



Low-density functionalized amorphous carbon nanofoam as binder-free Thin-film Supercapacitor electrode

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ABSTRACT

Nanoporous carbon materials containing small domains of sp^2 -carbon with highly disordered structures are promising for supercapacitor applications. Herein, we synthesize amorphous carbon nanofoam with 98% volumetric void fraction and low mass density of around 30 mg/cm³ by pulsed laser deposition at room temperature. With the unavoidable oxygen functional groups on the nanoporous surface, carbon nanofoam and nitrogen-functionalized carbon nanofoams are directly grown on the desired substrate under different background gases (Ar, N₂, N₂-H₂), and employed as supercapacitor electrodes. Among the background gases used in synthesis, the use of nitrogen yields nanofoam with higher thickness and more N-content with higher graphitic-N. From the test of amorphous carbon nanofoam supercapacitor device, nitrogenated amorphous carbon electrode shows a higher areal capacitance of 4.1 mF/cm² at 20 mV/s in aqueous electrolyte, a better capacitance retention at higher current, and excellent cycle stability (98%) over 10,000 charge-discharge cycles are achieved compared to not-functionalized counterpart prepared under Ar background gas (2.7 mF/cm² and cycle stability of 88%).

1. Introduction

Amorphous carbon (*a*-C) has been broadly investigated fundamentally due to its typical characteristics including the presence of all sp , sp^2 and sp^3 hybridization, low-range order, huge amounts of defects, and plenty of active sites for electrochemical reactions, etc [1–3]. Depending upon the sp^2/sp^3 contribution and hydrogen content, *a*-C is mainly categorized into graphite-like, diamond-like, and polymer-like [4]. Each category shows unique optical, mechanical, and electrical properties, and is extensively used for energy storage, electronics and other applications [1,5]. A recent study anticipates freestanding monolayer amorphous carbon for magnetic recording devices and flexible electronic applications [6]. Among the carbon nanostructures, *a*-C nanofoams (NFs) have received significant attention due to their porous structure with high surface area, huge void fraction, [7] low mass density, [8,9] hydrophilicity, [7] unconventional magnetism [10,11], excellent thermal properties [12]. Moreover, porous carbon NF has been explored as a

suitable active material for Na-ion storage, [13] supercapacitors, [14] catalysis, [15] solar steam generation, [16] and Faradaic desalination of brackish water [17]. It was also used as a target in ion acceleration schemes by interaction with ultra-intense laser pulses [18,19], as mechanical platform to decorate nanoparticles such as Pt/Pd for electrochemical detection of cancer cells or Au and Ag to enhance the charge storage performance for supercapacitor applications [20].

Carbon NF were first synthesized by pulsed laser deposition (PLD) [21,22]. Although several synthesis techniques such as hydrothermal methods, [8] sol-gel methods, [23] pyrolysis [24], laser processing of a graphene oxide followed by transfer of the film [25] etc. were employed to obtain this unique nanostructure [12,26], they have their own limitations. For example, an ultralightweight carbon NF prepared by hydrothermal method needs 48 hours of synthesis at a temperature more than 165 °C, [27] while high temperature is one of the essential parameters to obtain NFs using pyrolysis method [24]. PLD has the advantage of growing the material at room temperature within

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relatively low deposition time and on any substrate [7]. To obtain porous structures like carbon NF in PLD, deposition is carried out at high deposition pressure and substrates are placed outside the shock wave front of plasma plume. Moreover, it has been shown that the mass density of carbon NF can be controlled by tuning the deposition gas type and pressure [9]. Till now, in most cases, ablation of a graphite target is performed in inert gases (Ar, He etc.) [9,3] while the role of other gases such as nitrogen and hydrogen on the deposition of *a*-C NF has not been explored in detail.

Heteroatoms (e.g. nitrogen, sulphur, phosphorous) doping into the carbon matrix is one of the common adoptable strategies to enhance the charge-storage performance of electrode material [28]. It has been reported that N-doped carbon NF derived from amino acid chelate complex exhibited an excellent charge-storage performance and was used for solar energy harvesting applications [14]. Also, nitrogen incorporation into the *a*-C matrix or nitrogenated *a*-C (*a*-C:N) showed a significant effect on the capacitance, work function and semiconductor properties [29,28]. Femtosecond pulsed laser deposited *a*-C:N film showed excellent electron transfer kinetics, and is anticipated as a promising material for electrochemical detection of electroactive pollutants [30]. In our previous report, [7] we showed that nitrogenated graphite-like *a*-C NF, grown by PLD at room temperature, could be a potential candidate for electrochemical energy storage application. However, the role of hydrogen- and nitrogen-content in the structure of *a*-C NF and its impact on the potential application such as supercapacitor is not addressed so far.

To elucidate this role, the present report focuses on the deposition of pristine and functionalized *a*-C NF directly on the substrates (silicon and carbon paper current collector) by pulsed laser deposition at room temperature. The pristine *a*-C NF was deposited under Ar background gas, whereas functionalized *a*-C NFs were prepared under N₂ and N₂-H₂, named *a*-C:N NF and *a*-C:N:H NF, respectively, keeping other synthesis parameters constant. The growth rate, thickness and mass density and structural properties of those NFs were thoroughly investigated and correlated with the plasma plume chemistry under different background gases. Finally, as-grown NF was employed as a binder-free and conductive additive-free electrode for aqueous electrochemical energy storage applications.

2. Experimental methods

2.1. Synthesis methodology

a-C NF were prepared by PLD using graphite (1 inch diameter) as the target with a purity of 99.99% (purchased from Testbourne B. V.). The graphite target was placed on a rotating/translating holder, while the Si (100) and carbon paper substrates were placed on the rotating substrate holder at a distance of 38 mm from the target. The *ns*-PLD setup exploits the second harmonic ($\lambda = 532$ nm) of a Q-switched Nd:YAG laser (pulse duration of 5–7 ns), with a repetition rate of 10 Hz and a fluence of 2.7 J/cm². Prior to the deposition, the chamber was evacuated down to the base pressure of 2×10^{-3} Pa using first a rotary pump followed by a turbomolecular pump. Thereafter, desired background gases, Ar, N₂ and 95% N₂-5% H₂, were injected into the deposition unit. The deposition pressure was maintained at 500 Pa for each 15 min deposition. The deposition unit was vented, and the as-deposited NFs were taken out to examine the morphology, structure, and electrochemical properties as supercapacitor electrodes.

