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Carbon nanofibers by pyrolysis of self-assembled perylene diimide derivative gels as supercapacitor electrode materials†

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Carbon nanofibers (CNFs) have a wide range of applications and are commonly prepared under harsh conditions with small quantities. A green method for the preparation of CNFs under mild conditions with the scalable potential is highly challenging. Here, we describe a facile water-based room-temperature approach to producing gel fibers from a perylene diimide derivative via self-assembly, gelation, freeze-drying, and then to generating CNFs by subsequent pyrolysis under Ar. The entangled CNFs, with relatively uniform diameters around 20-50 nm, can be prepared as thin films or monoliths. The CNFs doped with elements N and Sn can be readily produced. The CNFs are characterized by various techniques and particularly evaluated as electrode materials for supercapacitor by cyclic voltammetry and galvanostatic discharge. A non-ionic surfactant (Pluronic F-127) can be easily incorporated into the self-assembly process, which produces the CNFs with a higher surface area $520 \text{ m}^2 \text{ g}^{-1}$ and a specific capacitance of 346 F g^{-1} at the scan rate of 1 mV s^{-1} or 192 F g^{-1} at the current density of 1 A g^{-1} . The CNF electrodes are highly stable. Quite surprisingly, the specific capacitance increases with repeated testing, achieving an impressive 226 F g^{-1} for 1000 charge/discharge cycles at 4 A g^{-1} .

1. Introduction

Carbon nanostructures, such as fullerenes, carbon nanotubes, graphene, and carbon nanofibers (CNFs), have attracted great interests because of their remarkable physical and chemical properties and wide range of applications.¹ CNFs can be prepared by different approaches on a relatively large scale and hence are potentially cost-effective. CNF-based materials have been applied in areas such as hydrogen storage, catalyst support,² gas sensing,³ electrochemical biosensors,⁴ supercapacitors,⁵ and water treatment.⁶ CNFs may substitute for the more expensive carbon nanotubes or graphenes for some applications.^{7,8} CNFs can be prepared either by templating or template-free approaches. In the template-free methods, CNFs are conventionally formed by vapor growth or catalytic decomposition/growth of carbon precursors in the gas phase and also by the widely used electrospinning method.^{2,9-11} In the templating approach, anodic aluminium oxide (AAO) membranes are widely used as hard templates,¹² whilst other materials such as crab shell can also be used.¹³ Preformed nanowires or *in-situ* formed and assembled nanowires may be used as templates to form CNFs in solvothermal processes.^{14,15} Apart from the solvothermal

processes where the carbonaceous materials are directly formed, CNFs are usually prepared by decomposition of small molecules or carbonization of carbon-rich polymers. For templating methods, the templates will have to be removed to generate the CNFs, normally by washing or etching procedures.

The vapor-growth approach involves the use of high temperature and high vacuum. As a result, the carbon materials are usually prepared in small quantities. Electrospinning is a highly versatile method for preparation of fibers from different types of polymers, but is generally slow (restricted by the injection rate). Volatile organic solvents or harsh conditions are commonly used to produce the fibers of desired polymers by electrospinning. CNFs are obtained after carbonization of the polymer nanofibers. The preparation of CNFs by carbonization normally requires the pre-formed carbon-rich nanofibers of polymers or other organic materials. A green (*e.g.*, use of water rather than organic solvents) and template-free approach (to avoid the procedures/costs of producing and removing templates) with the ability for easy scale-up (essential for applications) and under mild conditions (*e.g.*, room temperature synthesis) is highly desirable for the synthesis of CNFs.

Perylene diimides are multi-aromatic molecules, have an extended quadrupolar π system, and are utilized in many fields, including biosensing, light emitting diodes, field effect transistors, photovoltaic cells, and pigments.^{16,17} Due to their strong hydrophobicity, self-assembly of perylene diimides can form nanostructures in various organic solvents via π - π interaction/stacking and interaction of side chains. For example, 0-dimensional or 1-dimensional nanostructures are

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formed by self-assembly via the modification of side chains and the change of solubility with “poor” or “good” solvents.^{18,19} Water soluble perylene diimides are investigated by modification of perylene diimide with ionic substituents at the imide positions and/or bay positions. The aggregation of the molecules is prevented in water due to the electrostatic repulsion and steric hindrance.²⁰ In order to get biocompatible hydrogels, perylene diimide derivatives have been produced by reaction of perylene-3,4:9,10-tetracarboxylic dianhydride with amino acids. Once dissolved in water, the gelation/self-assembly of such perylene diimide derivatives may be initiated conveniently by change of pH or crosslinking with melamine.^{17,21-24} These hydrogels consist of entangled nanofibers, showing semiconducting and photo-switching behavior.²⁵ The dried gels may maintain the nanofibrous structure and exhibit air-stable photoconductivity.²³ These nanofibers have recently been used as templates for the synthesis of hybrid and supermicroporous nanotubules.²⁶

By utilizing the properties that perylene diimides are molecules with high carbon content and can form nanofibrous hydrogels in water under mild conditions, we describe here a highly efficient method to produce CNFs via the self-assembly of perylene diimide derivatives (PI) and subsequent carbonization. Further surfactant templating is introduced to form the CNFs with higher surface area. The potential of using these CNFs as high performance supercapacitor electrodes is demonstrated.

2. Experimental section

Materials and reagents: Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA, 97%), 5-aminoisophthalic acid (94%), imidazole (ACS reagent, ≥99%), triethylamine (TEA, ≥99%), potassium stannate trihydrate (K_2SnO_3 , 99.9%), NaOH, glucono- δ -lactone (GdL), melamine (MM, 99%), and non-ionic surfactant Pluronic F-127 were purchased from Sigma-Aldrich and used without further purification. Standard analytical grade solvents and de-ionized water were used routinely.

