

Electronic Supplementary Information (ESI)

Fluorescent Triboelectric Nanogenerator Manufactured by Flexible Janus Nanobelt Array Concurrently Acting as Charge-generating Layer and Charge-trapping Layer

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Experimental Sections

Chemicals

Terbium oxide (Tb_4O_7 , 99.99 %), concentrated nitric acid, benzoic acid (BA), 1,10-phenanthroline (phen), anhydrous ethanol, benzoylperoxide (BPO), aniline (ANI), (1S)-(+)-camphor-10 sulfonic acid (CSA), ammonium persulfate (APS), methylmethacrylate (MMA), *N,N*-dimethylformamide (DMF), $CHCl_3$, acetone, carbon nanotubes (CNTs) with the length of 50 μm , polyvinylidene fluoride (PVDF, $M_r \approx 400000$), and polyvinylpyrrolidone (PVP-K90, $M_r \approx 1300000$) were purchased from Aladdin Reagent (Shanghai) Co., Ltd.. All the chemicals were analytically pure reagents and directly used as received without further purification. $Tb(BA)_3phen$ complexes and poly(methyl methacrylate) (PMMA) were synthesized according to the references ^{S1-S2}.

Preparation of Spinning Dopes

In order to explore the optimal doping ratio of CNTs to PMMA, the mass percentage of CNTs to PMMA was varied from 0%, 1%, 3%, 5% to 7%. A certain quantity of CNTs was added into the mixture of DMF (2.00 g) and $CHCl_3$ (14.00 g) and then ultrasonically dispersed for 90 min at room temperature. Subsequently, a certain amount of PMMA was added into the above mixture and stirred for 24 h at room temperature, and spinning dopes 1 (defined as spinning dope 1-1 to 1-5) used to prepare CNTs/PMMA composite nanobelt, named as were formed. The specific amounts of used substances of spinning dope 1-1 to 1-5 were summarized in Table S1.

Table S1 Compositions of spinning dope 1-1 to 1-5

Spinning dope 1	CNTs (g)	PMMA (g)	DMF (g)	$CHCl_3$ (g)	CNTs: PMMA (%)
1-1	0.00	1.00	2.00	14.00	0
1-2	0.01	1.00	2.00	14.00	1
1-3	0.03	1.00	2.00	14.00	3
1-4	0.05	1.00	2.00	14.00	5
1-5	0.07	1.00	2.00	14.00	7

[PANI/CNTs/PMMA]/[$Tb(BA)_3phen$ /PMMA] Janus nanobelts were prepared by using two spinning dopes, including conductive spinning dope (named as spinning dope 2) and luminescent spinning dope (marked as spinning dope 3). In this work, PANI doped with camphor sulfonic acid (CAS) was synthesized after the conductive spinning dope 2 was prepared. Spinning dope 2 was obtained through following process: firstly, a certain amount of CNTs was added into $CHCl_3$ (14.00 g) and ultrasonically dispersed for 90 min at room temperature. Then, a certain amount of ANI and CSA were dissolved into the above-mentioned mixture under magnetic stirring for 30 min at room temperature (marked as solution 1). Meanwhile, a certain amount of APS was dissolved into DMF (2.00 g) and stirred for 30 min at ambient temperature (defined as solution 2). The two solutions were simultaneously frozen for 20 min at 0 °C in a refrigerator and then solution 2 was added into solution 1 by inches under magnetic stirring for 3.5 h in an ice-water

mixture, and then PMMA (1.00 g) was added into the mixture. Spinning dope 2 was formed under magnetic stirring for 12 h at room temperature and the color of spinning dope 2 changed from light brown to dark green. In order to achieve different conduction, the mass percentage of PANI to PMMA was varied from 0%, 3%, 5%, 7%, 10%, 12%, 15% to 30%. The green color of spinning dope 2 gradually deepened when the mass percentage of PANI to PMMA was increased, indicating that doped PANI was successfully prepared in this process. The specific amounts of used substances for spinning dope 2 were listed in Table S2. Tb(BA)₃phen (0.15 g) and PMMA (1.00 g) were added into the mixture of DMF (2.00 g) and CHCl₃ (14.00 g) under magnetic stirring for 12 h at room temperature to acquire spinning dope 3.