2.2. Microscopy and spectroscopy

A field-emission scanning electron microscope (FE-SEM, ZEISS SUPRA 40, Jena, Germany) was employed to probe the morphology of carbon NFs. Energy Dispersive X-ray (EDX) spectroscopy was used at the acceleration voltage of 5 kV to evaluate the local chemical composition, using a Peltier-cooled silicon drift detector (Oxford Instruments) and the

Aztec software for quantification. A specific MATLAB code (named EDDIE software) was used to calculate the mass density (ρ) of NFs with the input of area under Si, carbon and oxygen contents, an average thickness of the NF, and the details of each element such as atomic number and mass number [31]. The volumetric void fraction of carbon

NFs was estimated using the relation of $\% \text{ porosity} = \left(1 - \frac{\rho_{a-C \text{ NF}}}{\rho_{\text{graphite}}}\right) \times 100$, where density of graphite is (ρ_{graphite}) of 2.2 g/cm³.

Surface elemental compositions and bonding environment of NFs were examined by X-ray photoelectron spectroscopy (XPS) using a non-monochromatized X-ray source (Mg anode, photon energy 1253.6 eV), maintained at a power of 200 W. The kinetic energy of the photoemitted electrons was measured using a hemispherical analyzer with a 150 mm mean radius, PHOIBOS150 from SPECS GmbH. The spectra were acquired with a pass energy of 20 eV, with an energy resolution of 0.9 eV (full width at half maxima, FWHM). The pressure in the measurement chamber during the XPS measurements was about 1×10^{-10} Torr. The fitting details are provided in our previous report [7]. Briefly, peaks were fitted after Shirley background subtraction using CasaXPS software, and at.% of elemental compositions were extracted from peak area ratios after correction by Scofield relative sensitivity factors (C = 1.0, N = 1.77, O = 2.85) [32]. For C1s, the asymmetric *sp*²-C peak is fitted with Gaussian-Lorentzian lineshape (GL (30)) with asymmetric factor (T200) and other symmetric carbon peaks with GL(30) by setting the range of FWHM to 1.2–2 eV. The FWHM of oxygenated carbon peaks, deconvoluted O1s peaks, and deconvoluted N1s peaks are set to 1.8–2.2 eV. The *sp*³-C peak is shifted by 0.7–1 eV from *sp*²-C and hydroxyl/ether, carbonyl and carboxylic groups are shifted approximately 1.5, 3, and 4.5 eV higher, respectively.

A Renishaw InVia Raman spectrometer was used to collect the spectra of carbon NFs. Each Raman spectrum was recorded using the 514.5 nm excitation radiation from an Ar⁺ laser source with a power of 0.4 mW, an 1800 line/mm grating spectrometer and a 50× objective lens, with 20 accumulations for 10 s each.

2.3. Electrochemical measurements

The electrochemical performances of the NFs were investigated in a 2-electrode configuration using Swagelok Cell (SKU: ANR-B01, Singapore), and basic 6 M KOH (ACS reagent, Sigma-Aldrich, ≥85%) was used as the aqueous electrolyte. The cell was assembled by sandwiching modified separator-soaked-electrolytes between two symmetric carbon NFs grown directly on carbon paper (Figure S2 of supplementary Material). Prior to the test, electrodes and modified separator were dipped into the electrolyte solution for 1 hour, and the cyclic voltammetry was conducted within the electrochemical stable voltage range of 0–0.8 V at 100 mV/s for 400 cycles. Cyclic voltammograms at different scan rates ranging from 20 to 1000 mV/s and charge-discharge at different currents from 125 to 500 μ A were recorded using a Palmsens4 electrochemical workstation (PALMSENS, The Netherlands). The areal capacitance was calculated using the equation: $C_A = \frac{\int IdV}{A \cdot \nu \cdot V}$, where I is the current, ν is the scan rate, A is the geometric area of the electrode and V is the voltage of the device. The areal capacitance of the device from charge-discharge profile was estimated using the relation of $C_{\text{areal}} = \frac{I_d \cdot t_d}{A \cdot V}$, where I_d and t_d are the discharge current and the discharge time, respectively. Single electrode capacitance = $4 \times$ device capacitance. The volumetric capacitance of electrode materials, C_V , is estimated by dividing the areal capacitance by the total thickness of both electrodes. Energy density (E) and power density (P) of devices were estimated via the relations of $E = 0.5 C_{\text{areal}} V^2$ and $P = (E \cdot \nu)/V$, respectively.

3. Results and discussions

3.1. Morphological investigation

Typical top-view and cross-sectional scanning electron micrographs of NFs are displayed in Fig. 1. Morphology-wise, there are no distinguishable changes that can be seen for the NFs grown in different background gases. The estimated mass densities (ρ) of the *a*-C, *a*-C:N and *a*-C:H:N NF are 32.6, 43.3 and 42.6 mg/cm³, respectively (Table 1). This fact reflects that the NFs containing nitrogen are similar to each other but different from pristine ones (*a*-C). Secondly, the NF can be categorized as an ultralightweight material, whose density is much lower than the heavy carbons (mass density > 1 g/cm³ for, e.g., diamond, graphite, and *a*-C) and other carbon nanostructures (with mass density in the range of 100–300 mg/cm³ for, e.g., carbon nanotubes, nanoporous carbons, and carbon aerogels) [8]. Fig. 1 also confirms that NF is highly porous in nature. The estimated volumetric void fraction of all three NFs is around 98%, which is noticeably higher than the other carbon-based nanostructures such as carbon nanosheets prepared by plasma-enhanced chemical vapour deposition (71%) [33]. Such amount of porosity offers higher electrolyte ions accessibility to the electrode surface leading to high charge-storage performance [34]. A noticeable difference between the NFs synthesized under different background gases is the thickness. The deposition rate for *a*-C, *a*-C:N, and *a*-C:N:H NF is found to be 0.85, 2.01 and 1.84 mm/min, respectively. The difference in growth rate of NF under the different background gases is attributed to the nature of background gas used during the deposition, as discussed below.