Synthesis of perylene diimide derivative (PI): The perylene diimide derivative with four carboxylic acid groups (PI) was synthesized as reported previously.¹⁷ Briefly, PTCDA (0.20 g), 5-aminoisophthalic acid (0.23 g), and imidazole (1.60 g) were heated at 127 °C for 6 hours under nitrogen atmosphere. Then ethanol (20 cm³) was poured into the hot mixture, refluxed for 6 hours and then cooled down and left overnight to precipitate out the solid. The precipitate was filtered and washed with ethanol. The product was dried at 60 °C under vacuum oven to get 0.32 g deep red powder (yield: 88%).

Preparation of the CNFs: To form the gel, 10.0 cm³ stock solutions of PI (20 mM) were prepared by dissolving PI in 0.06 M NaOH solution (denoted as N), 12 mg cm⁻³ K_2SnO_3 solution (denoted as K), or TEA solution with a molar ratio of PI:TEA of 1:6 (denoted as T). 0.5 cm³ of these solutions and 0.5 cm³ water or 40 mM MM solution in water were added to a test tube, followed by addition of 13 mg GdL (2 molar equivalent). Mixing was achieved by shaking the test tubes for approximately 10 seconds. After this, the samples were allowed to stand, with gelation taking place over 30~120 min

at room temperature. The samples were denoted as X + GdL or X + MM + GdL, where X (N, K, or T) indicates the base in the PI solution.

The formed gels could be washed using water, acetone and cyclohexane in order. The gels were soaked in water for 30 minutes, replaced with fresh water 3 times; then washed with acetone using the similar procedure and soaked in acetone overnight. Finally the hydrogels were soaked in cyclohexane for 5 hours before freeze-drying. All the hydrogels with and without washing treatment were frozen in liquid nitrogen and then freeze-dried in a freeze-dryer (Vis Advantage) for 48 h. Finally, the as-obtained dry samples were pyrolysed in a Nabertherm furnace (model R 50/500/12) under an Ar atmosphere at 2 °C min⁻¹ to 200 °C for 2 h, 3 °C min⁻¹ to 800 °C for 3 h to form the black product. 1.0 g dry samples could yield approximately 0.23 g of carbon materials. The CNFs were prepared from both washed and un-washed gels.

Preparation of the F-127 templated CNFs: The F-127-templated gels were formed by mixing 0.5 cm³ of PI in TEA solution with 0.5 cm³ aqueous 40 mM MM solution containing 0.05 mg cm⁻³ F-127. GdL was subsequently added (13 mg cm⁻³ based on the mixed solution) to initiate the gelation at room temperature. The gels were washed, freeze-dried, and carbonized using the procedures described above.

Characterization: The fiber structure was observed by a Hitachi-S4800 scanning electron microscope (SEM) with an energy dispersive X-ray (EDX) microanalysis detector (INCA7200, Oxford Instrument). A small piece was cut from the monolith using a blade and then adhered to a stud using double-sided carbon tape. The CNFs were imaged directly. The dry gels were coated with gold using a sputter-coater (EMITECH K550X) for 2 minutes at 25 mA before SEM imaging. The Brunauer-Emmett-Teller (BET) surface area and pore volume by N₂ sorption at 77 K were determined using a Micromeritics ASAP 2020 adsorption analyzer. Samples were degassed for 10 h at 150 °C before N₂ sorption analysis. Powder X-ray diffraction (PXRD) patterns were collected on a Panalytical X' Pert Pro Multi-Purpose Diffractometer in high-throughput transmission geometry. Cu anode was operated at 40 kV and 40 mA. Samples were pressed into the well of aluminium plate. XRD patterns were measured over 5-50°2 θ with a scan time of 60 minutes. Thermal stability of PI nanofibers was assessed using a thermalgravimetric analyzer (TGA, TA instruments, Q5000IR). The samples were heated to 800 °C at a rate of 5 °C min⁻¹ under N₂ atmosphere. Elemental analysis data was obtained from a Thermo FlashEA1112 series CHNSO elemental analyzer. The surface of the samples was studied on a VG ESCA LAB-220i XL X-ray photoelectron spectrometer (XPS) with an exciting source of Al. A hand-held pH meter (HANNA instruments) was used to monitor the pH change during the course of gelation. The pH meter was calibrated using pH 4 and pH 7 buffer solutions, and then rinsed with de-ionized water. The probe was inserted into the solution and pH readings were recorded.

Electrochemical measurements: The working electrode was prepared by casting a polytetrafluoroethylene (PTFE) impregnated sample onto a glass carbon electrode with a

diameter of 3 mm. Typically, a slurry of the active material (90%) with PTFE (10%) in N-methylpyrrolidone (NMP) with a concentration of 5 mg cm^{-3} was made, then an accurate volume ($2 \mu\text{L}$) was pipetted onto the surface of the glass carbon electrode, before allowing the NMP to evaporate in an oven overnight. Due to the very low bulk density of the CNFs, a small mass of the CNFs could form a dense film and cover the surface of the working electrode to give reliable test data.²⁷ A three-electrode cell system was used to evaluate the electrochemical performance by cyclic voltammetry (CV, CHI 660D electrochemical analyzer) at room temperature. The electrolyte used was 2 M H_2SO_4 aqueous solution. The voltage cycled from 0.1 V to 0.8 V. A platinum wire (or sheet) and an Ag/AgCl electrode were used as the counter and the reference electrodes, respectively. The capacitance value was obtained from the CV curves according to the equation: $C_{\text{avg}} = \int i dV / 2(\Delta V \nu)$, where $\int i dV$ is calculated by integrating the total area in the CV plot, i is the response current density, ΔV is the potential by measuring its voltage span from the CV plot, ν is the potential sweep rate, m is the mass of active materials, the value divided by 2 because both the charge and discharge process exist in a cycle.