Table S2 Compositions of the spinning dope 2

Spinning dope 2	CNTs (g)	ANI (g)	CS A (g)	APS (g)	PMM A (g)	DMF (g)	CHCl ₃ (g)	CNTs:PMMA (%)	PANI:PMMA (%)
2-1	0.03	0.00	0.00	0.00	1.00	2.00	14.00	3	0
2-2	0.03	0.03	0.04	0.06	1.00	2.00	14.00	3	3
2-3	0.03	0.05	0.06	0.10	1.00	2.00	14.00	3	5
2-4	0.03	0.07	0.08	0.14	1.00	2.00	14.00	3	7
2-5	0.03	0.10	0.11	0.20	1.00	2.00	14.00	3	10
2-6	0.03	0.12	0.13	0.24	1.00	2.00	14.00	3	12
2-7	0.03	0.15	0.16	0.30	1.00	2.00	14.00	3	15
2-8	0.03	0.30	0.31	0.60	1.00	2.00	14.00	3	30

In this work, PVP and PVDF were used for co-spinning to improve the electrospinnability of spinning solution for preparing PVDF/PVP nanofibers membrane. PVDF (2.00 g) was added into the mixture of DMF (4.00 g) and acetone (3.00 g) and stirred for 40 min at 50 °C, and then PVP (0.60 g) was added into the mixture. After stirring the mixture for 6 h at room temperature, spinning dope 4 used to prepare PVDF/PVP composite nanofibers membrane was formed. A mixed spinning dope (marked as spinning dope 5) for preparing PANI/CNTs/Tb(BA)₃phen/PMMA composite nanobelt array (CNA) was fabricated and the specific process was as follows: CNTs (0.03 g) were added into CHCl₃ (14.00 g) and ultrasonically dispersed for 90 min at room temperature. Then, a certain amount of ANI (0.05 g) and CSA (0.06 g) were dissolved into the mixture under magnetic stirring for 30 min at room temperature (marked as solution 1). Meanwhile, APS (0.10 g) was dissolved into DMF (2.00 g) and stirred for 30 min at room temperature (defined as solution 2). The two solutions were simultaneously frozen for 20 min at 0 °C in the refrigerator and then solution 2 was added into solution 1 by inches under magnetic stirring for 3.5 h in an ice-water mixture, and then PMMA (1.00 g) and Tb(BA)₃phen (0.15 g) were added into the mixture. Under magnetic stirring for 12 h at room temperature, spinning dope 5 was obtained.

Synthesis of CNTs-CNA, JNN and CNA

In order to explore the optimal doping ratio of CNTs in PMMA, CNTs/PMMA composite nanobelt array was prepared by uniaxial electro-spinning *via* regulating the mass percentages of CNTs to PMMA from 0%, 1%, 3%, 5% to 7%, and the samples were named as (PMMA/CNTs)_p-CNA (p represents the mass percentages of CNTs to PMMA, p=0, 1, 3, 5, 7%). 4 mL of the spinning dope 1 was dumped into a 10-mL plastic injector with a plastic spinneret and the applied voltage was 10 kV. The roller was used as the collector and the distance between the tip of plastic spinneret and the collector was 15 cm, and the rotating speed of roller was 1200 r·min⁻¹ for the whole process. Operating temperature and relative air humidity were respectively 25 °C and 25%, and (PMMA/CNTs)_p-CNA (p=0, 1, 3, 5, 7%) was obtained after 4 h-electrospinning. The electrospinning device for preparing (PMMA/CNTs)_p-CNA (p=0, 1, 3, 5, 7%) was shown in Fig. S1a. Next, [PANI/CNTs/PMMA]/[Tb(BA)₃phen/PMMA] Janus nanobelt non-array (named as JNN) was prepared by using spinning dope 2-3 and spinning dope 3. The wire netting was used as a collector and other experimental conditions were the same as those for fabricating (PMMA/CNTs)_p-CNA (p=0, 1, 3, 5, 7%). The electrospinning device for preparing JNN was illustrated in Fig. S1b. PANI/CNTs/Tb(BA)₃phen/PMMA composite nanobelt array (marked as CNA) was obtained when 4 mL of spinning dope 5 was applied, and other experimental conditions were the same as those for fabricating (PMMA/CNTs)_p-CNA (p=0, 1, 3, 5, 7%). The electrospinning device for preparing CNA was illustrated in Fig. S1c.