Upon laser irradiation, as the plasma plume forms and expands, the ablated species move towards the substrate, and finally get deposited on its surface. During ablation in a high-pressure background gas, a shockwave front forms and propagates until the so-called stopping distance is achieved, resulting in plume spatial confinement, and enhanced visible glowing related to the number of collisional events occurring between ablated and gas species [35]. Thus, it is obvious that the plume propagation length, flux distribution, evolution of shockwaves, plasma dynamics, kinetic energies, and/or arrival rates of the various constituents within the plume, and backward motion of ablated species are

deeply affected by the background gas, chiefly in terms of chemical reactivity and atomic weight. Therefore, the type of background gas plays a crucial role in determining the structural quality, deposition rate, thickness, and mass density of deposited materials. In turn, one can visualize the shape evolution of the time-integrated plasma plume from Fig. 2. The distance between the cloud center and the shockwave front is estimated to be 2.96, 3.22 and 3.37 cm for *a*-C, *a*-C:N, and *a*-C:N:H NF, respectively. Ar possesses a heavier molecular weight (atomic mass of 39.948 amu), yielding higher cloud density and hence a shorter propagation of the shockwave front compared to the lighter gas (N₂, atomic mass of 14.007 amu). At the same time, the backward motion of ablated species becomes more dominant when a heavier gas is used. To validate this assumption, we placed the substrates on the target-side and studied the impact of back-ablated species. It has been evidenced that the *a*-C NF deposited on target side under Ar (*a*-C NFT) has the maximum thickness of 29.5 mm (Figure S1). On the other hand, the maximum thickness for *a*-C:N NFT and *a*-C:N:H NFT is found to be 14.9 and 11.2 mm, respectively (Figure S1). Eventually, we have seen in our previous work that the deposition of the ablated species in the backside is the result of ballistic aggregation under highly reactive species, while the diffusive aggregation occurs for the film deposited on the frontside substrate [7]. Compared to a previous report where carbon NF was deposited at 300 Pa, [7] here the carbon NF was deposited at 500 Pa in order to obtain highly porous structure. Therefore, the investigation on the deposition formed by backward ablated species (Fig. 2d-f) indicates that use of lighter mass is advantageous to lower the backward motion of ablated species and to synthesize the nanostructure on the frontside with higher yield. However, the lower deposition rate of *a*-C:N:H NF compared to *a*-C:N NF could be due to the etching of *sp*-C, *sp*²-C and *sp*³-C by atomic hydrogen at different rates along with the possibility of CH-like species formation inside the plasma plume [36]. Further detailed investigation on the plasma diagnostic is the subject of research.

3.2. Structural investigation

The Raman spectra of the three NFs are shown in Fig. 3a. All the spectra present typical *sp*² features in the 1300–1600 cm^{−1} range,

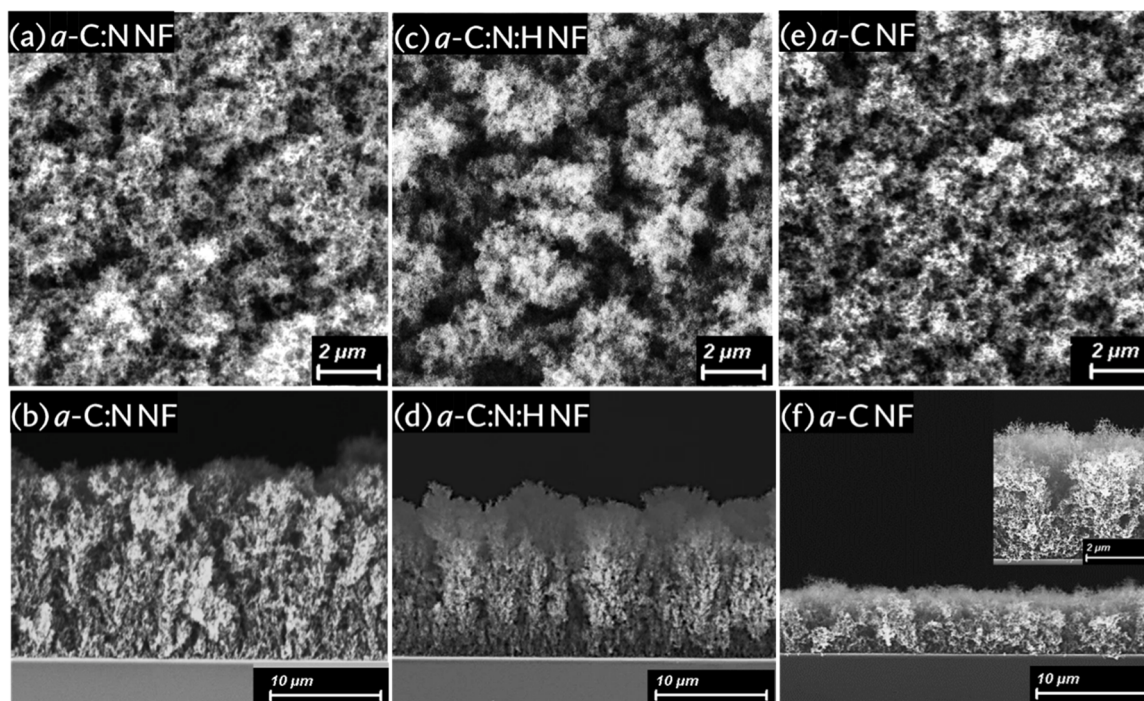


Fig. 1. Scanning electron micrograph of carbon nanofoam. (a-b) *a*-C:N NF, (c-d) *a*-C:N:H NF, and (e-f) *a*-C NF.

Table 1

Physico-chemical and electrochemical properties of amorphous carbon nanofoams.

Nanofoam (Background gas used in PLD)	Morphological result			Raman extracted parameters			XPS result			Charge-storage properties of device		
	Avg. Thickness (μm)	Mass density (mg/cm^3)	Vol. void fraction (%)	G-peak Position (cm^{-1})	G-peak Full width at half maximum (cm^{-1})	Intensity ratio of D- to-G peak	C/O/ N (at. %)	sp^2 sp^3	Graphitic- N (at.%)	Areal (vol.) capacitance in mF/cm^2 (F/cm^3) at 20 mV/s	rate performance (%) at 1000 mV/s	cycle stability after 10,000 cycles at 125 μA (%)
$\alpha\text{-C:N}$ (N_2)	10.1	43.3	98	1583	125	0.71	60.1/ 32.1/ 7.8	2.86	57.2	4.1 (2)	22	98
$\alpha\text{-C:N:H}$ (95% N_2 -5% H_2)	9.2	42.6	98	1584	118	0.54	57.5/ 39.4/ 3.1	1.88	32.7	1.2 (0.7)	18	88
$\alpha\text{-C}$ (Ar)	4.3	32.6	98.5	1575	138	0.51	55.2/ 42.2/ 2.6	2.56	35.7	2.7 (3.1)	36	73

