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Supporting Information

Exploring the twin functional properties of paper-like carbyne enriched carbon for maintenance-free self-powered system

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S1. Experimental section

S1.1 Materials

Polyvinylidene fluoride powder (- $(C_2H_2F_2)_n$ -), ethanol (C_2H_5OH), N-methyl pyrrolidone (C_5H_9NO), acetone (C_3H_6O), tetrahydrofuran (C_4H_8O) and potassium hydroxide (KOH) chemical were bought from the Dae Jung Chemicals and metals, South Korea. The chemicals in this work are research grade and used as such without further purification.

S1.2 PVDF membrane preparation

The free-standing PVDF membrane were prepared via facile solvent casting process. Briefly, 10 % of PVDF powders was dissolved in mixture of $C_5H_9NO \& C_3H_6O$ in the weight ratio of 70:30 via ultrasonication process¹. After complete dissolution of the PVDF powders in C_5H_9NO , the viscous solution was cast into a petri dish and allowed to dry at a temperature of 70 °C for 12 h. Finally, the free-standing PVDF membrane was peeled off from the petri dish and used as the starting materials for the preparation of free standing carbyne-enriched carbon.

S1.3 Preparation of Free-standing paper like carbyne-enriched carbon films via exclusion of halogenation from PVDF membrane

The free-standing paper like carbyne-enriched carbon (P-CeC) films were prepared via exclusion of halogen from PVDF film membrane vis dehydrohalogenation process². Briefly, the PVDF membrane $(4 \times 4 \text{ cm}^2)$ was immersed in solution containing the mixture of potassium ethylate and tetrahydrofuran in the weight ratio of (60:40) and allowed to ultrasound irradiation by means of a bath-type sonicator over 1 h. During this time period, the removal of halogen from the PVDF membrane is indicated by the colour change in the PVDF membrane. After the completion of reaction, one can notice the complete transformation from white to metallic black colour which indicated the successful removal of halogen from the PVDF membrane. Finally, the P-CeC film were washed with ethanol repeatedly (remove the

residual ions) and dried in vacuum oven for 30 min. The prepared P-CeC film is used as such for the further characterization. The thickness of the PVDF and P-CeC film is found to be \sim 194 and \sim 189 µm as analyzed using screw-gauge (MITUTOYO, range 10-25000 µm).

S1.4 Instrumentation

A Rigaku X-ray diffractometer system with Cu Kα radiation (operated at 40 KeV and 40 mA) was employed to examine the phase purity of the prepared PVDF membrane and P-CeC films. The change in the bonding nature of the PVDF membrane and P-CeC films were studied using FT-IR spectrum (700–4000cm⁻¹). The surface morphology and elemental mapping analysis of the PVDF membrane and P-CeC films carbyne films were examined using Field Emission-Scanning Electron Microscope (JEOL Instruments (JSM6700F). The chemical composition of surface existing in the PVDF membrane P-CeC films was investigated using X-ray photoelectron spectroscopy (XPS) measurements using ESCA-2000, VG Microtech Ltd. The Raman spectrum of the PVDF membrane and P-CeC films were obtained using a LabRam HR Evolution Raman spectrometer (Horiba Jobin-Yvon, France). The topographical image, line profiler, and surface potential mapping (KPFM) of PVDF membrane and P-CeC films were probed using an Atomic force microscopy (UPS, AXISNOVA, Kratos Inc.) study of P-CeC film were performed using He I (21.2 eV) as a photon source.

S1.5 Electrical performance of free-standing P-CeC film triboelectric nanogenerator:

The as prepared free-standing P-CeC film is used as a positive layer in the fabrication of a triboelectric nanogenerator by keeping commercial Kapton film (fixed with aluminium foil electrode) as a negative layer. Finally, the TENG device has been fabricated using positive (P-CeC film) and negative layer (Kapton) in the arc like structure. For control experiment we have also fabricated the PVDF based TENG using PVDF as negative and aluminium as positive layer in the arc like structure. The electrical output of both PVDF TENG and free-standing P-CeC TENG were examined using Keithley Electrometer, Model no: 6514³.

S1.6 Fabrication of flexible P-CeC based solid-state symmetric supercapacitor

The electrochemical device was fabricated in form of solid-state symmetric supercapacitor (SSC) by sandwiching the PVA-Na₂SO₄ gel electrolyte in between P-CeC film (1×1 cm²). The electrochemical performance of P-CeC SSC device were systematically analysed using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) analysis and galvanostatic charge–discharge (CD) analysis by Autolab PGSTAT302N electrochemical workstation. The specific capacitance, energy density and power density of fabricated P-CeC device were calculated according to previous report⁴.



Figure S1: Relative C 1s core level spectrum of PVDF membrane and P-CeC film



Figure S2: The laser Raman spectrum of PVDF membrane



Figure S3: (A) Cross sectional FE-SEM micrograph of PVDF film, (B) Overlay map of cross sectional PVDF film obtained using elemental mapping analysis, (C-E) signifies the elemental map of C, O, and F element present in the PVDF film.



