Fabrication of novel nitrogen-doped porous carbon nanospheres for

high-performance supercapacitors

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1. Experimental section

Chemicals

2,4-diamino-6-hydroxypyrimidine (> 98%, DHP), L-Lysine (> 98%,) and potassium bicarbonate (99.5%, $KHCO_3$) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Formaldehyde solution (37-40 wt. %) and hydrochloric acid (HCl, 36-38 wt. %) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals have not undergone additional treatment before use. All experiments were conducted using deionized water.

Synthesis of nitrogen-doped porous carbon nanospheres

Typically, DHP (0.126 g) and L-Lysine (0.075 g) were dissolved in deionized water (40 mL) until a transparent solution was obtained. Then, formaldehyde solution (2 mL) was added, and the reaction was carried out continuously at 30 °C and 500 rpm for 2 h. The resulting milky white suspension was centrifuged at 10000 rpm for 5 min and washed three times. Finally, the resultant samples were dried at 80 °C for 12 h to obtain nitrogen-doped polymer nanospheres, denoted as NPS.

Subsequently, NPS was pyrolyzed in a nitrogen atmosphere at 600 °C for 2 h. The obtained samples were uniformly mixed with $KHCO_3$ at a mass ratio of 1:2 and further carbonized and activated in a nitrogen atmosphere at 750 °C, thereby obtaining nitrogen-doped porous carbon nanospheres, denoted as NPCS.

To acquire a more comprehensive cognition of the synthesis process, with reference to the synthesis process of NPS, the usage dosage of L-lysine (0-0.125 g), the quantity of formaldehyde (1, 2 and 3 mL), the reaction time (5, 30 and 60 min), and the stirring rate (0, 250 and 750 rpm) were regulated independently, respectively.

Characterization

Scanning electron microscopy (SEM) images were acquired by means of the Nova NanoSEM 450 field emission scanning electron microscope with an acceleration voltage of 3 kV. The JEOL JEM-F200 field emission transmission electron microscope was used at a voltage of 200 kV to photograph transmission electron microscopy (TEM), scanning TEM (STEM), high-resolution transmission electron microscope (HRTEM) pictures, and element distribution mapping. Thermo VG ESCALAB 250 was used for X-ray photoelectron spectroscopy (XPS) examination, with an Al Kα X-ray source at 150 W (15 kV). The binding energy was adjusted in relation to the C 1s peak at 284.6 eV. The Elementar

Analysensysteme Vairo Macro EL Cube microanalyzer was used to determine the element composition of the samples. The Thermo Fisher Nicolet iN10 Fourier Transform Microscopic infrared spectrometer was used to characterize the FT-IR spectra of the resultant polymers. The Raman spectrum of the as-prepared sample was completed by the inVia Qontor Micro confocal Raman spectrometer. Solid-state ^{13}C cross-polarization magic angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectra were obtained on an Agilent DD2-500 MHz at 125.7 MHz, with a spinning rate of 10 KHz, 1000 scans, a 4 s pulse delay and a contact duration of 4 ms. The chemical shifts were referred to TMS. The X-ray diffraction (XRD) pattern was performed using a Rigaku D/Max 2400 diffractometer with Cu Kα radiation (λ = 1.5418 Å). Thermo-gravimetric analysis (TGA) was performed on a thermal gravimetric analyzer-TGR Q 500 at a heating rate of 10 °C min^{-1} under a nitrogen flow. The Beishide Instrument 3H-2000PM was used to analyze nitrogen adsorption-desorption isotherms at -196 °C and characterize the physical structure of each sample. The specific surface area was measured using the multipoint Brunauer-Emmett-Teller (BET) method. Nonlocal density functional theory (NLDFT) was used to calculate pore size distributions. The total pore volume of the sample to be studied was estimated using the adsorption data at P/P_0 = 0.99.