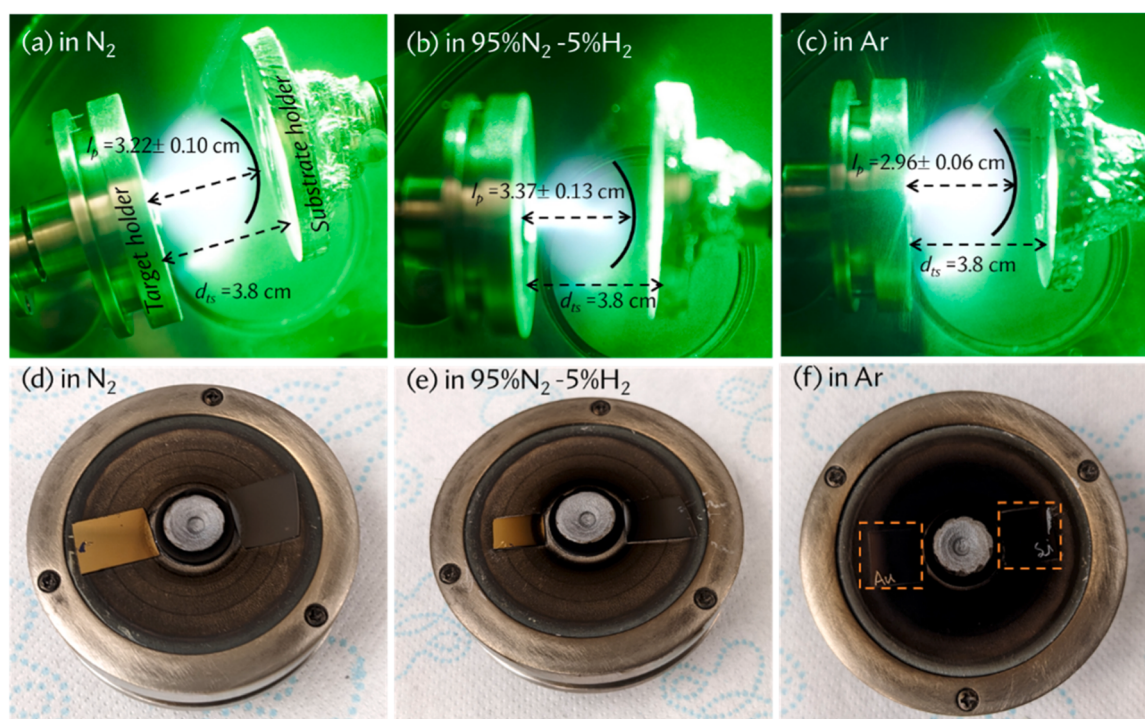


Fig. 2. Digital photographs of plasma plume for the nanofoam grown in (a) N_2 , (b) N_2 - H_2 and (c) Ar. The ablation occurs on the small graphite target by green laser with a fluence of $2.7 \text{ J}/\text{cm}^2$ and the background pressure of 500 Pa in all cases. (see experimental section for details). Optical photograph of target after the growth of nanofoams in (d) N_2 , (e) N_2 - H_2 and (f) Ar.

namely D-peak and G-peak, and a broad second order Raman band in the region 2800 – 3000 cm^{-1} where also CH bonds, when present, give contribution [37]. The three NFs, all prepared by ablating graphite in PLD under a background gas at room temperature, are amorphous as expected. Compared to $\alpha\text{-C}$ NF and $\alpha\text{-C:N}$ NF, a higher photoluminescence (PL) background is noticed for the $\alpha\text{-C:N:H}$ NF grown in N_2 - H_2 background gas, suggesting the incorporation of hydrogen in the carbon matrix [38]. The minimal PL background of $\alpha\text{-C}$ and $\alpha\text{-C:N}$ NFs may be attributed to the adsorbed water upon exposure in ambient environments or poor vacuum during the deposition. No evident differences in the Raman spectrum of NFs grown under different background gas can be seen in Fig. 3a. Anyway, a more quantitative analysis, based on fitting with deconvoluted peaks after background subtraction, reveals some structural differences among them (Fig. 3b). The D-peak was fitted with a Lorentzian lineshape, while the G-peak with a Breit-Weigner-Fano lineshape, and the position and FWHM of the

G-peak, and the intensity ratio D-to-G peaks (I_D/I_G) are reported in Table 1. Comparatively, $\alpha\text{-C}$ NF shows the lowest G-peak position with the largest FWHM (1575 cm^{-1} and $\sim 138 \text{ cm}^{-1}$, respectively), accompanied by I_D/I_G estimated to be 0.51. The G-peak position for both $\alpha\text{-C:N}$ and $\alpha\text{-C:N:H}$ is graphitic-like (about 1583 cm^{-1}), with similar FWHM, lower than for $\alpha\text{-C}$ NF, suggesting a larger amount of sp^2 clustering probably induced by nitrogen [36]. On the other hand, the intensity ratio, I_D/I_G , is higher for $\alpha\text{-C:N}$ NF than $\alpha\text{-C:N:H}$ NF (0.71 and 0.54, respectively), suggesting a lower disorder for the sp^2 clusters in presence of hydrogen. This fact is attributed to the nitrogen-induced sp^2 -clustering [39].

Elemental compositional of NFs is investigated by both bulk EDX (Fig. 4a, and Figure S3 of supplementary Material) and surface-sensitive XPS technique (Fig. 4b-c). Among the NFs, a higher amount of carbon content is obtained for $\alpha\text{-C:N}$ NF compared to the other two NFs from both the techniques (Table 1). While EDX results indicate that $\alpha\text{-C}$ NF

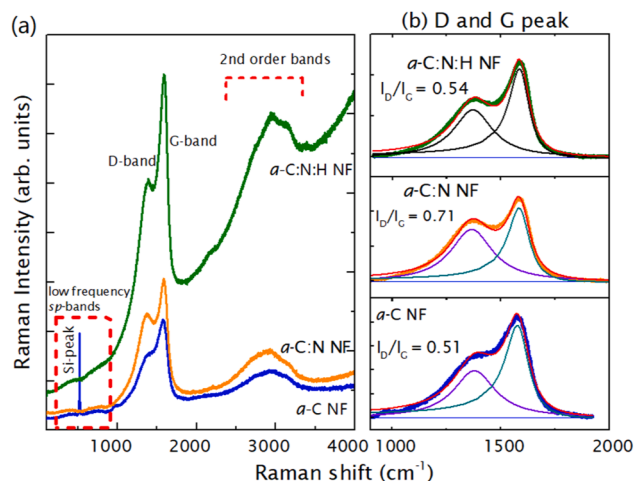


Fig. 3. (color online): Visible Raman spectra of (a) *a*-C, *a*-C:N and *a*-C:N:H nanofoams grown on Si substrate. (b) Magnified 1st order Raman spectra of nanofoams with deconvoluted peaks.

contains only carbon and oxygen (Figure S3 of supplementary Material), XPS showed the presence of 2.6 at.% of nitrogen along with them (Fig. 4c). The results obtained indicate that nitrogen and oxygen are physisorbed on highly porous *a*-C NF since the deposition was carried out under pure Ar gas environment. On the other hand, both the EDX and XPS results for *a*-C:N NF reflect the relatively higher nitrogen incorporation in the *a*-C matrix than the pristine NF. Although the N-content is hardly quantified from the EDX spectra of *a*-C:N:H NF, a closer look reveals a very weak signature of nitrogen (Figure S3 of supplementary Material). The result obtained here about the role of hydrogen is also in good agreement with the deposition rate, average thickness, mass density and graphitic quality of NF as obtained from the Raman spectroscopic results.