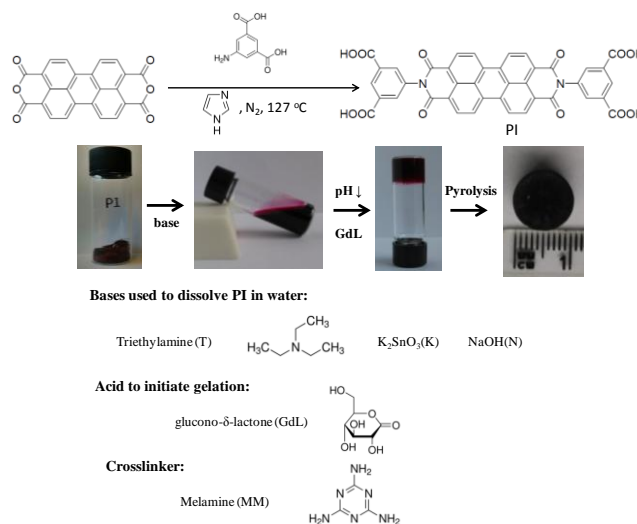
For the F-127 templated CNFs, in order to improve the stability, the working electrode was also prepared by casting a Nafion-impregnated sample onto a glassy carbon electrode. Typically, the CNFs were dispersed in an ethanol solution containing a Nafion solution (5 wt% in water) by sonication for 20 min, with a concentration of 5 mg cm^{-3} . The slurry ($2 \mu\text{L}$) was then deposited onto the glassy carbon electrode and dried in an oven, giving a loading of CNFs on the electrode at 0.14 mg cm^{-2} . The reliability of the test results was further investigated by increasing the CNF loading to 1.13 mg cm^{-2} , achieved by depositing $4 \mu\text{L}$ of the CNF dispersion in Nafion solution (5 mg cm^{-3}) and repeating 4 times. A three-electrode cell system was used to evaluate the electrochemical performance by CV and the galvanostatic charge-discharge method on a CHI 660D electrochemical workstation (Shanghai CH Instrument Co., China). The specific capacity was calculated by the equation: $C_g = (I\Delta t) / (m\Delta V)$ where I is the current loaded (A), Δt is the discharge time (s), ΔV is the potential change during the discharge process, and m is the mass of active material in a single electrode (g). The Ragone plot was obtained using the galvanostatic charge-discharge results from the 3-electrode system. The energy density (E) was calculated by $E = (C\Delta V^2) / 2$ while the power density (P) was calculated by $P = (Q\Delta V) / (2t) = E/t$.

3. Results and discussion

3.1 Preparation of CNFs from PI gels

Scheme 1 shows the synthesis of PI and the process to produce CNFs. PI has four carboxylic acid groups. However, the solubility is low in neutral water. Different bases, including K_2SnO_3 (denoted as K), NaOH (denoted as N), and triethylamine (TEA, denoted as T), were used to dissolve PI in aqueous solution. With the reduced solution pH by adding acid, the dark red solution gradually formed into a stable gel.

We firstly investigated how the bases and acids could be used to form the gels. The organic base TEA and inorganic base NaOH were initially chosen. This was to see if the use of different bases would have any impact on gel fibers. K_2SnO_3 was also selected because it was a weak base after hydrolysis in water and the element Sn might be incorporated into the CNFs after pyrolysis.²⁸ The presence of Sn/SnO₂ nanoparticles in CNFs can be very useful as electrode materials for lithium-ion batteries.^{29,30}



Scheme 1. Top: synthesis and chemical structure of PI molecule; Central: the process of fabricating carbon materials; Bottom: chemical structures of bases, acid and crosslinker used.

Gelation of PI solutions with TEA was investigated by adding HCl solution. The gels formed were inhomogeneous and brittle (see ESI, Fig. S1[†]). Glucono- δ -lactone (GdL) can hydrolyze slowly in water, which produces gluconic acid and results in a decrease in pH. GdL has been demonstrated to produce homogeneous and reproducible hydrogels from low molecular weight hydrogelators because of its controlled hydrolysis.^{24,31} In this study, it was found that homogeneous gels could be formed with GdL if the PI concentrations $> 0.5 \text{ mM}$ (see ESI, Fig. S1d[†]). Below this concentration, the gels were highly fragile. The optimal conditions to form homogeneous and strong gels were found to be 0.06 M for NaOH, 12 mg cm^{-3} for K_2SnO_3 , and PI:TEA = 1:6 respectively. GdL was added at 13 mg cm^{-3} based on the PI solution. In addition to the monolithic gel, a thin film (thickness around $50 \mu\text{m}$) could be formed simply by spreading PI + GdL solution between two glass slides, followed by gelation with time (Fig. S2). The thickness of the film could be easily adjusted by using a spacer between the slides to adjust the thickness of the precursor solution.

The formed gels were freeze-dried to produce dry red porous monoliths. Entangled but mostly discrete nanofibers were observed for T + GdL gels (Fig. S3[†]), while it was difficult to see separated fibers for the other systems. After

carbonization under Ar, the nanofibers appeared to aggregate/fuse for all the PI gels formed (Fig. S4†).