2. Supplementary experimental section

Pyrolysis procedure. The temperature was raised from room temperature to 100 °C at a heating rate of 10 °C min^{-1}; then the temperature was raised to 250 °C at a heating rate of 1°C min^{-1} and maintained for 1 h; next, the temperature was raised to 350 °C at a heating rate of 1°C min^{-1} and maintained for 1 h, and finally the temperature was raised to 600 °C at a heating rate of 2 °C min^{-1} and maintained for 2 h.

Activation program. 0.2 g of the sample after pyrolysis at 600 °C and 0.4 g of KHCO$_3$ were fully dissolved in 3 mL of deionized water. After stirring for 1 h at room temperature, the mixture was transferred to an oven and dried at 80 °C overnight. Subsequently, the dried mixture was activated in nitrogen at 750 °C for 90 min. Finally, the product was washed with 4 M HCl and deionized water until it was neutral, and then completely dried at 80 °C overnight to obtain nitrogen-doped porous carbon nanospheres.

Electrochemical measurement. The nitrogen-doped porous carbon nanospheres (NPCS), conductive carbon black and polytetrafluoroethylene (PTFE) were uniformly mixed at a mass ratio of 8:1:1. A small amount of deionized water was added to the mixture until it became thick, and then it was evenly coated on a 1×1 cm nickel foam current collector. It was dried at 65 °C overnight and pressed at 10 MPa

to obtain the working electrode loaded with the active material. The three-electrode system consists of a working electrode, a counter electrode (platinum plate), a reference electrode (Hg/HgO), and a 6 M KOH electrolyte. The assembly sequence of the symmetrical supercapacitor (two-electrode system) is positive shell, electrode sheet, separator, electrode sheet, gasket, spring, negative shell, and 50 μL of 6 M KOH electrolyte was uniformly added between the electrode sheet and the separator in turn. Finally, it was pressed under a pressure of 6 MPa. The electrode sheet is a nickel foam current collector loaded with the active material. Galvanostatic charge-discharge (GCD), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested on a CHI 760E electrochemical workstation. The specific capacitance (C, F/g) of the three-electrode system is calculated from GCD according to the following formula:

$$C = (I \, \Delta t) / (m \, \Delta V)$$

where I (A), Δt (s), m (g) and ΔV (V) represent the constant charge/discharge current, discharge time, mass of active substance and working voltage window, respectively.
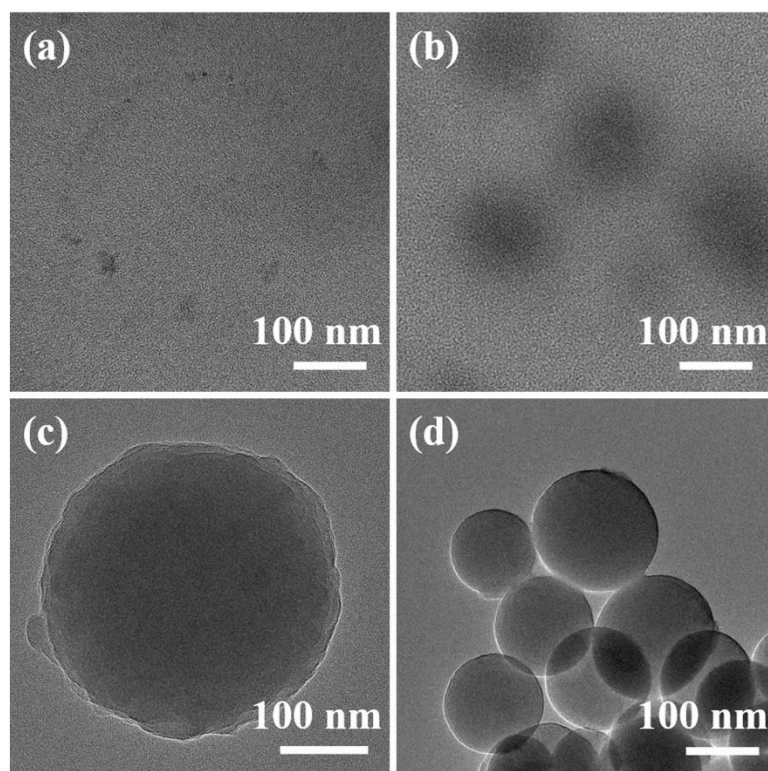
Fig. S1 TEM images of samples obtained (a) 30 min, (b) 80 min, (c) 140 min after the introduction