To gain deeper insight on the bonding between carbon, nitrogen and oxygen, high-resolution XPS spectra are deconvoluted. A high resolution

C1s spectra of *a*-C:N NF with deconvoluted peaks is shown in Fig. 4(d), which consists of *sp*-C (at around 282.6 eV) [40] *sp*²-C (at around 284.6 eV), *sp*³-C (at around 285.7 eV), C—O/C—N (at around 286.4 eV), C = O/C = N (at around 288.4 eV), and -COO (at around 290.4 eV). The high-resolution spectra of each element for *a*-C and *a*-C:N:H NF are provided in Figure S4 of the supporting file. The *sp*²-C/*sp*³-C ratio is reported in Table 1 for the three NFs, and it is found to be higher for *a*-C:N NF (2.86) compared to that of *a*-C NF (2.56) and *a*-C:N:H NF (1.88). A higher *sp*³-carbon content is likely for *a*-C:N:H NF as it is deposited in presence of hydrogen, which can form C—H bonds with *sp*³ hybridization. Incorporation of hydrogen in the NF is also confirmed by the high PL background in the Raman spectrum. The high resolution N1s spectra of NFs is also inspected to probe the different bonding of nitrogen, such as pyrrolic, pyridinic, graphitic and NO_x and satellite peak (Fig. 4e and S4). It has been seen that *a*-C:N NF contains higher graphitic nitrogen compared to the other two NFs (Fig. 4f). This can further confirm the graphitic-like *sp*² clustering when only nitrogen is present during the deposition. All the NFs also have COOH, COH, C = O and N—C = O functional groups, and variable relative content in the NFs (Fig. 4 g-h and Figure S4).

3.3. Electrochemical investigation

To exploit the NFs for potential applications, charge-storage performance was investigated and summarized in Table 1. Prior to the measurement, the voltage of device was optimized based on the cyclic voltammograms at different voltages keeping the scan rate fixed (Figure S5 of supplementary file). Fig. 5a shows the cyclic voltammograms of *a*-C:N NF at different scan rates of 20 to 1000 mV/s, whereas cyclic voltammogram of *a*-C and *a*-C:N:H NF are supplied in Figure S6(a-b) supplementary file. A quasi-rectangular cyclic voltammogram and unchanged shape at higher scan rate indicates near-ideal supercapacitor behavior of NFs. Since the average thickness of the NFs prepared under different background gases (Fig. 1d-f) are different, the volumetric cyclic voltammogram of all NFs is compared at 500 mV/s and shown in Fig. 5b. However, the shape of cyclic voltammogram of *a*-C:N is comparatively found to be better in terms of quasi-rectangularity than that of *a*-C NF

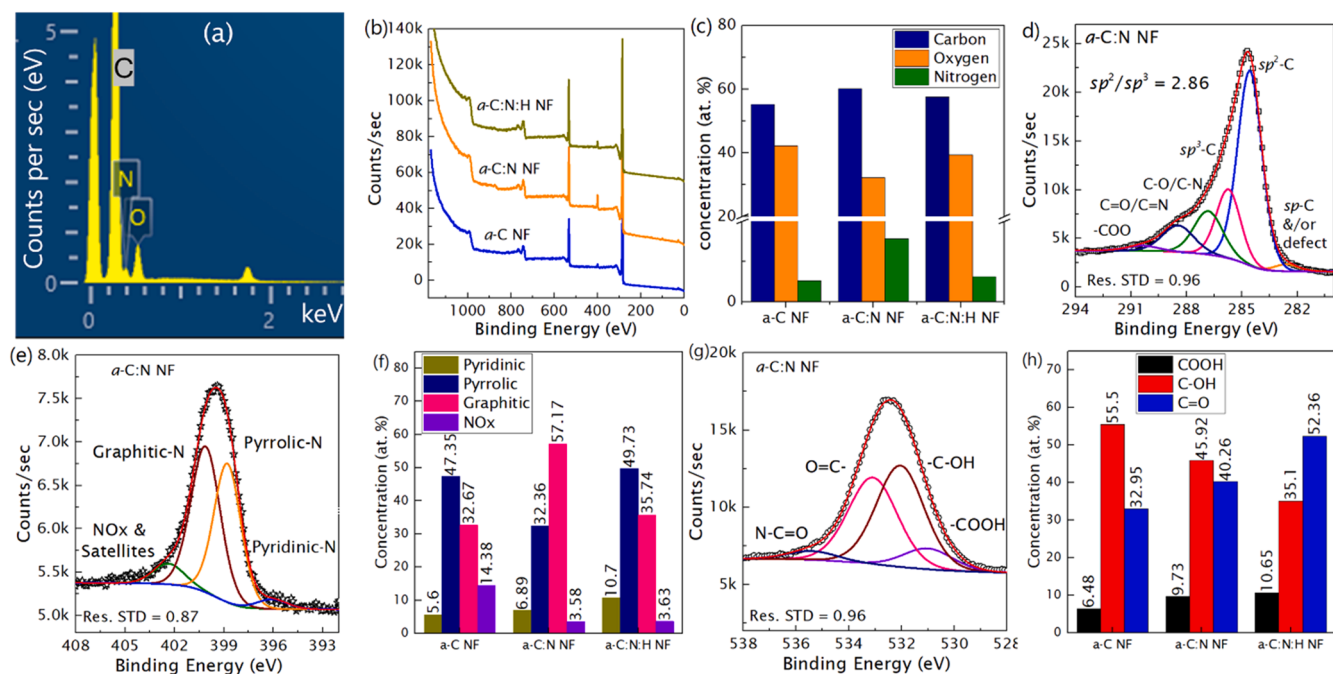


Fig. 4. (a) EDX spectra of *a*-C:N nanofoams. XPS (b) survey spectra, and (c) plot of elemental compositions of all nanofoams. High resolution (d) C1s, (e) N1s spectra of *a*-C:N nanofoams with (f) relative concentration of N-bonding of all nanofoams. (g) O1s spectra of *a*-C:N nanofoams with (h) relative concentration of O-bonding of all nanofoams.