For applications with CNFs, it is desirable to have uniform and discrete nanofibers, giving rise to higher and accessible fiber surface. It is postulated that the loss of nanofibers during carbonization could be due to presence of precursor and/or base/GdL in the freeze-dried samples. A sequential washing procedure with water/acetone/cyclohexane was employed to wash the as-formed gels. The final solvent was the volatile hydrophobic cyclohexane. This was to reduce the surface tension (limiting the impact on nanofiber morphology) and facilitate the removal of solvent (melting point 6 °C) by freeze-drying.^{32,33}

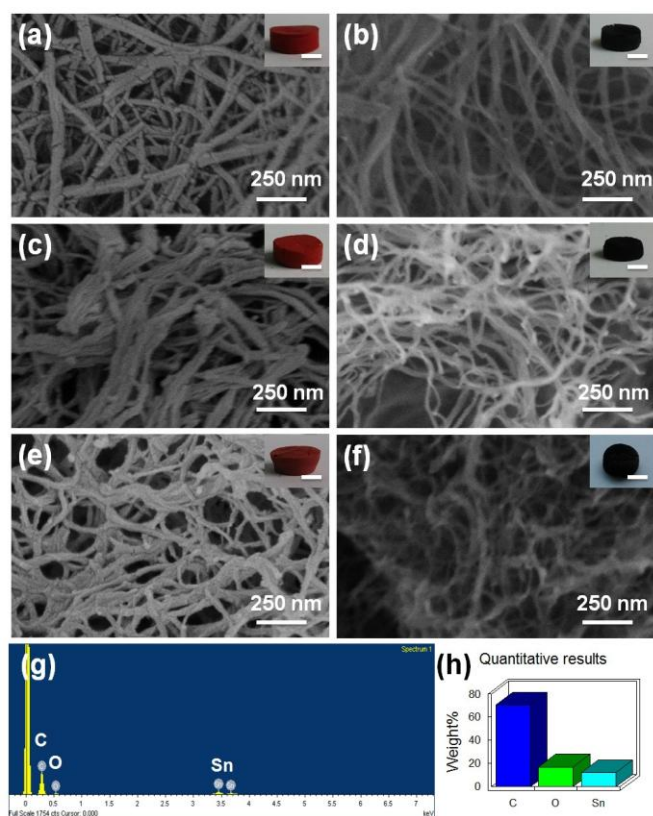


Fig. 1 SEM images of freeze-dried samples T + GdL (a), T + MM + GdL (c), K + MM + GdL (e), and the carbonized samples T + GdL (b), T + MM + GdL (d), K + MM + GdL (f). The EDX spectrum (g) and the corresponding element composition (h) of the calcined sample K + MM + GdL. The insets in (a-f) show the photos of the relevant monoliths. All samples were washed using water, acetone and cyclohexane in order. The scale bar of inset photos represents 5 mm.

After washing the as-formed gels and subsequent freeze-drying, there was no visible volumetric shrinkage. Randomly positioned and discrete nanofibers were observed (Fig. 1a). After carbonization, although there was small shrinkage of the monoliths, the nanofiber structures were retained (Fig. 1b). Discrete nanofibers with the diameters ranging from 20 to 50 nm were produced, which were continuous and relatively

uniform. The CNF film could be formed similarly but it was very fragile for handling. This study has then focused on the characterization and use of the CNF monoliths.

Nitrogen doped carbon has been reported to be a promising material for enhanced capacity and electronic conductivity by donation of its lone pair of electrons to the extended conjugated system.^{34,35} Melamine (MM), a N-rich compound, was used to crosslink PI in water to form gels.¹⁷ We hypothesized that carbonization of MM-crosslinked fibers could produce doped CNFs with higher N content. Hence, the gelation of PI solutions was performed with MM by mixing equal volume of PI solution and MM solution. The gels formed were very weak and brittle (Fig. S5†). In order to prepare strong and uniform gels, MM crosslinking was combined with the acid-triggered gelation. The PI solutions (20 mM, in 0.06 M NaOH, 12 mg cm⁻³ K₂SnO₃ or PI:TEA = 1:6) were mixed with equal volumes of 40 mM MM solution. Subsequently, GdL (13 mg cm⁻³) was added into the mixture solution. Uniform gels were formed for all the PI solutions.

The PI gels crosslinked with MM were subjected to the same washing procedure. After freeze-drying and carbonization, gel monoliths (red) and carbon monoliths (black) with discrete nanofibrous structures were obtained for T + MM + GdL and K + MM + GdL (Fig. 1c-f). The nanofibers were fused after carbonization for the N + MM + GdL fibers. For the K + MM + GdL sample, the Energy-dispersive X-ray (EDX) data showed the presence of Sn (15%) (Fig. 1g/h). Thermal gravimetric analysis (TGA) under N₂ was performed on the samples T + MM + GdL and K + MM + GdL (Fig. S6†). The initial mass loss could be attributed to the residual solvent or relatively volatile compounds until 150 °C. There was then continuous mass loss across the heating region until 800 °C. Perylene derivatives can be stable up to 400 °C.^{36,37} MM can completely sublime at a temperature of ~330 °C in an open system, which can be suppressed to a large extent if MM is heat-treated by the substances with a capacity to bridge the MM molecules. When MM was added as a cross-linker for PI, a large part of MM did not sublime. It is possible for MM to polymerize to give a carbon nitride allotrope (*g*-C₃N₄) at the high temperature.³⁸ The mass loss at 150–450 °C might be ascribed to the pyrolysis of the organic moiety of the hydrolysis product of GdL. When the carbonization temperature increased from 500 °C to 800 °C, the gradual weight loss indicated that N-doped carbon was produced slowly by the reaction between the semi-carbonized PI and the reactive nitrogen-containing species generated during the decomposition of carbon nitride.^{39,40} This test revealed a mass loss of about 79.27% for sample T + MM + GdL, and a mass loss of 76.71% for sample K + MM + GdL on heating to 800 °C at the rate 5 °C min⁻¹ under N₂. The elemental analysis found the carbon contents were higher (> 84%) with T+GdL and T+MM+GdL system (Table S1†). The N contents were in the range of 1.7 – 6.8 %.