of formaldehyde; (d) TEM image of NPS after pyrolysis at 600 °C.

Make an attempt to slow down the reaction rate by lowering the concentration of reactants so as to be capable of monitoring the sample state at different reaction stages. The usage amounts of DHP, L-lysine and formaldehyde are 0.042 g, 0.025 g and 0.67 mL respectively, and the usage amount of solvent remains unchanged. As shown in Fig. S1, a polymer was formed with the addition of formaldehyde to the solution of DHP and L-lysine. Different from the dissolution of DHP and L-lysine in water, the hydrophobic interaction of newly formed polymer induced the formation of small clusters (Fig. S1a, 30 min after adding formaldehyde). Those clusters known to be highly unstable and self-aggregated to form colloidal nanospheres (Fig. S1b, 80 min after adding formaldehyde) in order to minimize the total surface energy and grew into colloidal nanospheres, leading to the formation of NPS (Fig. S1c, 140 min after adding formaldehyde). The multiple small spheres in DLP could be indistinctly observed in Fig. 1c. After pyrolysis, solid carbon nanosphere was obtained due to the shrinkage of NPS (Fig. 1d, pyrolysis at 600 °C.), and activated carbon nanospheres (NPCS).[1]
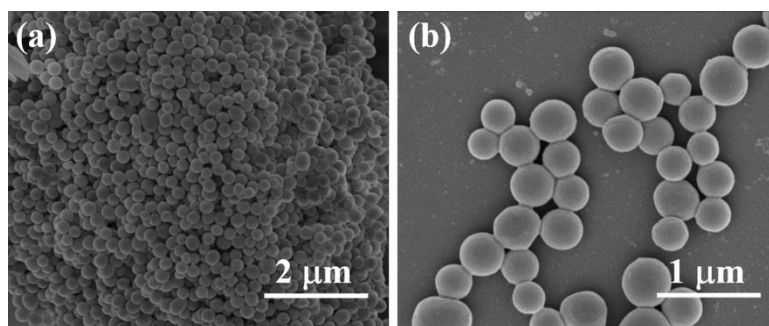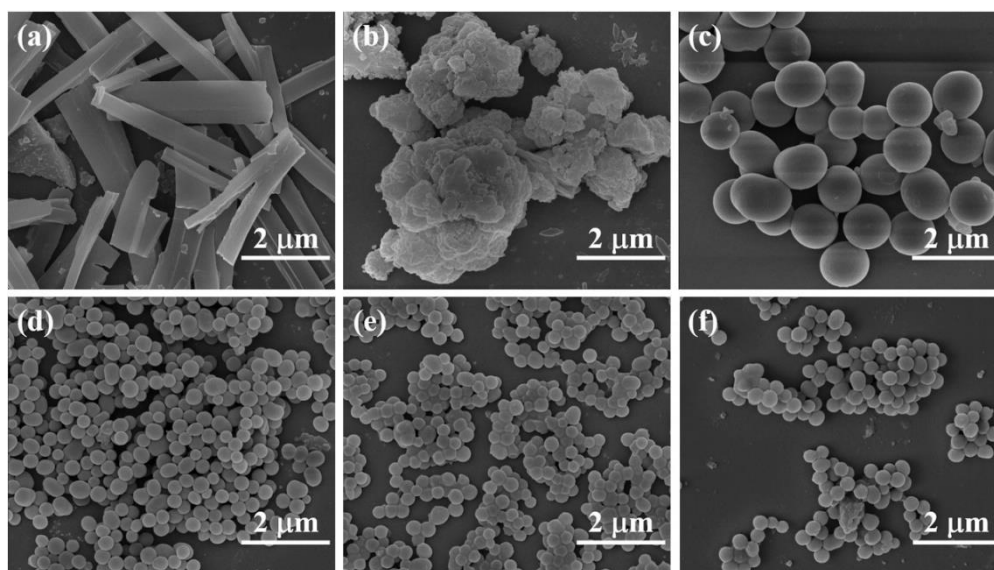
Fig. S2 SEM images of NPS.

