Preparation of two-dimensional microporous carbon from Pistachio nutshell with high areal capacitance as supercapacitor materials

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Two-dimensional (2D) porous carbon AC-SPN-3 possessing of amazing high micropore volume ratio of 83% and large surface area of about 1069 m² g⁻¹ is high-yield obtained by pyrolysis of natural waste Pistachio nutshells with KOH activation. The AC-SPN-3 has a curved 2D lamellar morphology with the thickness of each slice about 200 nm. The porous carbon is consists of highly interconnected uniform pores with the median pore diameter of about 0.76 nm, which could potentially improve the performance by maximizing the electrode surface area accessible to the typical electrolyte ions (such as TEA⁺, diameter = ∼0.68 nm). Electrochemical analyses show that AC-SPN-3 has significantly large areal capacitance of 29.3/20.1 mF m⁻² and high energy density of 10/39 Wh kg⁻¹ at power of 52/286 kW kg⁻¹ in 6 M KOH aqueous electrolyte and 1 M TEABF₄ in EC-DEC (1 : 1) organic electrolyte system, respectively.

Electrochemical capacitors (EDLC, known as ultracapacitors or supercapacitors) based on electrical double layer charge accumulation hold promise for a wide range of applications, including portable electric equipments, uninterruptable power sources, medical devices, load leveling and hybrid electric vehicles, and so forth²⁻⁴. Carbonaceous materials are the most common supercapacitor electrode active substances. The electrochemical performance of supercapacitors is highly determined by the adopted electrode materials with a rational design of the pore structure and morphology. There have been intensively investigated for supercapacitor electrode application such as activated carbons³⁻⁵, templated carbons⁴, carbon nanofibers⁵, carbon nanotubes⁶, carbide-derived carbons⁷ and graphenes⁸⁻¹⁰. Several interesting synthetic routes have been found to obtain the high quality carbons, including carbonization of organic/polymeric precursors¹¹⁻¹³, chemical vapor deposition¹⁴⁻¹⁹, excimer laser ablation of graphitic targets²⁰⁻²², arc discharge syntheses²³, arc discharge syntheses²³, sputtering/plasma based syntheses²⁵⁻²⁶, chemical methods, etc²⁷⁻²⁸. However, those methods have obvious shortages. For example, carbide-derived carbon (CDC) method is effective to prepare the high quality porous carbons where the carbons with high microporosity produced by extraction of other elements, such as Fe from iron carbide. Based on the equation of C/A = εₑε₀/d, where C is the specific capacitance per weight, A is the specific surface area of the electrode, and εₑ and ε₀ is the dielectric constant of the electrolyte and vacuum, respectively, the desolvated electrolyte ions derived from spatial restriction by the micropores were able to enhance the specific capacitance (C/A), since the desolvated electrolyte ions may approach the electrode surface more closely, decreasing the thickness d of the EDLC. In order for the chlorination reaction to proceed, highly corrosive HCl etc gases usually used and they were transported to the carbide/carbon interfaces and metals and metalloids were removed as chlorides, so the safety issues of the preparation process worth extra attention²⁹⁻³⁰.

Bio-inspired design strategies are powerful to prepare the medical materials and other functional materials³¹⁻³⁴. The natural wastes such as nutshell, fruit kernel, leaf, straw and so forth mainly containing cellulosesis and lignin biopolymers are widely utilized as feedstock for the activated carbons, and one could get value-add produces for diverse and growing carbon-based applications. It was reported that the cation and/or anion with large sizes limit the utilizations of conventional porous activated carbon electrodes since the ions either literally do not fit into pores or become diffusion limited at the required scan rates³⁵⁻³⁶. In order to enhance the quality of the activated carbons, the porous carbons were usually treated by pyrolyzing the waste materials with some chemical or physical additives as agents for further activation. Physical activation (i.e., by steam or
higher carbon yield than that used in physical activation. Recently, an
treatment process, resulting in lower energy cost and shorter time with
in the thin dimension48,49. Here, we report the preparation of 2D
materials since the ion transport length is significantly shortened
is facile and safety, possessing of high product yield (62.3 wt.%) and
easy for mass production. The microporous carbon products have high performance using as the EDLC electrode active materials.