3.2 Characterization and electrochemical evaluation of the CNFs

Fig. 2 shows the powder X-ray diffraction (PXRD) patterns of the gel fibers and the CNFs formed with MM in different base

solutions. Before carbonization, the PXRD patterns were similar, showing two diffraction peaks at $2\theta = 24$ and 26° (Fig. 2a). These results indicated a well-defined and compact π - π stacking of perylene cores in freeze-dried gel fibers.^{17,41} After carbonization, the PXRD patterns showed a broad peak at $2\theta = 16^\circ$ - 27° , indicating amorphous carbon materials (Fig. 2b). For the carbonized K + MM + GdL, there were sharp and strong peaks at $2\theta = 30.66^\circ$, 32.01° and 43.87° , corresponding to the (200), (101) and (220) planes of metallic Sn, respectively.⁴² This is a result of Sn^{4+} reduced to form metallic Sn by carbon during the high temperature carbonization process in Ar atmosphere.^{43,44} All the carbon materials formed from K_2SnO_3 solution showed the presence of metallic Sn by PXRD (Fig. S7 a/b[†]).

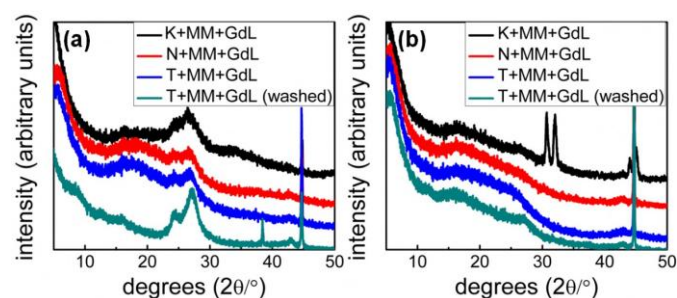


Fig. 2 PXRD patterns of samples K + MM + GdL, N + MM + GdL, T + MM + GdL, T + MM + GdL through washing treatment before (a) and after (b) carbonization.

XPS analysis of carbonized K + MM + GdL and N + MM + GdL showed the presence of C, N, and O, with the elements K and Sn specifically for the sample K + MM + GdL (Fig. 3a, b). The N1s spectrum can be fitted into four component peaks, which are located at 398.0, 400.01, 401.6 and 403.0 eV for the sample K + MM + GdL (Fig. 3c). These peaks are identified as pyridinic nitrogen (49.62%), pyrrolic nitrogen (31.17%), quaternary nitrogen (9.13%) and oxidized nitrogen (10.08%), respectively. Pentagonal pyrrolic nitrogen could be formed at low temperature, and converted to pyridinic and quaternary nitrogen as the carbonization temperature increased.^{34,35} The N content of 5.7% (atomic percentage) confirmed that the N doped carbon materials were produced successfully. The presence of elemental Sn was evidenced by two strong peaks of Sn $3d_{5/2}$ and $3d_{3/2}$ around 486.8 eV and 495.2 eV, which were attributed to ionic tin (Sn^{4+}), with a minor peak of Sn $3d_{5/2}$ at 485.1 eV attributed to metallic tin (Sn^0) (Fig. 3d). The oxide component dominated with a relative intensity of approximately 96%.⁴⁵ This seems contradictory to the finding of the PXRD pattern (Fig. 2b) where the strong diffraction peaks for metallic Sn are observed. Because the XPS only measures the surface of the materials with little penetration (5 nm), the Sn particles on the material surface were exposed to air during handling and could be readily oxidized to Sn^{4+} while they could maintain the metallic status inside the bulk material. As the PXRD analyzes the bulk powder sample, the strong diffractions from metallic Sn are thus observed while

the diffraction from the surface Sn^{4+} is negligible. The atomic percentage of Sn determined by XPS was approximately 4.10% (calculated with element peak areas with relevant atomic sensitivity factors for x-ray sources at 54.7°C). The first major peak in the XPS spectra (Fig. 3a, b) was for C1s, which may be devolved into a big peak at 284.8 eV (C-C bonds) and three minor peaks at around 286.0, 287.4 and 290.1 eV for the carbon atoms attached to oxygen atoms in the three different environment such as C-OH, C=O and COOH (Fig. S8[†]). The oxygen spectrum gave a peak at around 531.5 eV corresponding to the double bonded oxygen (Fig. S8[†]), which is contributed from SnO_2 .⁴⁶ Washed K + MM + GdL improved the nanofiber morphology but there was minimal impact on element status (Fig. S8[†] and Fig. S9[†]).

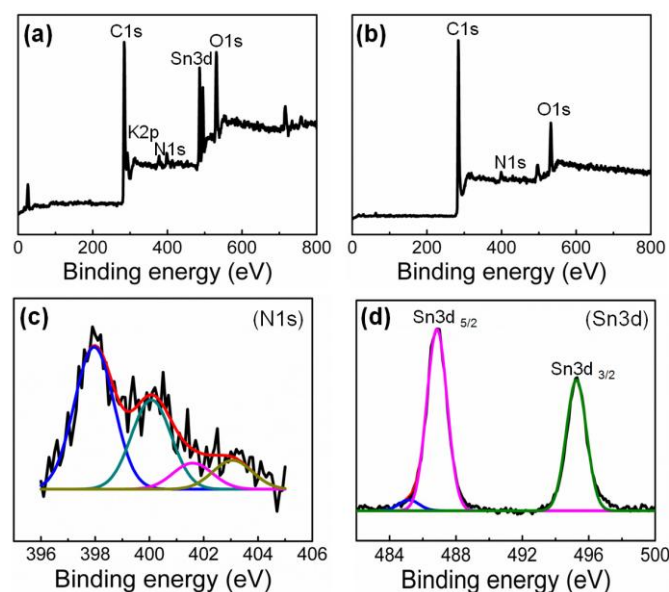


Fig. 3 XPS spectra of the calcined samples K + MM + GdL (a), N + MM + GdL (b), and the corresponding closer view and peak fitting for N1s (c) and Sn3d (d) of the calcined K + MM + GdL.

N_2 sorption analysis was employed to investigate the porosity of the representative carbon nanofiber materials. The BET surface areas of K + GdL, K + MM + GdL, N + MM + GdL and T + MM + GdL CNFs were 40, 123, 206, and $124\text{ m}^2\text{ g}^{-1}$, respectively. Such surface areas are typical for CNFs.² The N_2 isothermal curves showed the characteristics of micropores and some mesopores (Fig. S10[†]), with most of the pores in the micropore region formed during the carbonization process.

