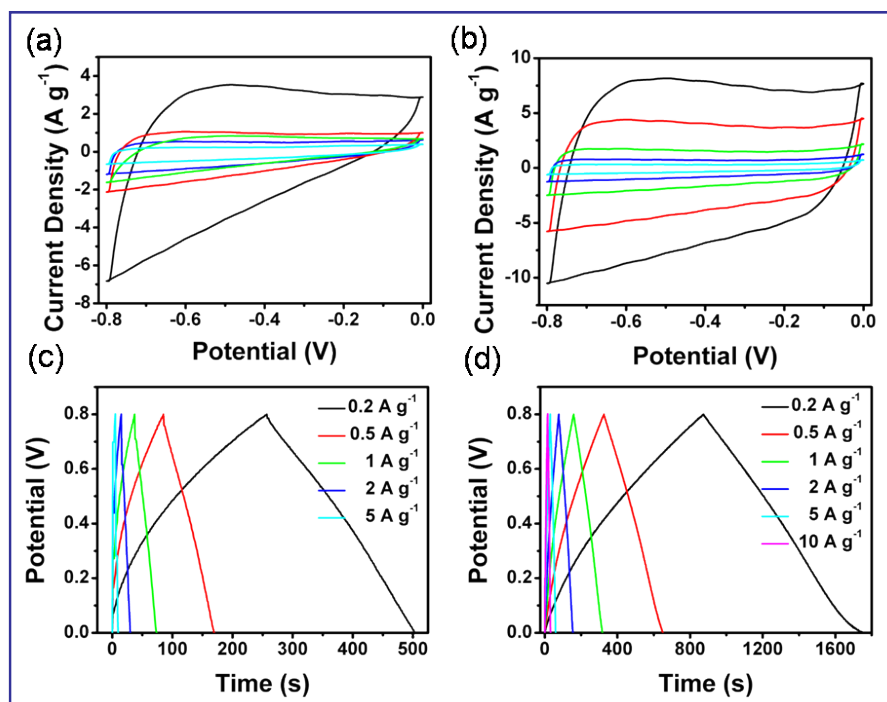


Fig. S10 The cyclic voltammetry of the contrast carbon (a) and sample HPC-1.5@0.077-2 (b) measured in 6 M KOH at varying scanning speeds: 100 mV s⁻¹ (black), 50 mV s⁻¹(red), 20 mV s⁻¹ (green), 10 mV s⁻¹ (blue), 5 mV s⁻¹ (sky blue). The galvanostatic charge/discharge curves of contrast carbon (c) and sample HPC-1.5@0.077-2 (d) measured in 6 M KOH at varying current densities.