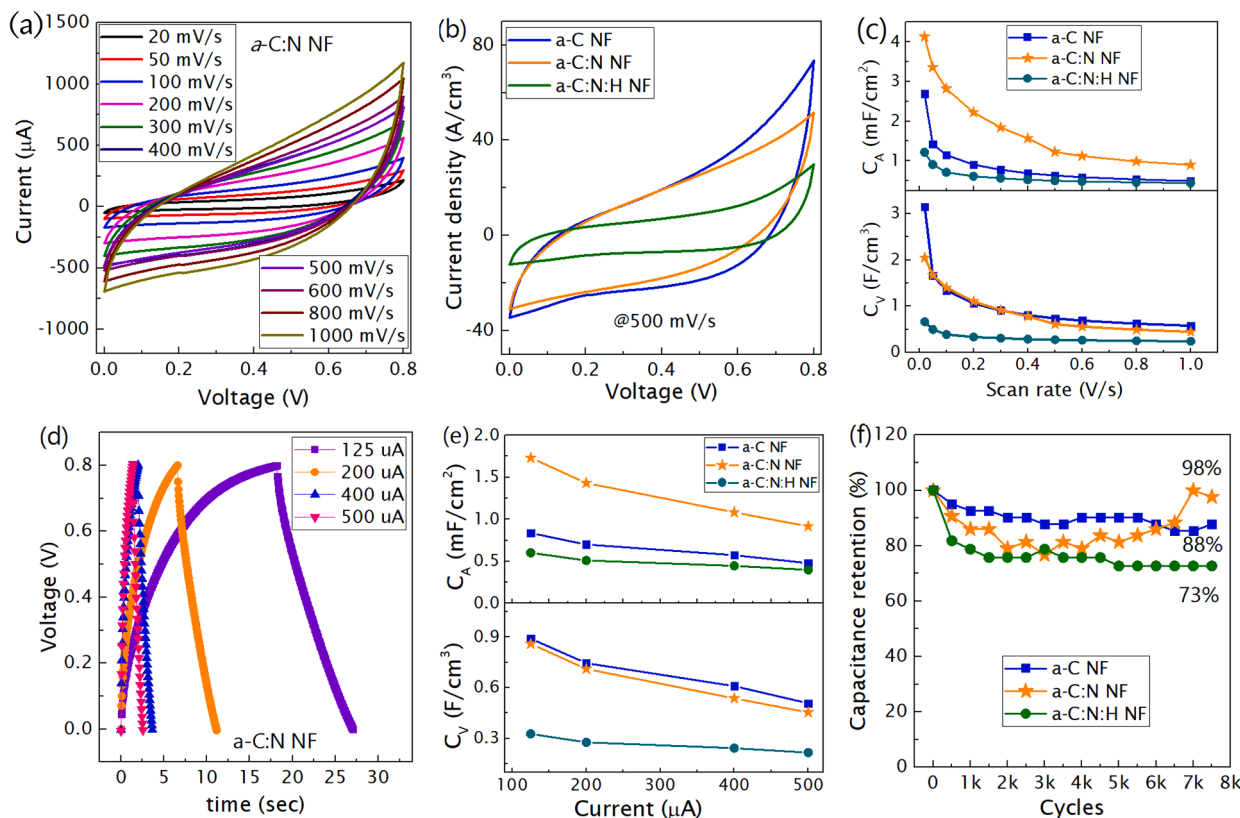


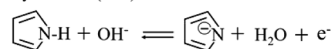
Fig. 5. (a) Cyclic voltammogram of *a*-C:N nanofoams at different scan rates of 20 to 1000 mV/s. (b) Comparative volumetric cyclic voltammogram and (c) areal and volumetric capacitance of *a*-C, *a*-C:N and *a*-C:N:H nanofoams. (d) Charge-discharge profile of *a*-C:N nanofoams at different currents. (e) Plot of volumetric and areal capacitance of nanofoams at different currents. (f) Cycle stability of nanofoams. In Figure (c) and (e), C_A is areal capacitance and C_V is volumetric capacitance.

(Fig. 5b). Both the areal capacitance and volumetric capacitance of the NFs are estimated from cyclic voltammogram at different scan rates and plotted in Fig. 5c. The estimated areal capacitance of *a*-C, *a*-C:N, and *a*-C:N:H NF devices is 2.7, 4, and 1.2 mF/cm² at 20 mV/s, respectively. The areal capacitance of carbon NFs-based symmetric supercapacitor device obtained from our study is found to be much higher than the device made of pristine (0.16 mF/cm² at 100 mV/s) and functionalized vertical graphenes (1.6 mF/cm²) [41], *sp*-carbon atomic wires wrapped polymer (2.4 mF/cm² at 20 mV/s), [42] CdS coated ZnO nanorods (0.03 mF/cm² at 50 mV/s), [43] TiO₂ nanogrid (0.74 mF/cm²) [44] and titanate hydrate nanogrid (0.08 mF/cm²) [44], etc.

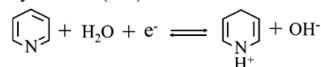
While compared volumetrically, *a*-C NF delivered relatively higher specific capacitance (3.15 F/cm³ at 20 mV/s) than the *a*-C:N NF (2.05 F/cm³) but the rate capacitance at 1000 mV/s for *a*-C and *a*-C:N NF is found to be 18% and 22%, respectively. The NF-based aqueous symmetric device exhibits comparable volumetric capacitance of supercapacitor device reported in the literature such as FEG/MoO_{3-x}/FEG (3.96 F/cm³ at 1 mA/cm², where FEG stands for functionalized partially exfoliated graphite), [45] Fe₂O₃ nanorod//MnO₂ (1.2 F/cm³ at 0.5 mA/cm²), [46] hydrogen-treated titania (H-TiO₂)@carbon nanowires//H-TiO₂@MnO₂ nanowires (0.71 F/cm³ at 10 mV/s), [47] and reduced graphene oxide//MnO₂ nanorod (0.72 F/cm³ at 10 mV/s) [48]. The charge-discharge test of NFs at different current densities was also performed, which is shown in Fig. 5(d) and Figure S6(c-d) in supplementary file. The areal and volumetric capacitance are also estimated at different current values and plotted in Fig. 5(e). The charge-discharge result of the NF-based symmetric supercapacitor devices agree with cyclic voltammogram result. The cycle stability test over 10,000 charge-discharge cycles at constant current indicates excellent stability of *a*-C:N NFs compared to other studied NFs. Although *a*-C:N:H NF is thicker compared to *a*-C NF, the higher areal (and volumetric) capacitance of *a*-C:N NF is attributed to the higher *sp*²/*sp*³-content, the