Table 1. Specific capacitance by CV testing for the CNFs with PTFE as glue to prepare the working electrode, Pt wire as counter electrode, Ag/AgCl as reference electrode, and a scan rate of 1 mV s^{-1} .

sample	Capacitance (F g^{-1})
K + GdL	25

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K + MM + GdL	59
K + MM + GdL (washed)	115
N + GdL	14
N + GdL (washed)	35
N + MM + GdL	45
N + MM + GdL (washed)	109
T + GdL	11
T + MM + GdL	53
T + MM + GdL (washed)	80
T + MM (+ F-127) + GdL (washed)	346

CNFs have been widely used as electrode materials.^{1,5} The most definite test of an electrode materials is to perform the test in a fully packaged cell. This is, however, not always practical. The specific capacitance can be satisfactorily evaluated by cyclic voltammetry (CV) and galvanostatic discharge, with the latter method correlating more closely to how a load is typically applied to a supercapacitor in the majority of applications.⁴⁷ The electrochemical cells can be a three-electrode or two-electrode system. The values obtained can be considerably different.⁴⁸ In this work, the potential of the CNFs as electrode material for supercapacitor was evaluated with a 3-electrode cell and 2 M H₂SO₄ solution as electrolyte.⁴⁹ The cyclic voltammograms of the electrodes coated with different CNF samples were recorded in a potential window from 0.1 to 0.8 V (vs Ag/AgCl) (Fig. 4). In order to see how the CNF morphology may influence the supercapacitor performance, the CNFs prepared from both washed and un-washed gels were tested. The specific capacitance of K + GdL, N + GdL, T + GdL CNFs were quite low at 25, 14 and 11 F g⁻¹, respectively. For the gelation initiated in K₂SnO₃ and TEA solution, the incorporation of MM into the gel by crosslinking PI molecules led to the CNFs with higher capacity (Fig. 4a, b, and Table 1). This was the case as well for gelation in NaOH solution (Table 1). When the as-formed gels were washed with water/acetone/cyclohexane, individually separated nanofibers were formed after carbonization (Fig. 1). The surface area of the CNFs with washing procedure was higher than that of the CNFs prepared without washing the gels (Fig. S11). Uniform CNFs structure and large specific surface area can facilitate penetration of the electrolyte solution through the electrode materials. The washing procedure seemed to affect the internal resistance of the electrode materials as well. For example, the charge/discharge curves of samples N+MM+GdL with and without washing at 10 A g⁻¹ showed that the samples without washing had a relative high internal resistance (IR drop) (Fig. S12). This resulted in enhanced capacitance for all the samples, particularly 115 F g⁻¹ for the washed K + M + GdL carbon sample.

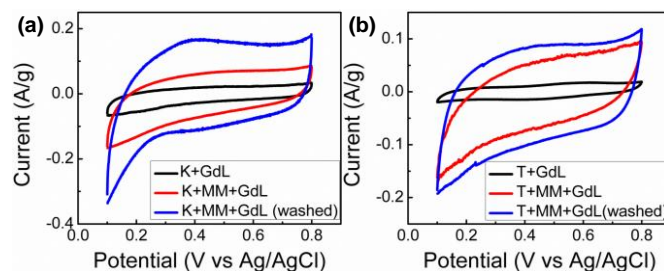


Fig. 4 Cyclic voltammograms recorded in 2 M H₂SO₄ by using different CNFs coated glassy carbon electrodes as working electrode with polytetrafluoroethene (PTFE) as glue, Pt wire as counter electrode, and Ag/AgCl electrode as reference electrode. The scan rate is 1 mV s⁻¹. (a) Comparison of the CNFs prepared from K₂SnO₃ (K) solution; (b) Comparison of the CNFs prepared from TEA (T) solution. The CNFs prepared from both washed and un-washed gels were tested.

3.3 Nonionic surfactant F-127 templated CNFs and improved supercapacitor performance

As the gel nanofibers are formed in a self-assembly process, it is easy to incorporate other molecules during self-assembly. The use of K₂SnO₃ as base to dissolve PI was an example for the preparation of Sn-incorporated CNFs, as described above. The micropores/mesopores present in the CNFs were formed during carbonization, but at a small quantity and hence a low surface area (Fig. S10[†]). CNFs with a high surface area may be highly beneficial for different applications.¹⁻⁶ Non-ionic surfactant (*e.g.*, Pluronic F-127) templating is a facile way to fabricate mesoporous CNFs and other type of mesoporous materials.^{12,50} Here, in order to produce surfactant templated CNFs, F-127 was dissolved in MM solution and then mixed with the PI-TEA solution. The gelation was initiated by adding GdL at 13 mg cm⁻³ based on the solution volume. The formed gel was washed, freeze-dried, and then carbonized in Ar. The template F-127 was removed simultaneously during carbonization.

Fig. 5a shows the randomly distributed but separated nanofibers for the F-127 templated material. N₂ sorption gave a BET surface area at 520 m² g⁻¹. The isothermal curve in Fig. 5b is typical of a microporous material. Indeed, the density functional theory (DFT) analysis indicates the pore sizes are mainly in the micropore region with the main peak centred around 0.8 nm (Fig. 5b inset). This is different from previous reports,⁵¹ where F-127 templating would usually result in the formation of mesopores.⁵⁰⁻⁵¹ We postulate that the micropores produced in the CNFs here may be the result that F-127 did not form the micelles (which is a pre-requisite for preparation of mesoporous materials) when participating in the PI gelation process. It is likely that F-127 molecular templating rather than the common micellar templating occurred in this preparation.