Fig. S3 SEM images of the samples prepared using different dosages of L-lysine. (a) 0 g, (b) 0.025 g, (c) 0.050 g, (d) 0.075 g, (e) 0.100 g, and (f) 0.125 g.

Table S1. Elemental analysis of the samples prepared by different dosages of L-Lysine

Samples	N (wt.%)	C (wt.%)
L-lysine (0 g)	34.08	33.84
L-lysine (0.025 g)	33.25	38.69
L-lysine (0.050 g)	27.26	41.09
L-lysine (0.075 g)	24.80	41.18
L-lysine (0.100 g)	24.09	42.82
L-lysine (0.125 g)	23.97	44.07

Combining the target of the nanoscale spherical morphology and the nitrogen content data, the polymer nanospheres synthesized by introducing 0.075 g of L-lysine are the best. Therefore, this sample is selected as the representative sample for this study.
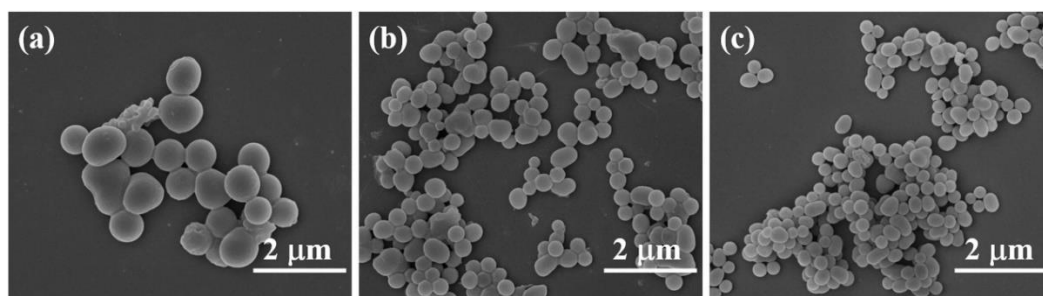
Fig. S4 SEM images of polymer nanospheres prepared using (a) 1.0 mL, (b) 2.0 mL, and (c) 3.0 mL formaldehyde, respectively.
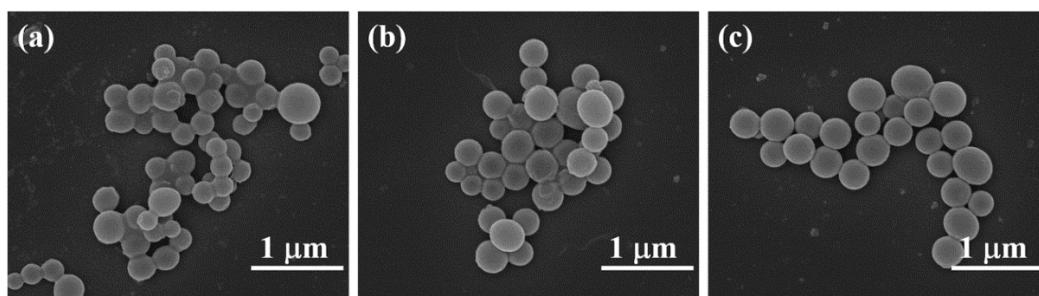

