

Ocean Wave Energy Generators Based on Graphene/TiO₂ Nanoparticle Composite Films

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Supporting Information

Preparation of graphene. First, graphite foil and platinum foil were inserted in 0.1 M (NH₄)₂SO₄ aqueous solution at a distance of 2 cm as anode and cathode, respectively. After applying a DC voltage

of 10 V, the exfoliated graphite powders were acquired. Then they were rinsed with deionized water and dimethylformamide (DMF) for at least three times each. Finally, the powders were dispersed in DMF with the assistance of bath ultrasonication for 10 min to obtain stable graphene/DMF dispersion at the concentration of 4 mg/mL.

Graphene/TiO₂ Ink Formulation. 5.3 mL graphene/DMF dispersion was centrifuged under 10,000 rpm for 10 min to separate the graphene nanosheets from DMF solvent, followed by discarding the supernatant DMF and harvesting the sedimented graphene. Meanwhile, 1.0 g Titania paste (transparent, 19.0 wt%, 20 nm in size, purchased from Sigma-Aldrich) was diluted with 5 mL ethanol (99.5%) and bath sonicated until a uniform dispersion was obtained. Finally, the diluted TiO₂ dispersion was mixed with the harvested graphene, together with 2 mL ethanol, and ultrasonicated for at least 20 min, followed by magnetic stirring at 400~500 rpm under a temperature of 60 °C until a viscous ink was obtained. The weight ratio of TiO₂: graphene in the final ink is around 9:1.

Fabrication of graphene/TiO₂ Film-Type Wave Energy Generators. The graphene/TiO₂ ink was used to fabricate rectangular films on glass substrates by blading. First, Scotch tapes were used to define an open area (typically $6.0 \times 1.5 \text{ cm}^2$ unless specified elsewhere) on a glass substrate. Then, a drop of graphene/TiO₂ ink was placed inside the open area and bladed with a scraper to spread throughout the open area. Subsequently, the film was annealed at 375 °C for 45 min to obtain a conductive graphene/TiO₂ film. Finally, silver pastes (or inks) were painted (or inkjet printed) onto both ends of the graphene/TiO₂ film as the two electrodes of the wave energy generators. Before the wave energy harvesting tests, the electrodes were sealed entirely with silicone to protect them from salt solution corrosion.

Characterization and Electrical Measurements. The structural characteristic of the graphene/TiO₂ films was studied through Raman Spectrometer (Raman Spectrometer HORIBA iHR 550) with a 633 nm wavelength laser at room temperature. Their morphology was characterized by SEM (Zeiss Ultra55). Their thickness was measured by a KLA-Tencor P-15 Surface Profilometer. The sheet resistance of all samples was measured by a multimeter, within the range of 0.5~ 1 kOhm/□. During wave energy harvesting tests, the graphene/TiO₂ film sample was fixed on a speed motor to control the inserting/pulling velocity and interval time between the cycles. Unless specified elsewhere, the inserting/pulling velocity and interval time for all the tests were 1 cm/s and 10 s, respectively. The time-resolved open-circuit voltage, or voltage-time (v-t) curve, across the graphene/TiO₂ film was recorded by a Keysight 34401A Digital Multimeter (controlled through Labview) under a sampling rate of 20 s⁻¹. To monitor the short-circuit current, a load resistor with a resistance of 100 Ohm was connected with the energy harvesters. Its voltage was monitored in the same way as the open-circuit voltage, and used to calculate the short-circuit current of the energy harvesters according to the Ohm' s law. The power was calculated following $P_{peak} = V_{peak} \times I_{peak}$, where P_{peak} , V_{peak} , and I_{peak} stand for the maximum output power, maximum open-circuit voltage and maximum short-circuit current, respectively.