The F-127 templated CNFs produced a significantly improved specific capacity of 346 F g⁻¹, compared to a capacitance of 80 F g⁻¹ for the non-templated CNFs prepared under the similar condition (Table 1). The CV curve was nearly

rectangular in shape, indicating good charge propagation within the electrode (Fig. S13[†]). Aqueous electrolyte solution was used in this study for the CV test. The electrochemical window for aqueous electrolytes is from 0 V to approximately 1 V.⁴⁸ The voltage range used in the CV tests in this study was 0.1 – 0.8 V⁴⁹ because there was a significant hump in current after 0.9 V, corresponding to irreversible chemical reactions (Fig. S14[†]).⁵² The concentration of H₂SO₄ solution was changed from 2 M to 1 M to see how this would impact the capacity by CV. The two curves were very similar (Fig. S15[†]). The specific capacitance (204 F g⁻¹) using 1 M H₂SO₄ aqueous solution as electrolyte solution was slightly less than that (215 F g⁻¹) of using 2 M H₂SO₄ solution at the scan rate of 10 mV s⁻¹.

Due to its improved electrode stability, a Nafion solution was used to impregnate the CNF sample and prepare the electrode. A specific capacitance of 320 F g⁻¹ was recorded for the rate of 2 mV s⁻¹. The specific capacitance decreased with the increase of scan rate but still reaching 118 F g⁻¹ at a scan rate of 200 mV s⁻¹ (Table S2[†]); whilst the shapes of all the curves were nearly rectangular (Fig. S16a[†]). The symmetric galvanostatic charge-discharge curves were obtained from the same working electrode with current densities ≥ 1 A g⁻¹ (Fig. S16c[†]). A high capacitance of 192 F g⁻¹ was obtained at the current density of 1 A g⁻¹. The value was reduced to 105 F g⁻¹ at the current density of 20 A g⁻¹ (Table S3[†]). The area loading of the CNFs on the working electrode was 0.14 mg cm⁻². This loading is thought to be low and may not be meaningful for real supercapacitor applications. The reliability of the test

results may be doubtful. To address these concerns, the area loading of the CNFs was increased to 1.13 mg cm⁻². As can be seen in Fig. 5c and 5d, the shapes of the CV curves are nearly rectangular and the specific capacitance results are comparable to the electrode with 0.14 mg cm⁻² CNFs. At low scan rates (< 20 mV s⁻¹) or low current density (2 A g⁻¹), the specific capacitance from 1.13 mg cm⁻² CNF electrode was lower (Table S2 & Table S3[†]). However, the specific capacitance was higher than the electrode with 0.14 mg cm⁻² CNFs when the scan rates or current density increased, indicating a better rate performance. The specific capacitance achieved at 20 A g⁻¹ was 121 F g⁻¹ (Table S3[†]). The specific capacitance of the F-127 templated CNFs is among the very high values for CNFs.^{5,15,35} F-127 is a water-soluble poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) triblock copolymer with high molecular weight (MW =12 600). The self-assembled F-127 acts as sacrificial templates during carbonization process. This has led to the formation of CNFs with higher surface area and more interconnected micropores/mesopores. Particularly, a relatively wide pore size distribution from 2-5 nm was observed. In this work, aqueous H₂SO₄ solution was used as aqueous electrolyte, and the size of the hydrated ion [SO₄²⁻(H₂O)₁₂] is about 5.33 Å.⁵³ The improved surface area and pore size distribution have contributed positively to the movement of the ions, leading to improved capacitance.

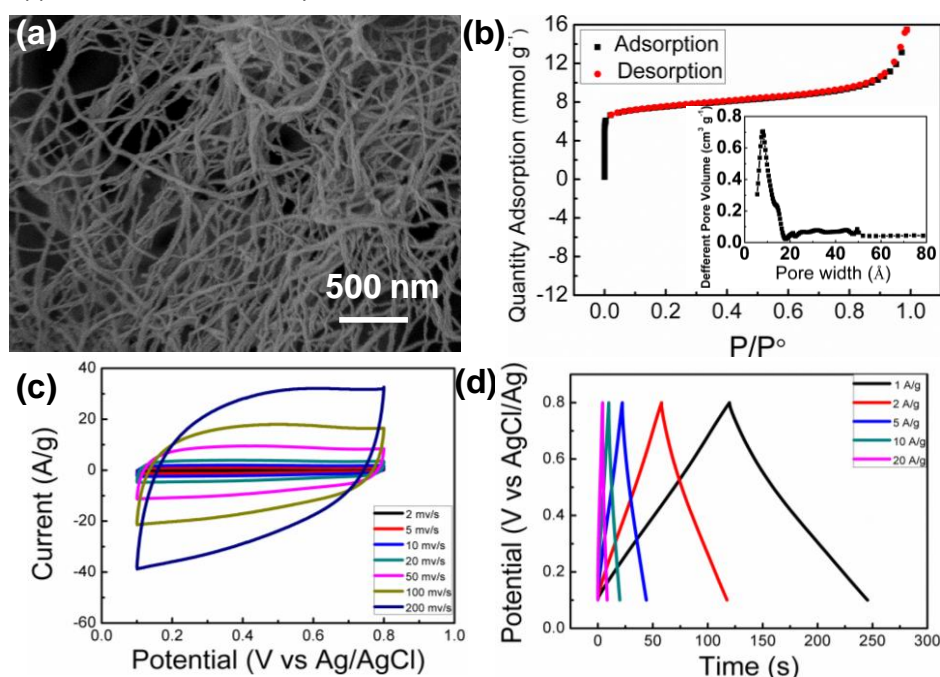


Fig. 5 F-127 templated CNFs (prepared from the washed gel) and the characterization data. (a) The SEM image showing the nanofiber morphology. (b) N₂ gas sorption isothermal curve and the pore size distribution (inset) calculated by DFT method. (c) Cyclic voltammograms at different scanning rates. (d) Constant current charge-discharge curves at different current density. The Nafion-glued CNFs as working electrode with a CNF area loading of 1.13 mg cm⁻², Pt sheet as counter electrode, and Ag/AgCl electrode as reference electrode.