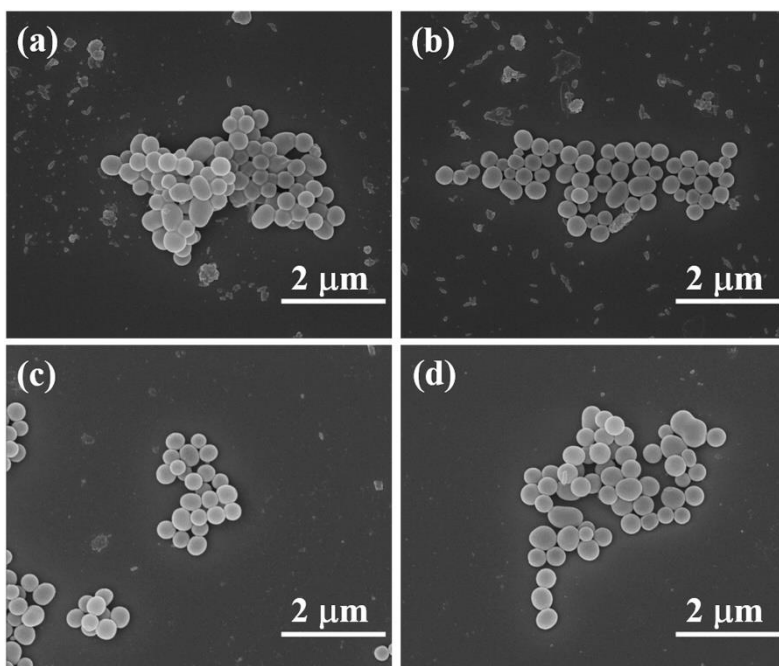Fig. S5 SEM images of polymer nanospheres prepared at (a) 5 min, (b) 30 min, and (c) 60 min.

