Electronic Supplementary Information

Remarkable solid-state proton conduction in sulfur- and nitrogen-functionalized few-layer graphene

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Chemicals:

Graphite powder (particle size 150 microns, Cat# 496588), ammonia (25%, NH_4OH), sodium hydrogen sulphite ($NaHSO_3$), hydrogen peroxide (50%, H_2O_2), and potassium permanganate ($KMnO_4$) were purchased from Sigma-Aldrich, Merck. Chlorosulfonic acid ($ClHSO_3$) was purchased from Alfa Aeser. Concentrated sulphuric acid (H_2SO_4) and acetone were purchased from Pallav chemicals and Spectrochem, India, respectively. Solvents and reagents have been purchased from commercial sources and utilized directly without additional purification.

Characterization:

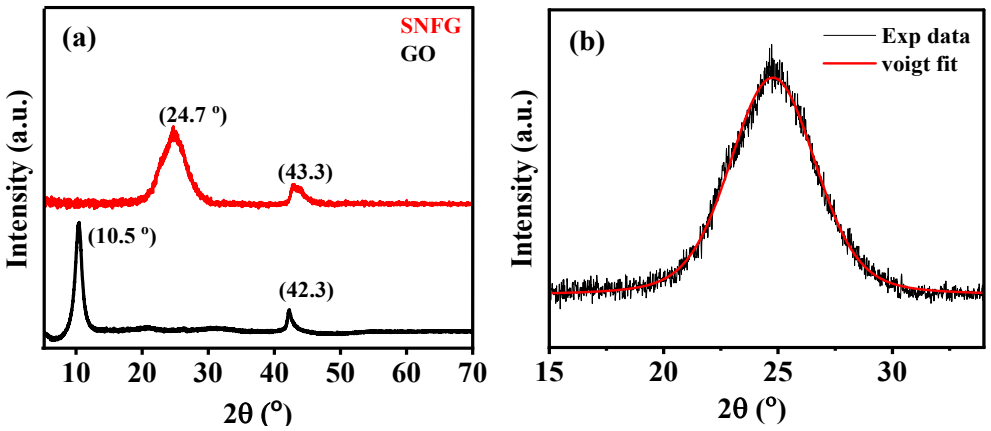
Powder X-ray diffraction (PXRD) spectra of the GO and SNFG were recorded using PANalytical Empyrean XRD using Cu Kα radiation (1.54 Å) in a 2θ range of 5-80°. Functional groups in SNFG were analysed using FT-IR spectroscopy. Spectra were collected using PerkinElmer Model UATR Spectrum

Two Instrument in the range of 500-4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) experiments were performed using Thermofisher with scan time 1 h per element for core level scan (Energy band of 20 eV, with pass setting of 23.5 eV, 0.025 eV step, 100 ms time per step, 5 cycles). Percentage elemental composition was calculated and analyzed by a fully automated PC controlled elemental analyzer. The Raman spectra of the material was recorded by Lab RAM HR 800 (HORIBA) with exciting wavelength of 532.8 nm. For morphological study, SEM were performed using high-resolution field emission scanning electron microscope (HR-FESEM) Zeiss of model ULTRA Plus at 20 kV. For sample preparation, samples were spread on carbon tape and dried. TEM experiments were performed using FEI Talos F200X instrument at an accelerating voltage of 200 kV. Samples were prepared by drop-casting a 0.5 mg suspension in 150 µL of isopropanol (IPA) onto a carbon-coated copper grid and allowing the solvent to evaporate under ambient conditions overnight. Thermal gravimetric analysis (TGA) was performed by Perkin Elmer TGA 4000 instruments in a temperature range from 30-900 °C at a scan rate of 10 °C/min with a N_2 flow rate of 10 mL/min. Nitrogen adsorption/desorption studies were conducted to provide insights into the porous properties of SNFG materials. Before performing the experiment, sample was degassed under a vacuum at 80 °C for 24 h. Pressure dependent water S4 adsorption/desorption measurements were performed using Quantachrome Autosorb, QUA211011 analyser. Prior to measurement, powdered samples were degassed at 80 °C for 24 h and water was adsorbed in vapour form. For two probe electrical conductivity measurement, solid pellets were made from the respective material by pressing them under hydraulic pressure and placed in a Swagelok cell for solid-state I-V measurement. For solid state proton conductivity study, humidity and temperature conditions were controlled in an ESPEC temperature-humidity programmable chamber (model SH-222). Experiments were carried out in the frequency range of 1 MHz-1 Hz using a two-probe setup by using the SP-240 BioLogic instrument as a frequency analyser.

