Enhancing Triboelectric Nanogenerator Performance Using Chitosan-Modified Multiwall Carbon Nanotubes

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Supporting information

Modification of MWCNTs with a 1,3-Propane sultone

Sulfonation of MWCNTs was performed according to following method ¹. 1 gram of MWCNTs was refluxed at 100 °C for 24 hours with 2 mL of 1,3-propane sultone and 20 mL of toluene present. After the reaction mixture was cooled down to room temperature and was centrifuged with ethanol and water mixture for 3 times. The final product, named (S@CNT), was prepared by vacuum drying the resultant mixture at 80°C for 36 hours.

Composite Membranes preparation

The composite membranes of CS/MWCNTs were fabricated using the solution casting method ².Briefly, a specific amount of MWCNTs was dissolved in ethanol, followed by an aqueous solution of CS/acetic acid (2 wt%.), and the bubbles were removed by homogenisation. Furthermore, the synthesised solution was transferred to the glass plate and placed for 24h at 50°C for vacuum drying. Finally, an H₂SO₄ (1.0M) solution was used to immerse the synthesised membrane for 48 hours, followed by drying the membrane for 24 hours at 30°C. The synthesised membranes of different ratios of the S@CNT content were name as CS/CNT-0.5, CS/CNT-1.0, CS/CNT-1.5 and CS/CNT-2.0 respectively.

Characterization

Several analytical approaches were used to characterise and measure the surface-modified MWCNTs and nanocomposite membranes. The FTIR spectra of the surface-modified MWCNTs and nanocomposite membranes were obtained using a Nicolet 6700 FTIR-ATR spectrometer operating within a wavelength range of 500-4000 cm⁻¹. Using a Rigaku D/max advanced wide-angle X-ray diffractometer and nickelled-filtered Cu K radiation (40 kV, 200 mA) as the X-ray source, the crystalline structures were examined. The measurements were carried out in a nitrogen environment that was regulated. A thermogravimetric analyser, model TA 50, was used to determine thermal characteristics. The analysis was carried out in a nitrogen atmosphere and spanned a temperature range of 30 °C to 700 °C. A scanning electron microscope (SEM, Hitachi FE-S4800) was used to analyse the cryo-fractured morphologies of the membranes. The elemental makeup of the samples was examined using an EDX spectroscope attached to the SEM. 200 kV was used as the high

voltage for the imaging. Using an MTS E43 Universal Testing Machine at room temperature, the mechanical characteristics of the samples were examined. The testing was done following the Chinese standard GB/T-1040.3 at a 2 mm/min testing speed. The dynamic fatigue tester system (Popwil Model YPS) was used to control the contact frequency to measure the performance of synthesised TENGs. The picometer (Keysight B2981A) and electrometer (Keithley 6514) were used to measure electrical characteristics like current and output voltage. The mechanical stability was measured through mechanical tensile tests using an Instron universal tester (Model 1185).



Figure S₁ long term stability of 0.5 CS /S@CNT (a) different temperature (b) at different RH (%)



Figure S₂. (a) Experimental setup of KPFM (b) KPFM results (c) working mechanism of KPFM.



Figure S₃ TGA of (a) S@CNT (b) CS/CNT composite membranes

| Sample | T5% | Tmax1 | Tmax2 | Char residue (wt. %) | | | |
|--------|-------|-------|-------|----------------------|--------|--------|--------|
| | | | | 500 °C | 600 °C | 700 °C | 750 °C |
| MWCNTs | 206.1 | 57.7 | | 88.24 | 67.60 | 33.07 | 15.42 |
| S@CNT | 101.2 | 79.3 | 235.4 | 68.38 | 60.25 | 39.70 | 28.87 |

Table S_1 Thermal properties of pristine and sulfonated MWCNTs from TGA Analysis

$Table \ S_2 \ Elemental \ Composition \ of \ Sulfur, \ Oxygen, \ and \ Carbon \ of \ Modified \ MWCNTs$

| Molar Fraction | | | | | |
|----------------|------|-------|-------|--|--|
| Sample | S | 0 | С | | |
| MWCNTs | 0 | 3.88 | 96.12 | | |
| S@CNT | 4.04 | 10.52 | 85.44 | | |

Table S₃ Mechanical features of the composite membranes

| Sample | Tensile strength (MPa) | Elongation at break (%) |
|------------|------------------------|-------------------------|
| CS/S@CNT-0 | 38.65 ± 1.57 | 3.71 ± 0.85 |
| CS/S@CNT-1 | 41.74 ± 1.4 | 10 ± 4.2 |
| CS/S@CNT-2 | 46.52 ± 2.24 | 6.38 ± 1.15 |
| CS/S@CNT-5 | 53.19 ± 7.5 | 3.86 ± 0.84 |

Table S4: Comparison of Triboelectric Nanogenerators (TENGs) with Different MaterialCombinations and Their Electrical Performance 3-5

| Serial No. | Tribopositive Materials | Tribonegative Materials | Open Circuit Voltage | Short Circuit Current | Power Density |
|---------------|----------------------------|----------------------------|----------------------------|-----------------------------|-------------------------|
| 1 | TPU | PVDF | 170 V | 1.5 μA | - |
| 2 | Nylon/Cu | PVDF-GnP | 134.4 V | 12.9 µA | - |
| 3 | Cellulose | PVDF | 90 V | 7.4 µA | $\frac{0.13}{mW / m^2}$ |

| 8 | CS-MWCNT [This Work] | PDMS | 244.9 V | 42 mA / m^2 | 4.22 <i>W</i> / <i>m</i> ² |
|---|-------------------------|---------------|----------------|----------------------|---|
| 7 | BMOF/FCF | PTFE/AI | 47 V | 7 μΑ | $\frac{1.1}{mW / m^2}$ |
| 6 | Polyurethrane | Polypropylene | 110 V | 7.28 µA | $\frac{0.9}{mW / m^2}$ |
| 5 | Poly Vinyl Alcohol | Polypropylene | 21.62 V | 1.72 μA | - |
| 4 | AI-foil | PDMS | 180 V | 6 µA | 0.72 μW |

References

- 1. T. A. Saad Ahmed, Amir Zada , Annum Afzal , Muhammad Khan , Amjad Hussain , Muhammad Hassan ,Muhammad Ali, Shiai Xu, *Membranes*, 2021, **11**, 450.
- 2. J. Wang, C. Gong, S. Wen, H. Liu, C. Qin, C. Xiong and L. Dong, *International journal of hydrogen energy*, 2019, **44**, 6909-6918.
- 3. A. Chen, C. Zhang, G. Zhu and Z. L. Wang, *Advanced Science*, 2020, 7, 2000186.
- 4. Y. Shang, Z. Wang, C. Yu, W. Xu, Z. Chen, B. Jiang and H. Zhang, *Nano Energy*, 2022, **103**, 107847.
- 5. C. Cao, Z. Li, F. Shen, Q. Zhang, Y. Gong, H. Guo, Y. Peng and Z. L. Wang, *Energy & Environmental Science*, 2024.