Fig. S6 SEM images of polymer nanospheres prepared under the condition of (a) 0 rpm, (b) 250 rpm,
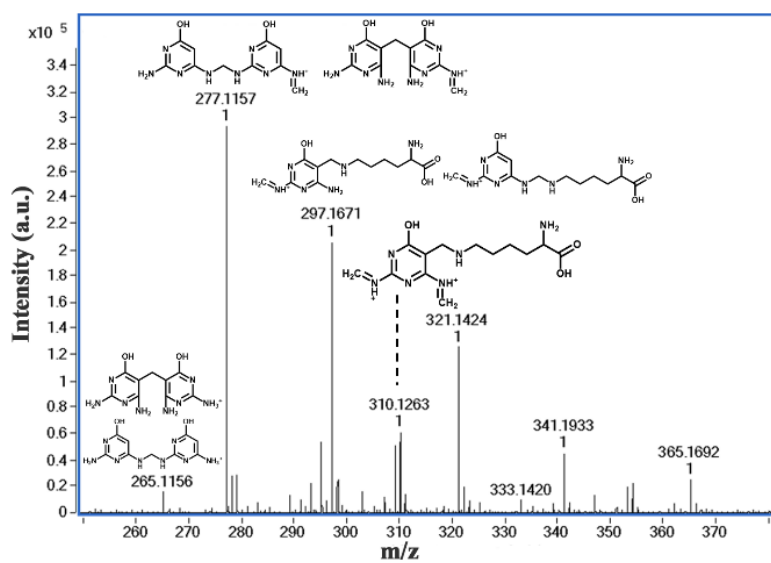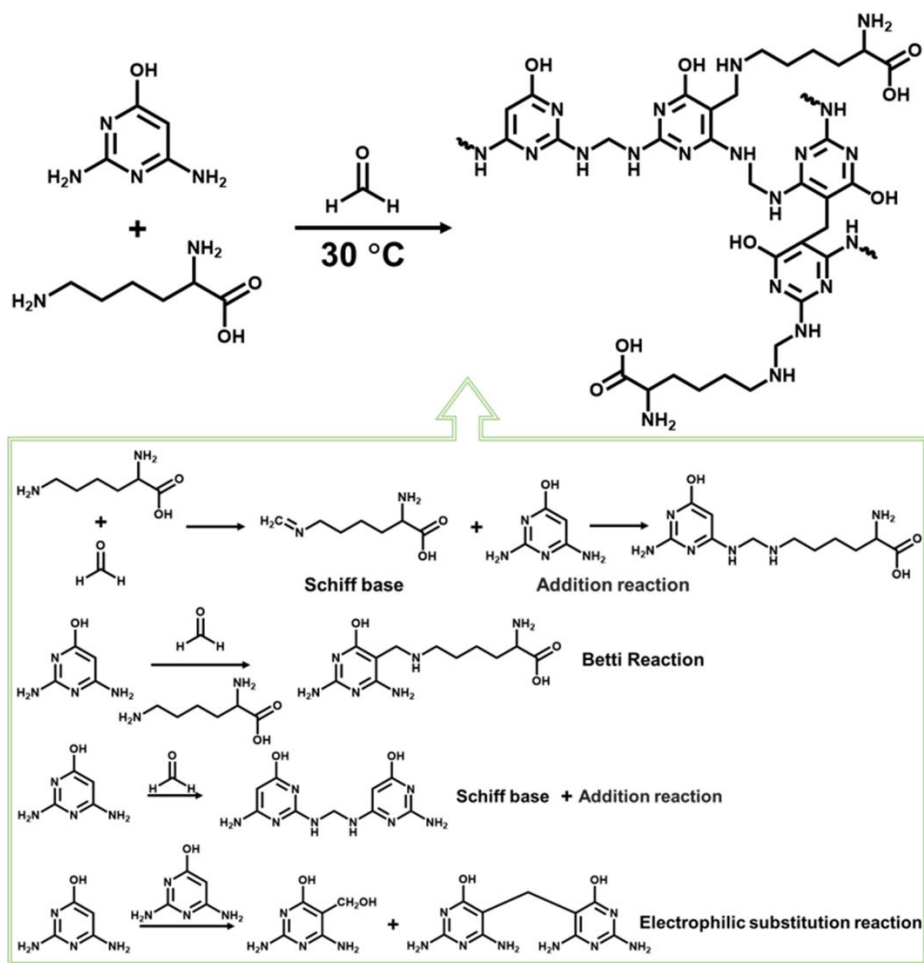
(c) 500 rpm and (d) 750 rpm.

Fig. S7 The positive ion TOF-SIMS spectrum of NPS.

Scheme S1 The possible chemical reactions during the synthesis of NPS.

After formaldehyde was introduced, the initial pH value of the reaction system was 6.5, and after 2 h of reaction, the pH value was 5.24.
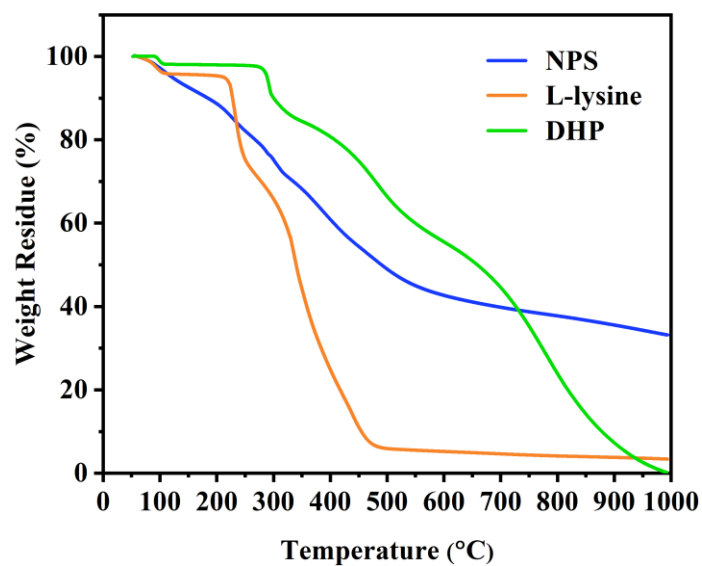

Fig. S8 TGA curves of DHP, L-lysine and NPS.