Synthesis:

Sulfur- and nitrogen-functionalized few-layer graphene (SNFG) was synthesized from the precursor graphite oxide (GO). First, GO was prepared from graphite via a modified Hummer's method following a

method previously reported by our group without addition of $NaNO_3$.[1] Thereafter, GO was modified to nitrogen- and oxygen-functionalized few-layer graphene (NOFG-D) employing Bucherer method wherein GO was treated with ammonia and sodium bisulfite in hydrothermal at 210 °C for 5 h following a previously reported method by our group.[2] Afterward, 80 mg of NOFG-D was sonicated in 40 ml of DMF solvent for 30 min and then reacted with different volume of chlorosulfonic acid (3, 6 and 9 ml) in an ice bath. The solution was stirred for 24 h in room temperature. It was then filtered and washed with water to remove excess of acid to obtain sulfur- and nitrogen-functionalized few-layer graphene (SNFG). Depending on the amount of sulfonic acid added (3/6/9 ml) during synthesis, the materials were named as SNFG-3, SNFG-6 and SNFG-9. SNFG-9 was found to be the best proton conducting material and for simplicity, this material has been mentioned as SNFG in the main manuscript.



PXRD analysis using Scherer equation

Figure S1: (a) PXRD pattern of SNFG and GO. (b) Voigt function fitting of SNFG.

Calculation for interlayer distance "d":

Using the Bragg's law:

$n\lambda = 2d\sin\theta$

where n is an integer

λ = wavelength of incident light

d = interlayer distance

n = 1, λ = 1.54 Å, $2\theta = 24.8°$, $\theta = 12.3°$

d= 1.54/2 sin (12.3°) = **3.6 Å**

Calculation for crystalline length 'L$_c$' and no. of layers 'N':

Scherrer formula is, $L_c = (K\lambda)/(\beta\cos\theta)$

K = dimensionless shape factor, typical value is 0.9 for L_c.

β = line broadening at full width half maxima in radian = β was determined by Voigt fitting

θ = 12.4= 0.216 radian

$L_c = (0.90\times1.54)/ (0.0765\times \cos (0.216))$

L_c = 17 Å

N = Number of layers

N = 17 /3.6 ≈ **5 layers**

Raman spectra

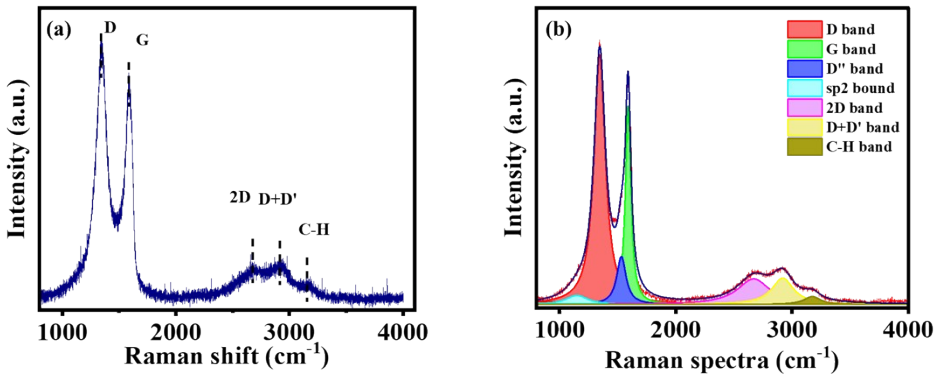


Figure S2: (a) Raman spectra of SNFG and (b) Fitting of Raman spectra.

One of the crucial methods for graphite material structure analysis is Raman spectroscopy for which Cançado et al. provided a suitable formula for computing the given grain size (Equation S1).[3]

$$L_a = (2.4\times10^{-10})\lambda_{laser}^4 (\frac{I_D}{I_G})^{-1} \ldots \text{(S1)}^4$$

Hence, L_a in this study was = $(2.4\times10^{-10}\times(532)^4)/2.58$=7.4 nm

Raman spectra of low frequency region was deconvoluted into four peaks (Figure S2a), sp^2 bound, D-band, D'-band, and G-band at 1113, 1346, 1512, and 1590 cm^{-1} respectively.[5] Similarly, fitting of the high-frequency region was deconvoluted into three peaks (Figure S2b), wherein peaks were centered at 2670, 2919, and 3173 cm^{-1} reflected 2D-band, D+D' band, and C-H band respectively.[6]

Thermo-gravimetric analysis (TGA)