presence of lower amount of COOH group in the structure, the higher N-content with higher graphitic-N compared and the relatively higher structural disorder, as discussed in XPS and Raman spectroscopic investigations (Table 1). In comparison to pristine *a*-C NF, better charge-storage performance of *a*-C:N NFs is due to the N-doping with graphitic-N and pyrrolic-N mostly. Incorporating N-doping enhances the density of states of *sp*²-carbon at the Fermi level, and the associated capacitance so called quantum capacitance can be enhanced [49]. Among the N-configurations, positively charged graphitic-N attracts the electrolyte anions, contributes in double layer formation by structural disorder, and improve the charge-transfer kinetics [28]. Other N-functional groups, in particular pyrrolic-N and pyridinic-N, are well-known to contribute the pseudocapacitance in alkaline medium via the relations as below:

Pyrrolic-N (N-5)



Pyridinic-N (N-6)



The areal and volumetric energy densities of symmetric supercapacitor at various areal and volumetric power densities are estimated and illustrated in Ragone plot (Fig. 6a-b). The charge-storage capabilities of *a*-C NF supercapacitors are found to be comparable with the existing reports and commercial devices (Fig. 6) [50–58]. We would like to highlight that the thickness of the film in most of the reports is lower than that of *a*-C nanofoam. For example, thickness of carbon electrode is 400 nm [50] whereas the thickness for *a*-C NFs are in the range of 4–10 μm. Low thickness and low mass density often result in high charge-storage performance [58]. The performance of *a*-C NF supercapacitor device in terms of areal power density and volumetric energy

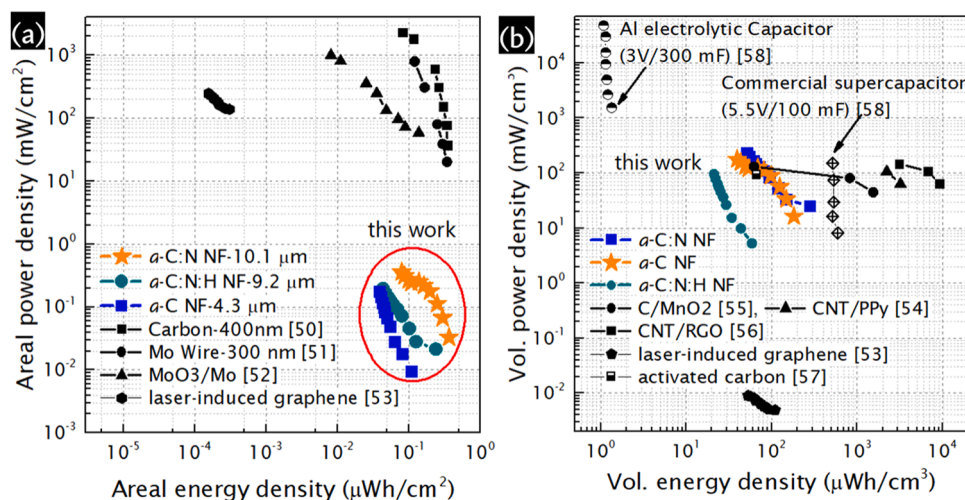


Fig. 6. (a) Areal and (b) volumetric Ragone plot of carbon nanofoam supercapacitor devices comparing devices with others in the literature. [CNT: carbon nanotube, PPy: Polypyrrole, RGO: reduced graphene oxide].

density can be enhanced further by improving the NFs optimized in the present study, which will be communicated soon in our next article. In summary, the performance of α -C NFs ensures its potential application towards macro- to micro supercapacitor devices where the thickness of the electrode is limited in the range of 10 μ m [59].

3.4. Post-mortem analysis

In order to check the morphology and structural quality of NFs, we have recorded the SEM images and Raman spectra of NFs before and after electrochemical investigations. For the after-electrochemical investigations, the NFs were washed with water several times to remove any residue of electrolyte and dried in an ambient environment. The morphology of α -C:N NFs before and after electrochemical investigations is shown in Fig. 7(a) and 7(b), respectively. As can be seen, the NFs are agglomerated but still maintain the foam-like morphology. Similar observations have been seen for the other NFs studied here and hence not shown. Fig. 7(c) is the linear background subtracted normalized Raman spectra of α -C:N NFs before and after the electrochemical test. Both spectra show the typical α -C features, and they almost overlapped on each other except for slight changes. To probe the slight changes, Raman spectra were deconvoluted as mentioned in the experimental sections and the result is shown in Table 2.

The advantages of carbon NFs prepared by PLD are as follows: (i) the carbon-based active materials do not need any binder and conductive additives to fabricate the electrode; (ii) unlike the chemical vapor

deposited graphene-based structure or carbon structure grown at high temperature (around 800 °C or more), [60] the deposition of carbon NF was conducted at room temperature and hence additional transfer process is not needed to use this materials for flexible supercapacitor applications; (iii) unlike the other carbon nanostructures, post treatment to improve the wettability (hydrophobic to hydrophilic) and hence charge-storage performance is not required [41] since the NFs are hydrophilic [7]; and (iv) N-incorporation using pulsed laser deposition is carried out at room temperature without a post-treatment in the presence of harmful NH_3 , thanks to the out-of-equilibrium growth conditions achieved during PLD. N-incorporation in the carbon matrix is usually challenging unless high temperature growth of nanocarbon with a N-precursor [5,14] or post-deposition annealing treatment under caustic and unsafe NH_3 at high temperature is performed. Table 3 highlights the α -C NFs electrode preparation and compares the properties with other similar carbon nanostructures.