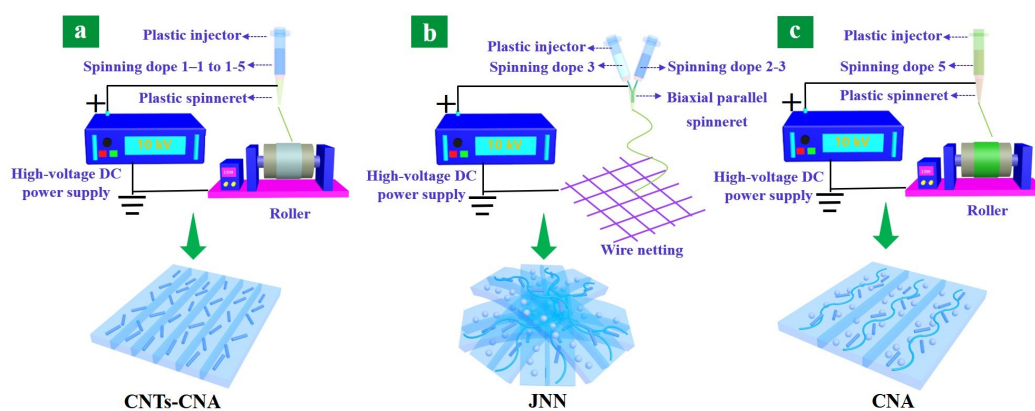


Fig. S1 Schematic diagrams of electrospinning devices for preparing CNTs/PMMA composite nanobelt array, named as (PMMA/CNTs)_p-CNA (p represents the mass percentages of CNTs to PMMA, p=0, 1, 3, 5, 7%) (a), [PANI/CNTs/PMMA]/[Tb(BA)₃phen/PMMA] Janus nanobelt non-array, named as JNN (b) and PANI/CNTs/Tb(BA)₃phen/PMMA composite nanobelt array, called as CNA (c)

Characterization Methods

The morphologies and structures of samples were characterized *via* a field emission scanning electron microscope (FESEM, XL-30) equipped with an energy-dispersive x-ray spectroscopy (EDS). An optical microscope (OM, CVM500E) was employed to analyze the structure of Janus nanobelts. The luminescence of samples was analyzed by a Hitachi fluorescent spectrophotometer

F-7000. The output performances of TENG were obtained with the KEITHLEY 6514. The water contact angle of samples was tested by DROP SHAPE ANALYZER-DSA25. The conductance of samples was tested by Hall effect measurement system (ECOPIA HMS-3000). The thickness of the sample was tested by electronic thickness gauge (204705061714) with the measurement range of 0-12.7 mm. All tests were performed at room temperature.

Results and Discussion

Morphology and structure

The thicknesses of JNA and PVDF/PVP nanofibers membrane are tested by Electronic Thickness Gauge, and the specific test methods are as follows: the uniform JNA and PVDF/PVP nanofibers membrane are selected and cut to the size of *ca.* 1.5 cm×2 cm, and then are gently placed on the test platform of Electronic Thickness Gauge, as shown in Fig. S2a and Fig. S2b. The thicknesses of JNA and PVDF/PVP nanofibers membrane are 142 and 143 μm , respectively.