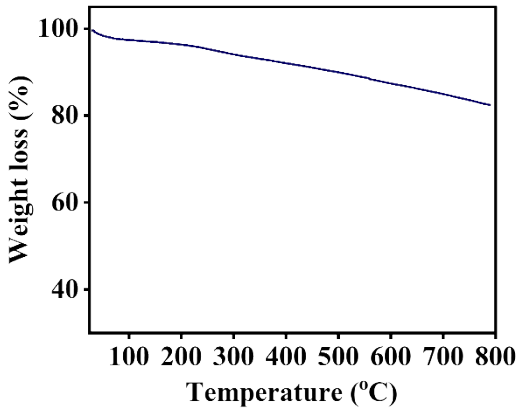


Figure S3: (a) TGA curve of SNFG.

N_2 adsorption/desorption isotherm

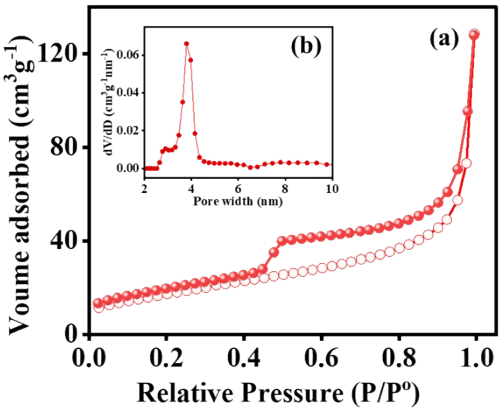


Figure S4: (a) Nitrogen adsorption/desorption isotherm at 77 K, (b) pore distribution using NLDFT method for SNFG.

N_2 adsorption/desorption profile for SNFG exhibited type-III/IV isotherm profile with hysteresis loop of H2 type (according to IUPAC classification) in the range of (0.45-1.0) for P/P_0.These findings revealed the mesoporous nature of the material. BET surface area and pore volume were 63 m^2/g and 0.12 cm^3/g respectively. The pore width was in the range of 3.8 nm, calculated using the NLDFT method (inset Figure S4b).

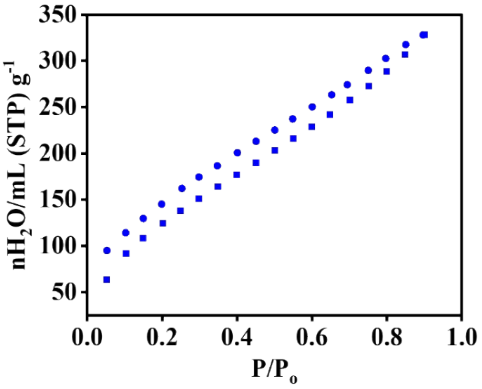


Figure S5: Pressure dependent reversible water uptake of SNFG.

Two probe electrical conductivity measurement

The prepared solid pellets were placed in a Swagelok cell for solid-state *I-V* measurement. Electrical conductivities were determined utilizing Equations S2-S4. *R* is the resistance calculated from the slope of the *I-V* curve. "*l*" and *A* are the thickness and area of the pellets (πr^2), respectively. κ and ρ are conductivity and resistivity, respectively. Typically, the thickness and area of the pellets were 0.20 cm and 1.130 cm^2, respectively.

$V = IR$ …… (S2)

$R = \rho\, {}^{l}/_{A}$ ……. (S3)

$\kappa = {}^{1}/_{\rho}$…… (S4)

In this study, κ was found to be 6.6×10^{-2} Scm^{-1}, calculated using "*l*", *A* and *R* values. *R* was calculated from *I-V* curve slope which was found to be 2.67 Ω.

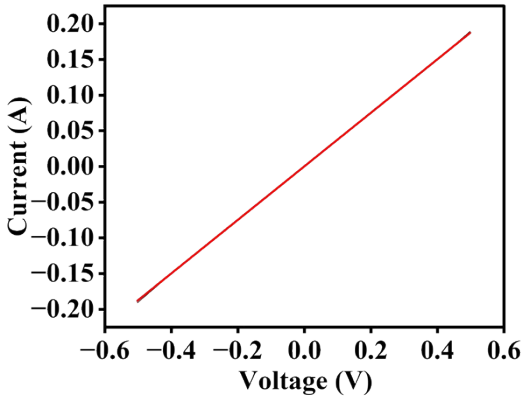


Figure S6: I-V curve of SNFG for electrical conductivity measurement.