4. Conclusion

In summary, a nitrogenated amorphous carbon nanofoam (α -C:N NF) directly on the current collector is synthesized by pulsed laser deposition at room temperature using nitrogen as a background gas. The α -C NF is highly porous with 98% volumetric void fraction, very lightweight with mass density of around 43 mg/cm^3 , and low range order. To validate the influence of nitrogen in α -C matrix, the deposition of NFs was also carried out using Ar and $\text{N}_2\text{-H}_2$ background gases, while keeping other

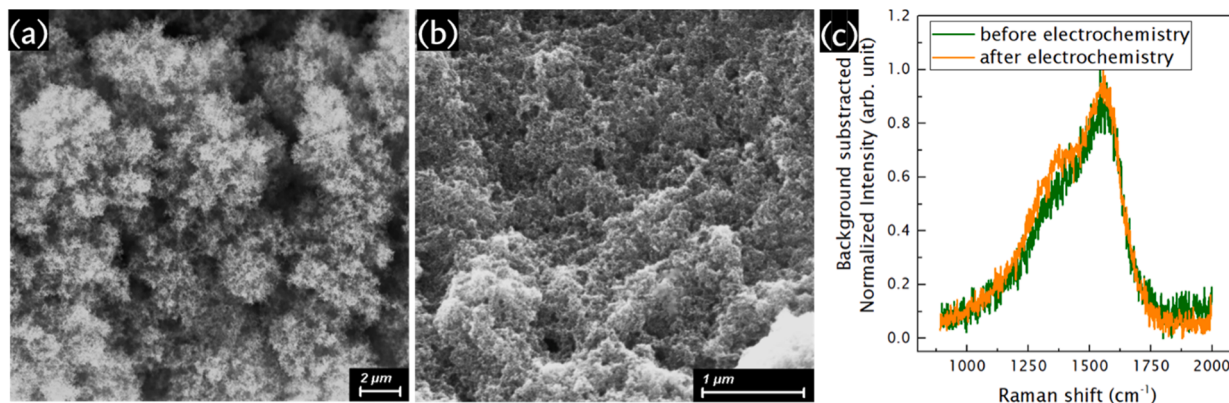


Fig. 7. Post-mortem analysis. Scanning electron micrograph of α -C:N NFs (a) before and (b) after electrochemistry. (c) Raman spectra of α -C:N NFs before and after electrochemistry. Here the substrate is carbon paper.

Table 2

Raman extracted parameters of carbon NFs before and after electrochemical investigations.

	a-C:N NF		a-C:N:H NF		a-C NF	
	Before electrochemistry	After electrochemistry	Before electrochemistry	After electrochemistry	Before electrochemistry	After electrochemistry
G-peak position (cm^{-1})	1568	1562	1562	1573	1578	1565
FWHM of G-peak (cm^{-1})	145	169	142	147	109	164
I_D/I_G	0.78	0.65	0.4	0.54	0.65	0.57

Table 3

Comparison of preparation method and properties of similar carbon nanostructures.

Carbon structures	Electrode fabrication strategy	Properties
Carbon/Graphene nanosheets/nanowalls [33]	Plasma enhanced chemical vapor deposition. Can be grown directly on any substrate at the temperature of 750 °C	mass density = 535 mg/ cm^3 , Porosity – 71%, hydrophobic
Ultrathin carbon NF [8]	Naphtalene-Mediated Hydrothermal Sucrose Carbonization. growth temperature = 155 °C for 5 hrs. Need to wash the product and further processing is needed to use as electrode	mass density = 85 mg/ cm^3
Carbon aerogels [61]	Pyrolysis of resorcinol–formaldehyde aerogel at temperature of 600–1100 °C	surface area (400–800 m^2/g) and ultrafine cell/pore size (<100 nm), bulk densities of 0.55–0.60 g/cm^3
Graphene aerogel [62]	Freeze casting at –100 °C followed by freeze-drying and thermal reduction at 800 °C under Ar environment	Lightweight, high porosity and high surface area
CNT scaffolds [63]	Pyrolysis at 1150 °C	Mass density = 20–240 mg/cm^3
N,P-doped a-C foam (char) [5]	combustion of epoxy-based intumescent composite followed by annealing at 600–900 °C in argon. The char was dispersed in 1 mL of isopropanol, and 50 μL of Nafion for ink preparation	Density = 1.7–2.0 mg/cc . surface area of 970.6–2498 m^2/g .
Carbon NF[25]	Laser irradiation of GO target and transfer to desired substrate by water-transfer process.	–
N-doped porous carbon NF[13]	Freeze-drying the transparent gel under liquid nitrogen and heat treatment at 600 °C followed by NH_3 treatment at 400 °C. Standard way the slurry was prepared to fabricate the electrode	Porous structure with measured surface area around 350 m^2/g
Pristine and N-containing a-C NF [This work]	Pulsed laser deposition, It can be grown directly on desired substrate at room temperature.	mass density = 30–50 mg/cm^3 , Porosity > 90%. hydrophilic

deposition parameters constant. Without the use of any binder and conductive-additives, the as-grown NFs are employed as supercapacitor electrodes. It has been seen that a-C:N NF with higher average thickness and more yield, higher sp^2/sp^3 content, more disordered structure, and higher N-content with more graphitic-N delivered better charge-storage performance compared to the other studied NFs. The aqueous symmetric supercapacitor device exhibited a high areal capacitance of 4.1 mF/cm^2 at 20 mV/s in aqueous electrolyte, excellent retention at high current, and 98% stability over 10,000 charge-discharge cycles.

Authors contributions

S.G. and C.S.C. planned and conceptualized the work. S. G. and A.M. performed the PLD deposition. S. G. did the Raman spectroscopy of

samples and interpreted the result with V.R., S. G. and M.R. did the electrochemical measurements and assisted in the analysis. F.G. and G. B. did the XPS measurements. S.G. wrote the draft and all co-authors revised the manuscript and approved the final version of the manuscript.

Data Availability statement

All the data of this study are available in the main manuscript and the Supplementary Information.

CRediT authorship contribution statement

Subrata Ghosh: Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Massimiliano Righi:** Investigation, Formal analysis, Data curation. **Andrea Macrelli:** Writing – review & editing, Methodology, Investigation. **Francesco Goto:** Investigation, Data curation. **Marco Agozzino:** Data curation. **Gianlorenzo Bussetti:** Writing – review & editing, Visualization, Validation. **Valeria Russo:** Writing – review & editing, Visualization, Validation, Supervision. **Andrea Li Bassi:** Writing – review & editing, Visualization, Validation, Supervision. **Carlo S. Casari:** Writing – review & editing, Visualization, Validation, Supervision, Conceptualization.

Declaration of competing interest

The authors declare no competing financial interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.cartre.2025.100516](https://doi.org/10.1016/j.cartre.2025.100516).

Data availability

Data will be made available on request.

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