Results
The Pistachio nutshell was pyrolyzed at 750°C (denoted as C-SPN) and activated with KOH labeled as AC-SPN-X, where X refers to the mass ratio between KOH and carbon materials. Figure 1 and Figure S1 show the scanning electron microscopy (SEM) images of natural Pistachio shell and C-SPN with different magnification times. Both natural Pistachio shell and C-SPN possess curved 2D lamellar structures and certain shrinkage could be observed for C-SPN (Fig. 1b), indicating that the C-SPN preserves a wealth of natural plant features of the Pistachio nutshell. The thickness of each slice of C-SPN is approximately 200 nm based on the SEM observation (insert in Fig. S1b). The surface of C-SPN is flat and smooth (Fig. S2 a and b). The rough surface with many pores could be observed after the activation (Fig. S2 c–h). The damages became more apparent when the mass ratios of KOH/C increased from 1 to 5. Figure 1 c and d shows the high resolution transmission electron microscopy (HRTEM) images of AC-SPN-3 that further highlights the porous structure. The AC-SPN-3 constructed of amorphous and graphitized carbons (Fig. S3) has highly interconnected pores with the pore size of about 0.5–1 nm (Fig. 1 c and d).

Figure 2a shows the X-ray diffraction (XRD) patterns of the C-SPN as well as AC-SPN-1, AC-SPN-3 and AC-SPN-5 porous carbon materials. All the samples have two broad diffraction peaks at around 20 = 24° and 43° in the XRD patterns, which are consistent with the graphitic carbon. The broad diffraction pattern at 20 value of about 24° may be attributed to the (002) reflection of the graphitic-type lattice. The weak diffraction pattern at around 43° corresponds to a superposition of the (100) and (101) reflections of the graphitic-type lattice, i.e., (10) reflection, indicating a limited degree of graphitization. The specific structure nature can be further elucidated by the Raman spectroscopy. In Figure 2b the peaks present at around 1320 cm⁻¹ (D-bands) are due to the breathing mode of K-point phonons with A1g symmetry, corresponding to the disordered carbon or defective graphitic structures37–41. The peaks at around 1580 cm⁻¹ (G-bands) are assigned to the E2g phonon of sp² carbon atoms37–39, which are characteristic feature of the graphitic layers and correspond to the tangential vibration of the carbon atoms. Thus, the intensity ratios of these two peaks partially depend on the graphitization degrees40, and the higher value of I_D : I_G indicating higher electrical conductivity may be expected. Figure 2c shows the Nyquist plot for different carbon materials in 6 M KOH in the frequency range from 0.01 Hz to 0.1 mHz. The inset in Figure 2c shows the conductivities of the C-SPN and AC-SPN-X electrodes as well as the ratios of I_D/I_G from the Raman spectra for the C-SPN and AC-SPN-X samples. The Nyquist plots are composed of two distinct parts: one is semicircle part at high frequency with the corresponding value of the first intersection of the curve with the real axis indicates the internal resistance of the electrodes, and the other is linear part at low frequency corresponding to the diffusion process of the electrolyte ions onto the surface of the electrode in the system. After fitting the Nyquist plots with the typical circuit model, we can conclude that the electrode containing AC-SPN-3 possesses the highest conductivity of 12.8 C cm⁻¹ among those carbon electrodes (inset in Fig 2c). Besides, the I_D/I_G value of AC-SPN-3 is relatively high compared to that of AC-SPN-1 and AC-SPN-5 (inset in Fig 2c), indicating that the AC-SPN-3 sample has the most abundant graphitic layers among the activated samples even though the presence of disorder in the structure51.

The porosities of the AC-SPN-3 were examined by the N₂ sorption measurements (Fig. 2d) with the related textural parameters including Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}), total pore volumes (V_t), micropore volumes (V_micropore), pore diameters (D_{por}) and the ratios of V_micropore/V_t summarized in Table 1. For comparison, the
textural parameters of the related typical porous carbons in the literatures are also listed in Table 1. The total BET surface of the AC-SPN-3 sample is about 1069 m$^2$ g$^{-1}$, which is parallel to that of the porous carbon CN2 (1061 m$^2$ g$^{-1}$) prepared by the template method and the porous carbons obtained by the CDC techniques where the carbide Ti$_2$AlC (1150 m$^2$ g$^{-1}$) or TiC (1000–1600 m$^2$ g$^{-1}$) was used as the precursor. This high surface area is favorable for the high performances of the AC-SPN-3 sample using as the supercapacitor electrode material. The total pore volume of AC-SPN-3 is 0.51 cm$^3$ g$^{-1}$ based on the N$_2$ desorption curve analyses, which is in the middle level among the porous carbons prepared from the natural products or wastes. The AC-SPN-3 material has a uniform pore size distribution with the pore diameter of about 0.76 nm, based on the HK method, which is close to and a little larger than the diameter of those carbon electrodes. And, N$_2$ sorption isotherms of AC-SPN-3. Typical I curves was observed, indicating uniform microporous structure. The inset is pore size distribution, showing the main pore size of 0.76 nm.