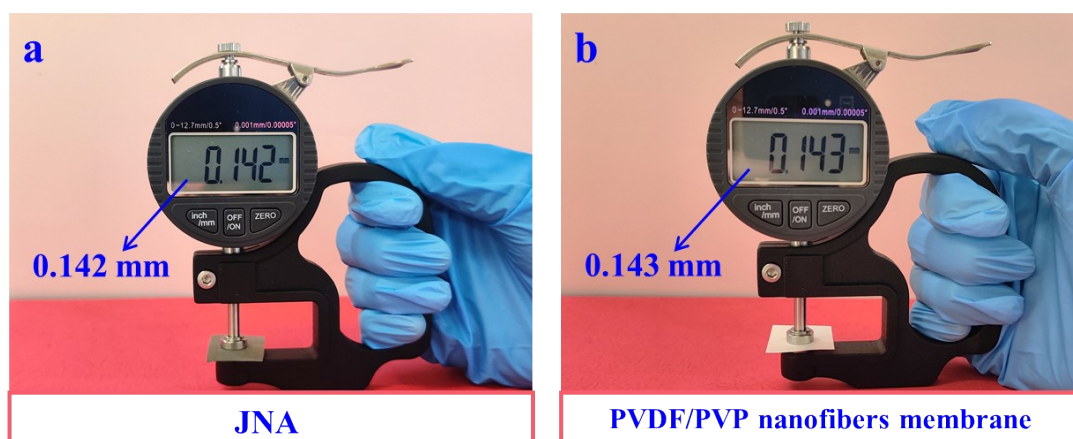


Fig. S2 Physical photos of the thickness test for JNA (a) and PVDF/PVP nanofibers membrane (b)

Output Performance

The output current and voltage of TENG-(PMMA/CNTs)_p-CNA (p=0, 1, 3%) are respectively changed from 1.90 μA and 42 V to 3.90 μA and 80 V when the mass percentage of CNTs to PMMA is varied from 0% to 3% in CNTs-CNA, as shown in Fig. S3. However, when the CNTs content continues to increase to 7%, the output current and voltage of the TENG-(PMMA/CNTs)_p-CNA (p= 5, 7%) begin to evidently decrease. The conductance of CNTs-CNA is increased from 8.107×10^{-11} to 1.287×10^{-10} S when the mass percentage of CNTs to PMMA is varied from 0%, 1%, 3%, 5% to 7%, as provided in Table S3. These results indicate that the reason for the different degrees of enhanced output performances may be related to the conductivity and charge transport ability of the triboelectric materials. When the mass percentage of CNTs to PMMA is changed from 0% to 3%, the content of CNTs is lower and the distribution of CNTs in CNTs/PMMA composite nanobelt is uniform. Appropriate amount of CNTs can form conductive channels which can appropriately accelerate the transport of triboelectric charges, so TENG-(PMMA/CNTs)_p-CNA (p=0, 1, 3%) can exhibit high output performance. However, the excessive CNTs are unevenly distributed in CNTs/PMMA composite nanobelt when the CNTs

contents augment to 5% and 7%. Excessive CNTs can form more conductive networks that results in higher charge combination ratio and more severe charge loss. Meanwhile, part of excessive CNTs can be distributed on the surface of CNTs/PMMA composite nanobelt, causing too higher surface conductivity of (PMMA/CNTs)_p-CNA (p=5, 7%), thus the generated triboelectric charges more easily dissipate into the air^{S3}. Therefore, the accumulation of triboelectric charges and surface charge density on the surface of CNTs-CNA are reduced, resulting in the evident decrease of output performance for TENG-(PMMA/CNTs)_p-CNA (p=5, 7%). As a result, the mass percentage of CNTs to PMMA is fixed at 3% in this work.