The thermo-gravimetric analysis (TGA) reveals that NPS is a gradual weight loss, significantly different from the stepped weight loss using DHP and L-lysine alone (Fig. S7). This result also supports that DHP is formed through chemical reactions among DHP, L-lysine and formaldehyde. Before 550 °C, it belongs to the rapid weight loss stage, with a residual mass rate of 45 wt.%. In the temperature range of 550-1000 °C, the weight loss is slow, and the final residual carbon is approximately 33 wt.%.
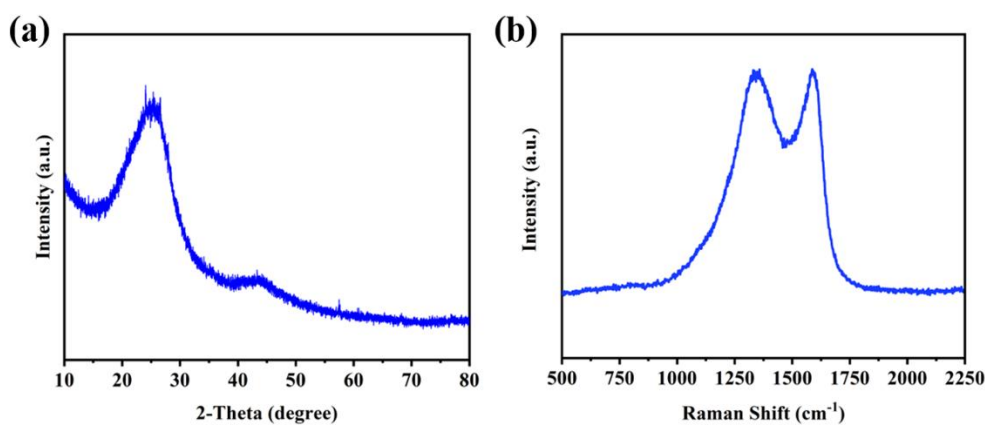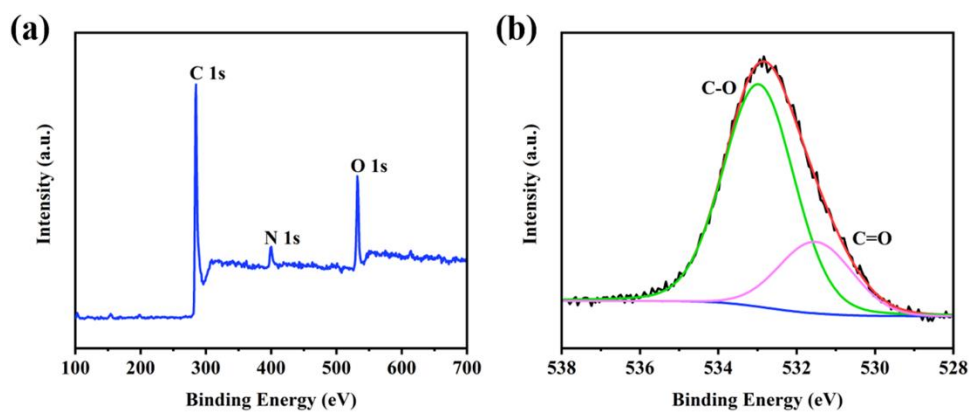

Fig. S9 (a) XRD pattern and (b) Raman spectrum of NPCS.

Fig. S10 (a) XPS survey and highly-resolved O 1s spectra.

References

1   J. Du, W.-C. Li, Z.-X. Ren, L.-P. Guo and A.-H. Lu, J. Energy Chem., 2020, **42**, 56-61.