Figure S4: (A) Cross sectional FE-SEM micrograph of P-CeC film, (B) Overlay map of cross-sectional P-CeC film obtained using elemental mapping analysis, (C & D) signifies the elemental map of C and O element present in the PVDF film.



Figure S5: FE-SEM analysis of PVDF film. (A-C) FE-SEM micrograph of PVDF film at different magnification (low to high), (D) Overlay map of PVDF film obtained using elemental mapping analysis, (E & F) signifies the elemental map of C, F element present in the PVDF film.



Figure S6: UPS analysis of prepared P-CeC film



Figure S7: Comparative current profiles of PVDF TENG and P-CeC TENG



Figure S8: 3D topographical micrograph of prepared PVDF membrane(A) & P-CeC film(B)



Figure S9: (A) Voltage profiles of PVDF TENG at various compressive force from 2 to 15 N.



Figure S10: (A) Rectified voltage profile of P-CeC TENG at various force (2 to 15N)



Figure S11: Electrochemical impedance spectroscopy analysis of P-CeC SSC device (A) Nyquist plot and (B) bode phase angle plot



Figure S12: Electrochemical impedance spectroscopy analysis of PVDF SSC device. (A) Nyquist plot



Figure S13: (A) CV profile of P-CeC SSC device connected in series measured in the voltage window of -1.8 to 1.8 V at the 100 mV s⁻¹ scan rate and (B) CV profile of P-CeC SSC device connected in series measured in the voltage window of 0 to 1.8 V at the scan rate 100 mV s⁻¹.



Figure S14: (A) charging graph of commercial capacitor (1 μ F) at the constant force of 10 N using P-CeC TENG and (B) charging graph of 1 μ F commercial capacitor at the constant force of 10 N using PVDF TENG



Figure S15: (A) Self charging properties of P-CeC based SPS at the mechanical force of 8 N

Table S1:	performance	metrics of	of P-CeC	based	SPS	with	other	reported	<u>Self-chargi</u>	ng
power syst	tem:									

S. No.	TENG material	SC material	SC connected (OVW)	SPS charge	Time (s)	Charge Storing efficiency	Ref
1.	Wrinkle PDMS	CNT	1 (1V)	800 mV	10,800	80 %	5
2.	Cut-Paper	Graphite	4 (3V)	2500 mV	750	83 %	6
3.	Silicone rubber	Graphite	6(4.8V)	1200 mV	900	25%	7
4.	EP-TENG	carbon	3(7.5V)	2000 mV	2200	26.6 %	8
5.	F-TENG	FSC	3 (3.6V)	2500 mV	900	69.4 %	9
6.	FS-FTENG	RuO ₂	4(3.2V)	1400 mV	2400	43.7 %	10
7.	P-CeC TENG	P-CEC	1(0.8V)	750 mV	380	93.75 %	TW

References:

- 1 A. Ambrosy and K. Holdik, J. Phys. E., 1984, 17, 856–859.
- 2 K. Krishnamoorthy, V. K. Mariappan, P. Pazhamalai, S. Sahoo and S. J. Kim, Nano Energy, 2019, 59, 453–463.
- P. Pazhamalai, K. Krishnamoorthy, V. K. Mariappan, S. Sahoo, S. Manoharan and S. J. Kim, *Adv. Mater. Interfaces*, DOI:10.1002/admi.201800055.
- 4 K. Krishnamoorthy, P. Pazhamalai and S. J. Kim, *Energy Environ. Sci.*, 2018, **11**, 1595–1602.
- Y. Song, X. Cheng, H. Chen, J. Huang, X. Chen, M. Han, Z. Su, B. Meng, Z. Song and
 H. Zhang, J. Mater. Chem. A, 2016, 4, 14298–14306.
- H. Guo, M. H. Yeh, Y. Zi, Z. Wen, J. Chen, G. Liu, C. Hu and Z. L. Wang, ACS Nano, 2017, 11, 4475–4482.
- H. Guo, M. H. Yeh, Y. C. Lai, Y. Zi, C. Wu, Z. Wen, C. Hu and Z. L. Wang, ACS Nano, 2016, 10, 10580–10588.
- N. Sun, Z. Wen, F. Zhao, Y. Yang, H. Shao, C. Zhou, Q. Shen, K. Feng, M. Peng, Y. Li and X. Sun, *Nano Energy*, 2017, 38, 210–217.
- 9 J. Wang, X. Li, Y. Zi, S. Wang, Z. Li, L. Zheng, F. Yi, S. Li and Z. L. Wang, Adv. Mater., 2015, 27, 4830–4836.
- 10 J. Chen, H. Guo, X. Pu, X. Wang, Y. Xi and C. Hu, *Nano Energy*, 2018, **50**, 536–543.