Figure 2 | XRD, Raman patterns and BET tests. (a), XRD profiles for pristine activated carbon (C-SPN) as well as the samples activated with KOH at different ratios (AC-SPN-1, AC-SPN-3 and AC-SPN-5). (b), Raman spectra of the resultant pristine activated carbon and samples after KOH activation. (c), The Nyquist plot for the carbon electrode in 6 M KOH with the insert of the conductivities of the C-SPN and AC-SPN-X electrodes as well as the ratios of $I_C/I_D$ from the Raman spectra for the C-SPN and AC-SPN-X samples. The AC-SPN-3 electrode possesses the highest conductivity of 12.8 C cm$^{-1}$ among those carbon electrodes. And (d), N$_2$ sorption isotherms of AC-SPN-3. Typical I curves was observed, indicating uniform microporous structure. The inset is pore size distribution, showing the main pore size of 0.76 nm.

Table 1 | Comparison of pore parameters and specific capacitances of the porous carbons prepared by different methods

| Sample | $S_{BET}$ [m$^2$/g] | $V_i$ [cm$^3$/g] | $V_{mic}$ [cm$^3$/g] | $D_{pore}$ [nm] | $V_{mic}/V_i$ [%] | Maximum capacitance [F/m$^2$] | Method (or Material) | Reference |
|--------|----------------|----------------|----------------|----------------|----------------|-----------------------------|------------------|-----------|
| AC-K3  | 2009           | 1.00           | 0.82           | 0.59           | 82             | -                           | Second activation | 55        |
| CN2    | 1061           | 0.68           | 0.36           | 3.1            | 53             | 0.11                        | Template         | 56        |
| CNX-1  | 1803           | 0.93           | 0.74           | 3.10           | 80             | 0.08                        | Template         | 57        |
| CS48A2 | 2737           | 1.43           | 0.81           | 2.40           | 57             | 0.07                        | Template         | 58        |
| C8C    | 1850           | -              | 1.25           | -              | <0.15          | CDC                         | 59               |
| C-Ti$_2$AlC | 1150 | -              | 2.25           | -              | <0.15          | CDC                         | 59               |
| CNS-700 | 1340           | 1.08           | 0.53           | -              | 60             | 0.07                        | Hemp            | 60        |
| HPC-1  | 2157           | 2.26           | 0.77           | 4.18           | 34             | 0.09                        | Animal bone      | 61        |
| AKO    | 1654           | 1.29           | 0.62           | 52             | 0.17           | Argan seed shell            | 62               |
| HFAC-2 | 1217           | 0.46           | 0.41           | -              | 88             | 0.46                        | Egg white        | 63        |
| AC-SPN-3 | 1069          | 0.51           | 0.42           | 0.76           | 83             | 0.293 (aqueous)/0.201 (organic) | Pistachio nutshell | Our work |
of (CH₃CH₂)₂N⁺ (TEA⁺, 0.68 nm), a typical ion of the solute TEABF₄ for the organic electrolyte of supercapacitor. It should be mentioned that AC-SPN-3 possesses a high micropore ratio with the Vₘₐₜ/Vₜ = 83%, which is much higher than that of the typical porous carbons prepared from the natural products or wastes, such as CNS-700 (60%, from Hemp⁵⁹), HPC-1 (34%, from animal bone⁶¹), or AKO (52%, Argan seed shell⁶²). Thus, high capacitor properties are anticipated for the AC-3-3 using as the electrode active material in the organic electrolyte system.