Experimental Details of the Proton Conductivity Measurements

50 mg of samples were finely ground and taken in a pellet maker. They were pressed with ~4 tons of pressure in a hydraulic press to make uniform pellet of diameter 6 mm and thickness 0.8-0.9 mm. These pellets were tightly packed in two probe-measurement cell. For each experiment the sample pellets were pre-equilibrated overnight. For each temperature dependent study sample was equilibrated for two hours at each humidity condition. Proton conductivities were calculated using Equation S5.

$$\sigma = \frac{l}{R * A} \quad \text{(S5)}$$

wherein, σ, *L*, *R*, and *A* represent the proton conductivity (S cm^{-1}), thickness (cm), resistance (Ω), and area of the pellet (cm^2) (A= πr^2, r is the radius of the pellet), respectively. Resistance (*R*) was obtained by fitting the semicircle of the Nyquist plot in the high-frequency domain.

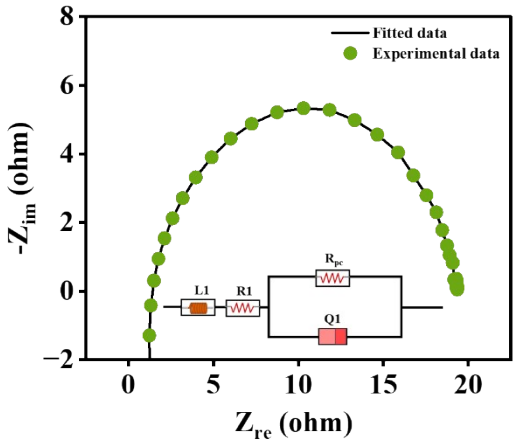
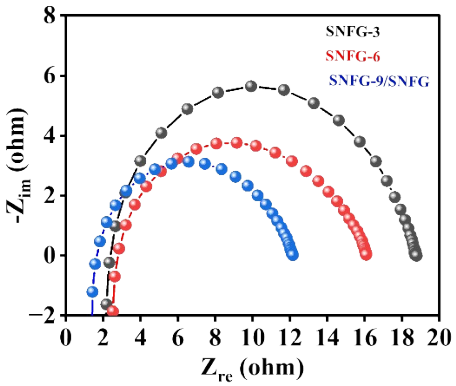


Figure S7: Experimental data fitting of Nyquist plot. Inset showing circuit diagram employed for fitting.



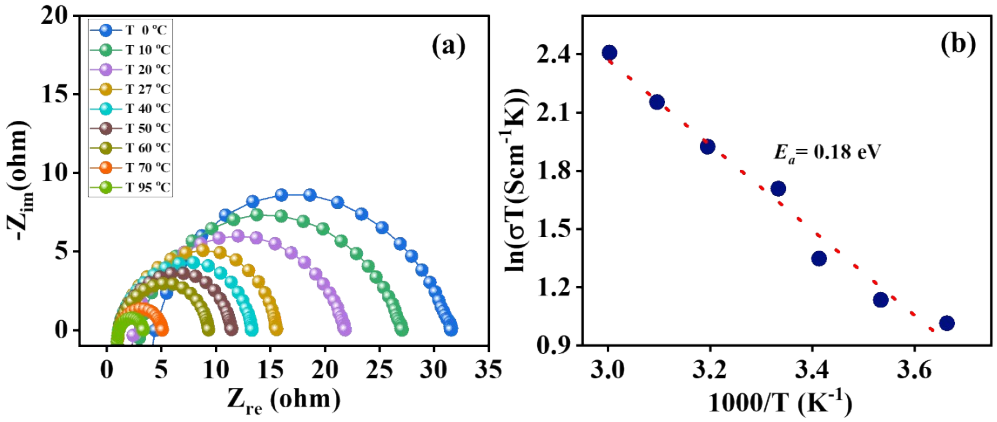


Figure S8: Solid state proton conduction for different SNFG materials at 50 ºC and 95 %RH.

Figure S9: (a) Nyquist plot from 0 to 95 ºC and (b) Arrhenius plot plots of ln(σ*T) vs T^{-1} for SNFG.

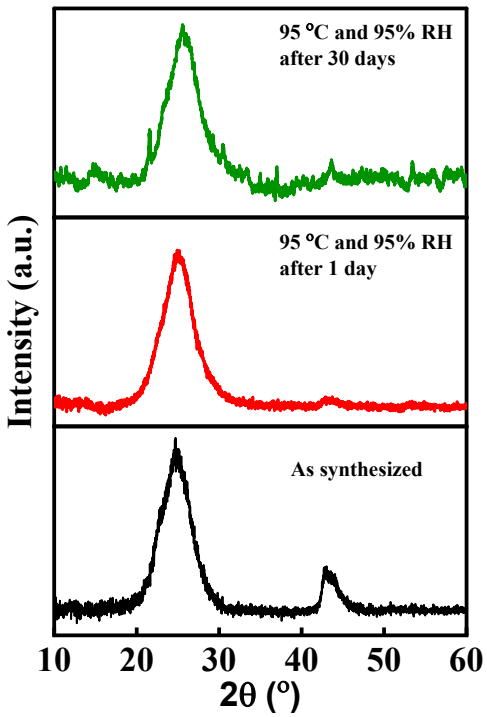


Figure S10: Overlay of PXRD pattern at different measurement conditions for SNFG.