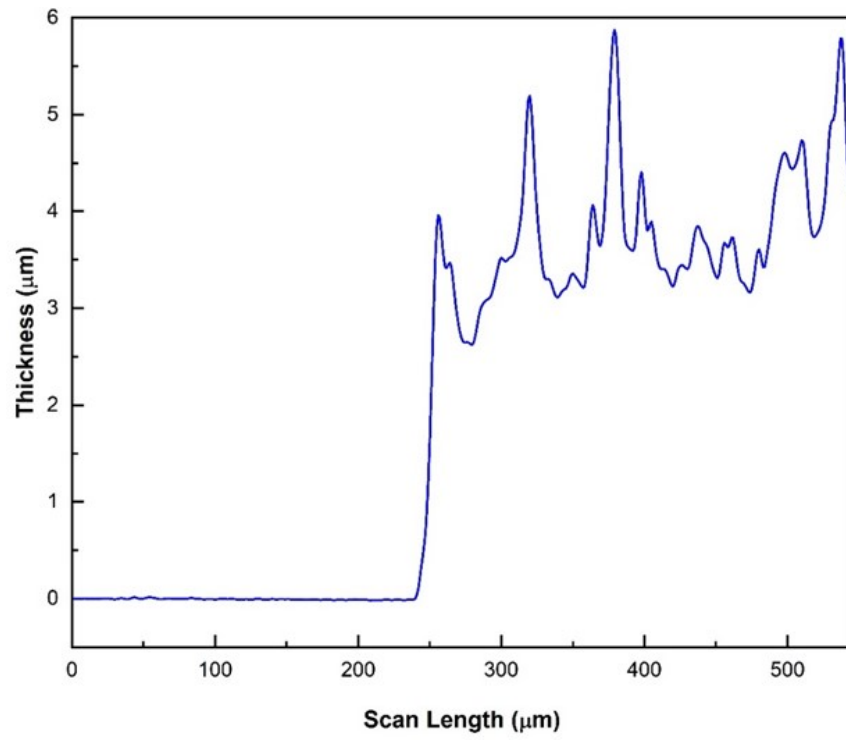


Figure S1 The thickness profile of a graphene/TiO₂ film.

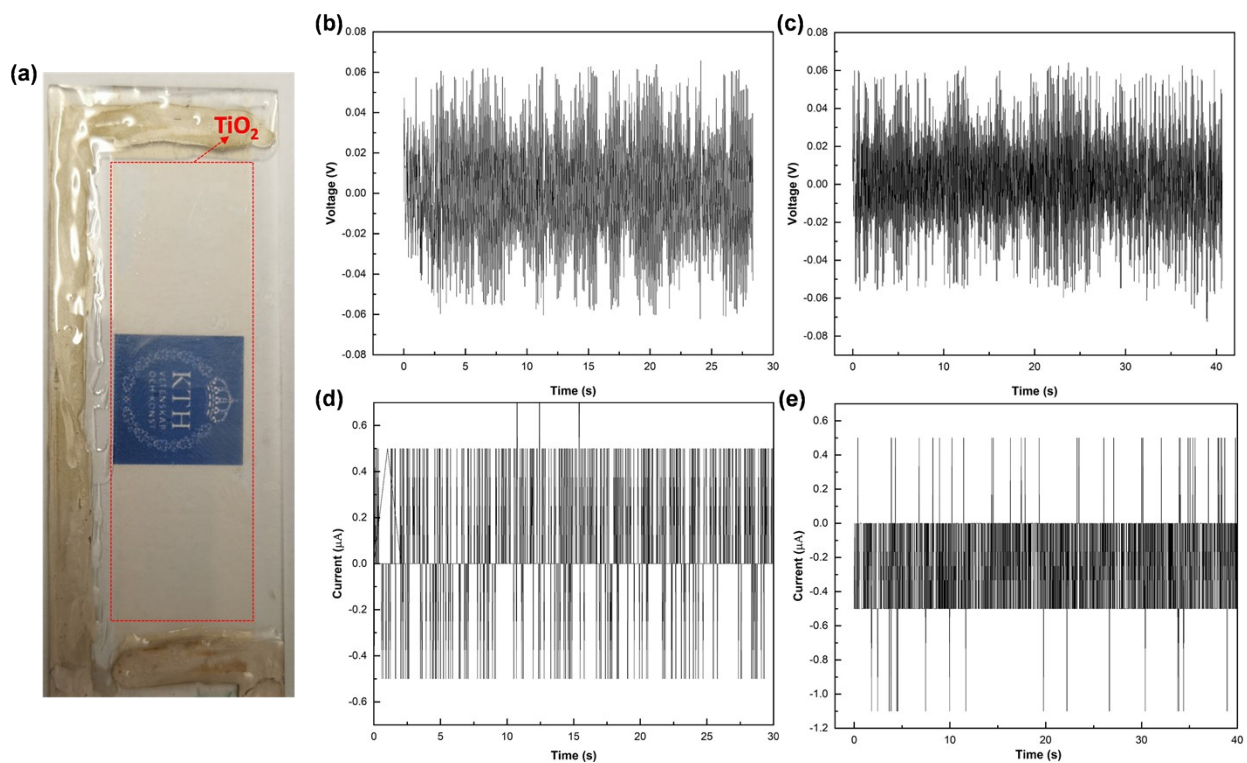


Figure S2 (a) Pure TiO_2 film on the glass substrate; (b), (d) Recorded voltage and current signals of pure TiO_2 film in air (not contacting any liquids); (c), (e) Recorded voltage and current signals of pure TiO_2 film during a series of movement into and out of 0.6 M NaCl solution. All the measurements were conducted at the same velocity of 1 cm/s and the same interval time of 10 s. No apparent voltage/current signals were observed during the tests, demonstrating that the pure TiO_2 film in this system cannot produce electricity.