The electrochemical properties of the C-SPN as well as AC-SPN-1, AC-SPN-3 and AC-SPN-5 samples were investigated in 6 M KOH aqueous electrolyte system. Without activation the C-SPN cyclic voltammetry (CV) curves (Fig. S4a) are disorder due to the low ion transport properties. Much better CV curves could be found for the AC-SPN-1 and AC-SPN-5 samples (Fig. S4 b and c). Quasi-rectangular shape curves were observed from the CV data for AC-SPN-3 (Fig. 3a), indicating the best electrochemical property of AC-SPN-3 sample among the C-SPN and AC-SPN-X samples. 1 M tetraethylammonium tetrafluoroborate (TEABF₄) in EC-DEC (1:1) organic electrolyte system was chosen to investigate the behavior of the AC-SPN-3 sample, where tetramethylammonium tetrafluoroborate (TMABF₄) tetraethylammonium tetrafluoroborate (TEABF₄), tetrabutylammonium tetrafluoroborate (TBABF₄) possessing of the effective cationic size of TMA⁺ 0.50 nm, TEA⁺ 0.68 nm, TPA⁺ 0.92 nm and TBA⁺ 1.11 nm was used as the solute, respectively. The CV result of AC-SPN-3 in the TEABF₄ electrolyte system (Fig. 3b) was obviously higher than that in the TMABF₄, TPABF₄ and TBABF₄ electrolyte systems (Fig. S5). The effective cationic size of the TEA⁺ ion (0.68 nm) is the closest to the median pore diameter (0.76 nm) of AC-SPN-3 among the TAA⁺ ions. Thus, the obtained higher CV values of AC-SPN-3 in the TEABF₄ electrolyte system can be clearly seen that the curves show triangular nature in the scan rates. When the current density increases, the specific capacitance decreased caused by the inner resistance throughout the current range of 0.2–1.5 A g⁻¹, indicating its excellent capacitive properties. The specific capacitance of AC-SPN-3 is about 215 F g⁻¹ at the current density of 0.2 A g⁻¹, and the specific capacitance is about 261 F g⁻¹. When the IR drop enhances along with the increase of the current densities. The AC-SPN-3 possesses typical triangular shapes with a little galvanostatic discharge decrease caused by the inner resistance throughout the current range of 0.2–1.5 A g⁻¹, indicating its excellent capacitive properties. The special capacitance of AC-SPN-3 is about 214, 180, 158, 132, 108 and 97 F g⁻¹ at the current density of 0.5, 1, 2, 3, 6 and 8 A g⁻¹, respectively, in the organic electrolyte of TEABF₄ system (Fig. 4b). It can be clearly seen that the curves show triangular nature in the scan rates. When the current density increases, the specific capacitance value decreases because of the limited diffusion of the active ions on the electrode surface in the case of fast charging. Figure 4c shows the Ragone plots of the AC-SPN-1, AC-SPN-3 and AC-SPN-5 samples in the two-electrode configuration. The AC-SPN-3 has a high energy density of 10 Wh kg⁻¹ at the power of 52 kW kg⁻¹ in 6 M KOH electrolyte system. Much higher energy density of 39 Wh kg⁻¹ at the power of 286 kW kg⁻¹ was observed in the TEABF₄ electrolyte system. Likewise, the desolvated TEA⁺ ions with the effective cationic size of 0.68 nm, similar to the median pore diameter (0.76 nm) of the AC-SPN-3, may approach the AC-SPN-3 electrode surface more closely (insert in Fig. 4c), decreasing the thickness d of the EDLC and leading to a higher specific areal capacitance⁶³. The obviously high electrochemical properties of the AC-SPN-3 is the result of the beneficial synergistic effects of the large number of highly interconnected
uniform micropores with suitable size and high surface areas and the abundant curved 2D lamellar graphitic layers with thin nanometer dimensions present in the carbon matrix.

Discussions
Bio-inspired design strategy has been implemented to prepare the two-dimensional lamellar microporous carbon supercapacitor electrode active material with large surface area. The high quality material has been obtained by pyrolysis of natural waste Pistachio nutshell followed by KOH activation, the method is facile and safety, the yield is high, and scalability of the process is quite easy. The microporous carbon possesses a curved lamellar morphology inheritance of the natural plants feature in the scale of micron/nanometer. The material exhibits very high areal electrical double layer charge accumulation capacities in both aqueous and organic electrolyte systems in comparison with those of currently reported activated graphene, porous carbon from template methods, carbide-derived carbons and most of porous carbons from the pyrolyses of the natural products or rests, due to the strong synergistic effects of the large number of highly interconnected uniform micropores with suitable size and high surface areas and the abundant curved 2D lamellar morphology with thin nanometer dimensions. This result is obviously valuable for the utilization of inexpensive, abundant and sustainable natural waste of Pistachio nutshell, i.e., typically turn “waste” into wealth.

Methods
Materials preparation. The Pistachio nutshell were collected in large quantity, typically turn “waste” into wealth.

The carbon sample was degassed at 330 °C for 12 h. The electrochemical measurement experiments were carried out on a CHI660e electrochemical work station (Shanghai Chenhua Instruments Co.) at room temperature. The working electrodes were prepared by loading a slurry containing 80 wt.% porous carbon (about 2.3 mg), 10 wt.% poly(vinylidene fluoride) (PVDF) in N-methylpyrrolidone and 10 wt.% acetylene black on a nickel foam. After the electrode materials were loaded, the working electrode was pressed and dried in vacuum at 80 °C for 12 h. In a three-electrode system, the above loaded nickel foam as working electrode was investigated with a Pt counter electrode and Ag/AgCl reference electrode in 6 M KOH solution and 1 M TAABF4 in EC-DEC (1:1) organic electrolyte as the electrolyte. The charge-discharge measurements were carried out using coin cells CR2032. A total of 2032 stainless steel coin sells with two symmetrical carbon electrodes separated by a porous polymeric separator were assembled with the aqueous and organic electrolytes. Electrochemical impedance spectroscopy (EIS) measurements were conducted for the working electrode in a frequency range of 0.01 Hz to 1 mHz. The EIS data were analyzed using Nyquist plots, which represent the real part (Z′) and imaginary part (Z″) of impedance.

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