Table S1. Percentage composition of nitrogen and sulfur for SNFG.

Elements	XPS	CHNS
N Atm %	5.1	5.0
S Atm %	0.6	0.7

Table S2. Percentage composition of different functionalization from deconvoluted C1s spectra of SNFG.

Sample	C=C	C-N	C-OH	C=O	O-C=O
	63.4	16.1	7.7	10.5	2.1

Table S3. Percentage composition of different functionalization from deconvoluted N1s spectra of SNFG.

Sample	Primary -N	Pyridinic-N	Pyrrolic-N	Graphitic-N	N-oxide
	20.4	10.9	19.5	13.9	16.1

Table S4. Percentage composition of different functionalization from deconvoluted O1s spectra of SNFG.

Sample	C=O	O=S=O	O=C-OH
	62	35.6	2.3

Table S5. Percentage composition of deconvoluted S 2p spectrum of SNFG.

Sample	S $2p_{1/2}$	S $2p_{3/2}$
	52.9	47.1

Table S6. TGA comparison of various graphene materials.[7]

Sample	% Weight loss (500-800 °C)
GO	~30
OFG	~70
NOFG	~32
NOFG-D	~40
SNFG	~8.4

Table S7. Proton conductivity at different temperature and 40% RH of SNFG.

Temperature (ºC)	Conductivity (S cm^{-1}) × 10^2
27	1.15±0.15
40	1.24±0.08
50	1.35±0.05
60	1.47±0.24
70	1.79±0.05
80	2.37±0.12
95	4.61±1.90

Table S8. Proton conductivity at different temperature and 95% RH of SNFG.

Temperature (°C)	Conductivity (S cm^{-1}) × 10^2
0	1.01±0.07
10	1.09±0.10
20	1.31±0.12
27	2.75±0.05
40	3.15±0.05
50	3.45±0.25
60	3.68±0.36
70	4.10±0.50
80	5.70±0.50
95	8.65±1.95

Table S9. Comparison of proton conductivity of present study with reported values of different materials.

Sample	Proton conductivity (S cm^{-1})	References
GO sGO	5.7×10^{-3} (90 °C, 90% RH) 9.1×10^{-3} (90 °C, 90% RH)	*Electrochim. Acta,* 2019, **297**, 240-249
GO (Bulk sample)	4.0×10^{-4} (27 °C, 60 % RH)	*Angew. Chem. Int. Ed.,* 2014, **53**, 6997-7000
PEGO	1.0×10^{-2} (80 °C, 60% RH)	*Adv. Funct. Mater.,* 2015, **25**, 4480-4485
HRFG-96	3.9×10^{-2} (95 °C, 95% RH)	*J. Phys. Chem. C,* 2022, **126**, 6135-6146

OFG	8.7×10^{-3} (80 °C, 95% RH)	*Chem. Commun.,* 2016*,* **52**, 12661-12664
3DGO-NS	2.8×10^{-1} (60 °C, 90% RH)	*ChemPlusChem,* 2022, **87***,* e202200003
GO-HPS	1.5×10^{-1} (RT, 80% RH)	*Chem. Asian J.,* 2017, **12***,* 194-197
NOFG	3.6×10^{-3} (95 °C, 95% RH)	*J. Phys. Chem. C,* 2022, **126***,* 10534-10545
IMBA-rGO2	3.9×10^{-3} (40 °C, 90% RH)	*ACS Appl. Mater. Interfaces,* 2020, **12***,* 10829-10838
GO/FA	1.7×10^{-2} (25 °C, 90% RH)	*RSC Adv.,* 2017, **7**, 21901-21905
SNFG	**8.65×10^{-2} (95 °C, 95% RH)**	***This work***

Table S10. Comparison of proton conductivity of SNFG before and after thermal annealing at 70 °C and 95 % RH.

Before annealing (S cm^{-1})	**After annealing (S cm^{-1})**
4.10×10^{-2}	4.62×10^{-2}

References:

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