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The overall performance of the F-127 templated CNFs electrode is shown in a Ragone plot (Fig. 6a), obtained from the galvanostatic charge-discharge data at different current densities.⁵² The highest gravimetric energy density achieved was around 13 Wh kg⁻¹. As a trend, the energy density decreased with the increase of power density. To investigate the electrochemical stability of the F-127 templated CNF electrode materials, galvanostatic charge/discharge measurements were performed repeatedly at a current density of 4 A g⁻¹. Interestingly, the specific capacitance increased slightly with more test cycles (Fig. 6b). This phenomenon perhaps resulted from the activation process. At the initial stage, active materials had not been fully used. After repetitive charge/discharge cycles, the electrochemically active materials would be fully exposed to the electrolyte. The specific capacitance of the F-127 templated CNF materials could reach a high value of 226 F g⁻¹ at 1000 charge/discharge cycles, indicating that the capacitance of F-127 templated CNF materials was very stable. This is among the highest specific performance for a high current density at 4 A g⁻¹ (Table S4† and the relevant referenes). What's more, the previously reported methods for fabricating CNFs (such as electrospinning, templating, and vapor growth) require the use of harsh conditions or volatile organic solvents. Instead, our method has used water as solvent and form gel fibers under mild conditions, which is green and sustainable. Because the gel fibers can be formed in any vessel with the change of pH in aqueous solutions, this method may be easily scaled up to produce a large quantity of CNFs.

4. Conclusions

In summary, we have developed a water-based approach to prepare CNFs from a perylene diimide derivative via a simple gelation and carbonization procedure. Triethylamine was used to help to dissolve and could produce the best discrete CNFs compared to NaOH and K₂SnO₃. However, the use of K₂SnO₃ as base resulted in the incorporation of Sn/SnO₂ into the CNFs. Melamine was employed to crosslink the precursor molecules and produce N-doped CNFs after carbonization. It was necessary to wash the as-formed gels with water/acetone/cyclohexane in order to produce CNFs with relatively uniform separated CNFs with the diameters around 20–50 nm. The CNFs showed BET surface areas in the region of 100–200 m² g⁻¹. The specific capacitance measured by CV was quite low for the CNFs prepared from un-washed gels (aggregated carbon nanofibers), but could be improved to over 100 F g⁻¹ for the CNFs prepared from washed gels (separated carbon nanofibers). More interestingly, a non-ionic surfactant Pluronic F-127 could be easily incorporated during the

gelation process, which produced the CNFs (diameters around 50 nm) with much improved surface area at 520 m² g⁻¹ and specific capacitance of 346 F g⁻¹ at the scan rate of 1 mV s⁻¹ or 192 F g⁻¹ at the current density of 1 A g⁻¹ with a CNF area loading of 0.14 mg cm⁻². Increasing the CNF loading (1.13 mg cm⁻²) produced comparable capacitance results. The specific capacitance was lower at low current density but became higher at the current density > 2 A g⁻¹, with a specific capacitance of 121 F g⁻¹ at 20 A g⁻¹. The stability test of the CNFs electrode showed a specific capacitance of 226 F g⁻¹ for 1000 charge/discharge cycles at 4 A g⁻¹. Although porous carbons can be prepared by carbonizing easily available biomaterials and demonstrate some excellent applications, there are very limited controls on porosity, composition and the form of the materials (e.g., thin films).⁵⁴ The method developed here may be easily modified and optimized to prepare various doped and functional nanofibrous materials with desired fiber diameter, pore structure, and material format, which are highly important for a range of applications.

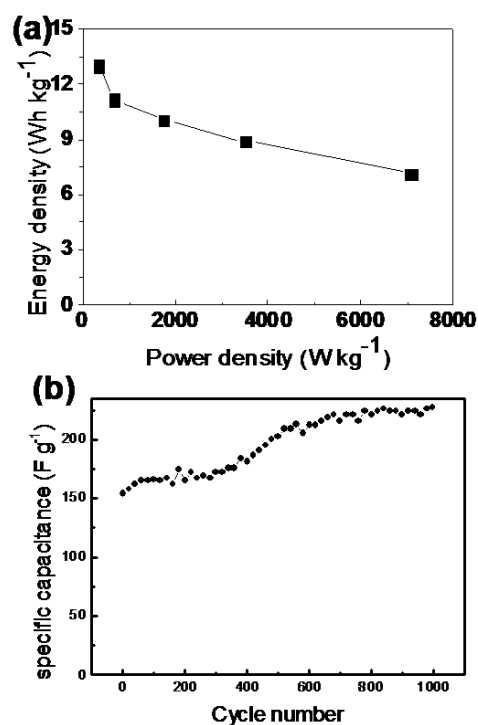


Fig. 6 (a) Ragone plots of the prepared supercapacitor for the electrode prepared from F-127-templated CNFs. (b) The graph showing the stability of the F-127-templated CNF electrode for up to 1000 charge/discharge cycles at current density of 4 A g⁻¹

with a CNF area loading of 0.14 mg cm⁻². The other test conditions were the same as used in Fig. 5.

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A water-based approach to fabricating CNFs from a perylene diimide derivative (PI) via a simple gelation process and a carbonization procedure is described. The CNFs materials can be easily produced with doped N or Sn/SnO₂. Importantly, the use of non-ionic surfactant Pluronic F-127 as templates can generate CNFs with a high surface area at 520 m² g⁻¹ and high capacitance as electrode materials for supercapacitors.

Keyword: carbon nanofiber, self-assembly, perylene diimide, pyrolysis, capacitance

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Title: Carbon nanofibers by pyrolysis of self-assembled perylene diimide derivative gels as supercapacitor electrode materials