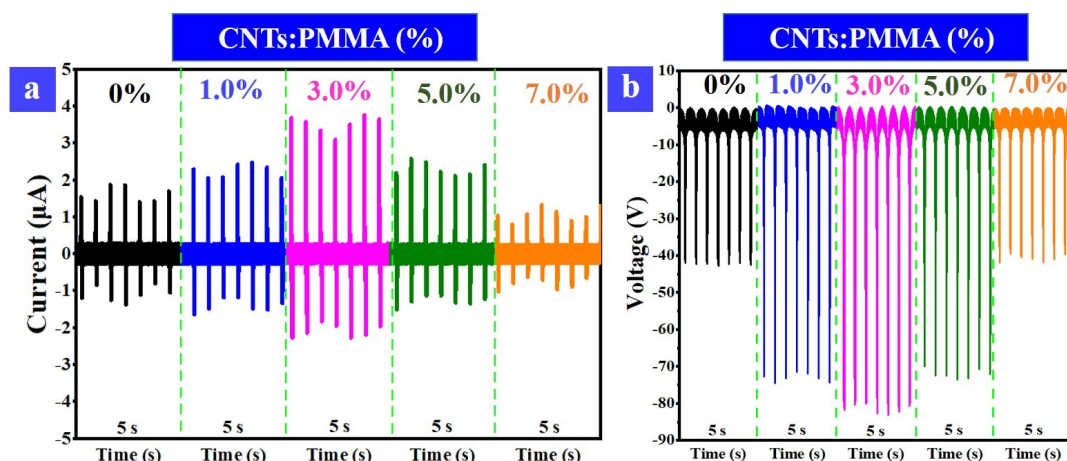


Fig. S3 Output current (a), output voltage (b) of TENG-(PMMA/CNTs)_p-CNA (p=0, 1, 3, 5, 7%) when different mass percentages of CNTs to PMMA in (PMMA/CNTs)_p-CNA (p represents the mass percentages of CNTs to PMMA, p=0, 1, 3, 5, 7%)

Table S3 Conductance of samples

Samples	Conductance (S)
(PMMA/CNTs) _{0%} -CNA	8.107×10^{-11}
(PMMA/CNTs) _{1%} -CNA	9.628×10^{-11}
(PMMA/CNTs) _{3%} -CNA	1.019×10^{-10}
(PMMA/CNTs) _{5%} -CNA	1.235×10^{-10}
(PMMA/CNTs) _{7%} -CNA	1.287×10^{-10}
JNA (PANI:PMMA=0%)	1.116×10^{-10}
JNA (PANI:PMMA=3%)	1.255×10^{-10}
JNA (PANI:PMMA=5%)	1.307×10^{-10}
JNA (PANI:PMMA=7%)	1.345×10^{-10}
JNA (PANI:PMMA=10%)	1.435×10^{-10}
JNA (PANI:PMMA=12%)	1.590×10^{-10}
JNA (PANI:PMMA=15%)	2.193×10^{-10}

JNA (PANI:PMMA=30%)	4.500×10^{-8}
JNN (PANI:PMMA=3%)	9.927×10^{-11}
CNA (PANI:PMMA=3%)	1.121×10^{-10}

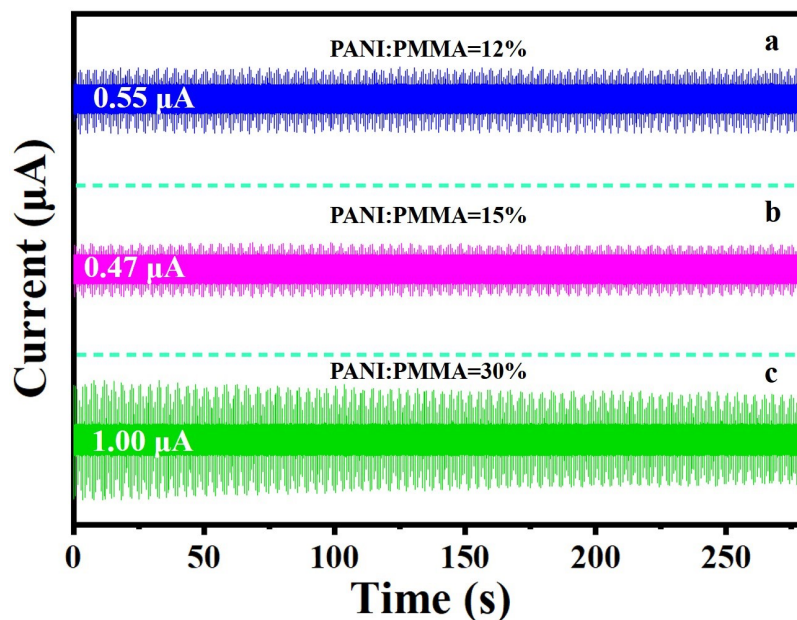


Fig. S4 Output current of TENG-JNA when the PANI content respectively is 12% (a), 15% (b) and 30% (c) in JNA

Table S4 Performances comparisons of TENG-JNA built by us and similar TENG assembled by others using nanomaterials

Literature	Contact area (cm ²)	Maximum output current (µA)	Maximum output voltage (V)
ACS Appl. Mater. Interfaces, 2018, 10, 25660-25665.	5×5	5.68	138
J. Li, Adv. Mater. Technol., 2018, 1700370.	4×4	4.50	170
Adv. Mater. Technol., 2019, 1900859.	2×2	3.80	140
ACS Appl. Mater. Interfaces, 2019, 11, 12452-12459.	3×3	7.00	300
Nano Energy, 2020, 78 105358.	2×2	7.00	160
Nano Energy, 2021, 80 105549.	5×5	8.50	166
Chem. Eng. J., 2021, 130200.	2×4	7.50	135

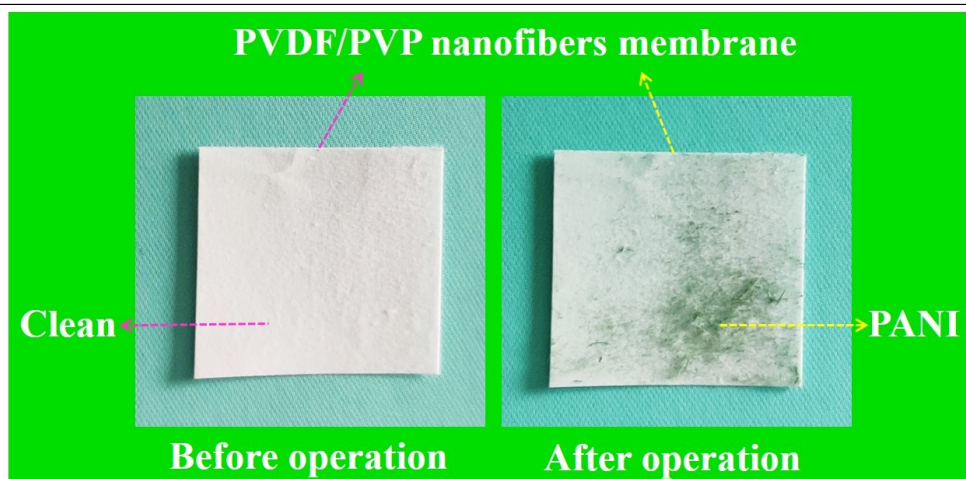


Fig. S5 Physical photos of PVDF/PVP nanofibers membrane before and after the operation of TENG-JNA when the PANI content is 30% in JNA

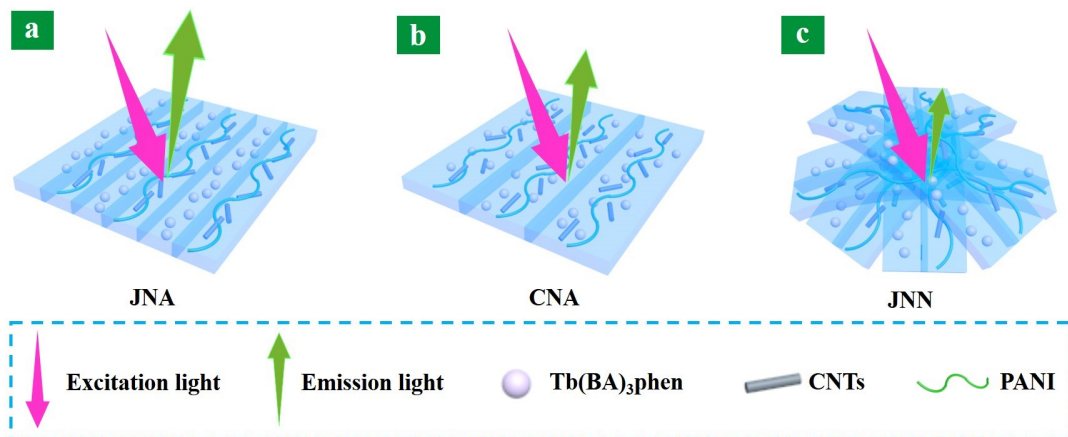


Fig. S6 Schematic illustrations of excitation and emission lights in JNA (a), CNA (b) and JNN (c)

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