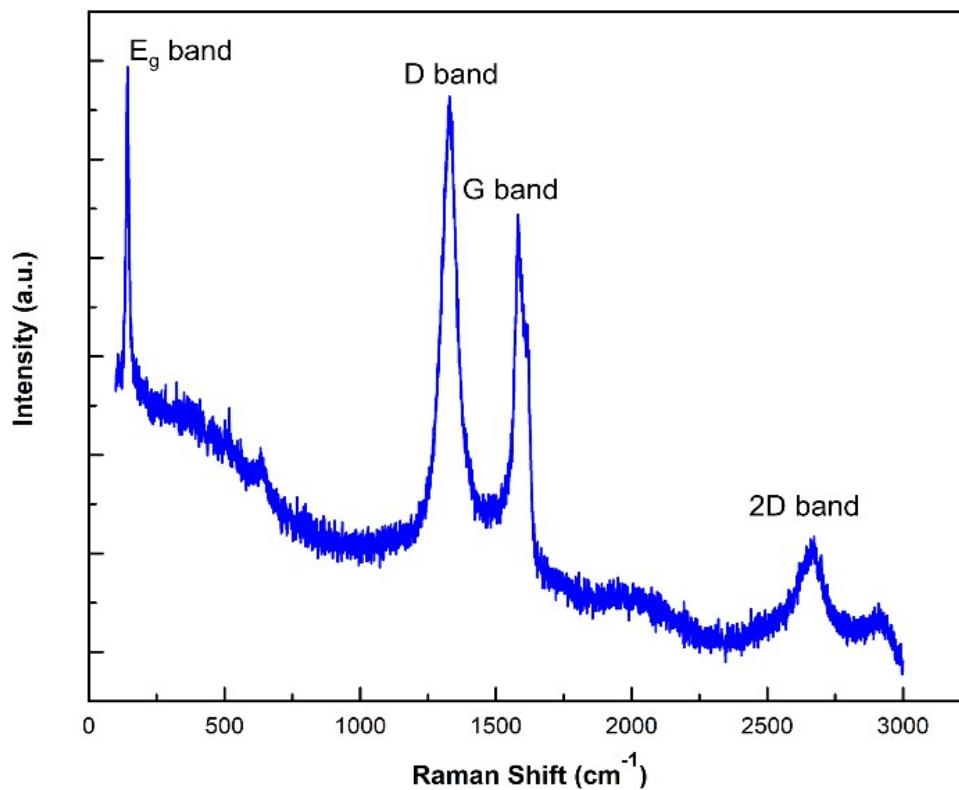


Figure S3 Raman spectrum of graphene/TiO₂ film sample onto a glass substrate. The E_g band refers to TiO₂, and the D band, G band and 2D band refer to graphene. The intensity of G band and 2D band is 84.39 and 51.77, respectively, resulting in a ratio of 1.63, larger than the value of 0.3 for monolayer graphene.^{S1} The 2D-band is broad as compared with the sharp peak for monolayer graphene. These confirm the multilayer structure of our graphene.

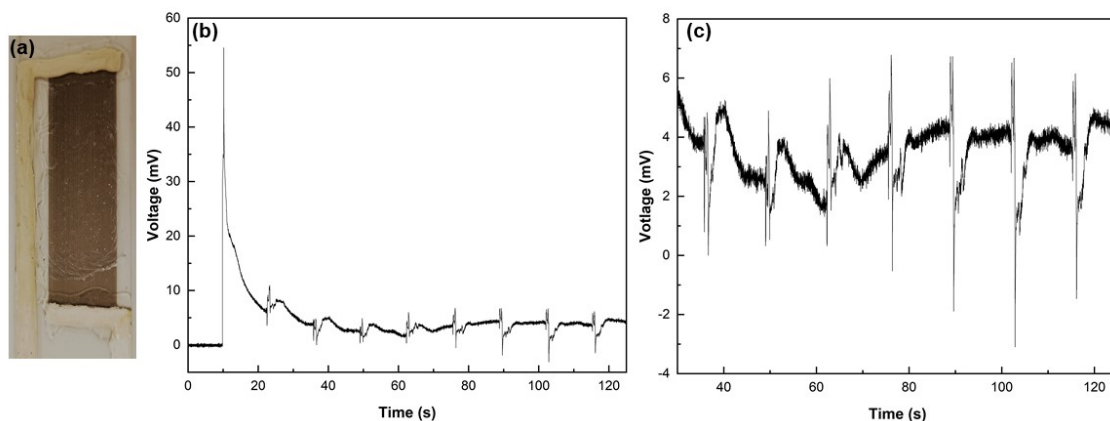


Figure S4 (a) Photograph of an inkjet printed pure graphene ocean wave generator. The graphene film was printed with 10 passes through the same inkjet printing process as in Ref. 25. (b) Recorded voltage signals of the pure graphene film during a series of movement into and out of 0.6 M NaCl solution at the velocity of 1 cm/s. (c) An enlarged view of some cycles in (b).

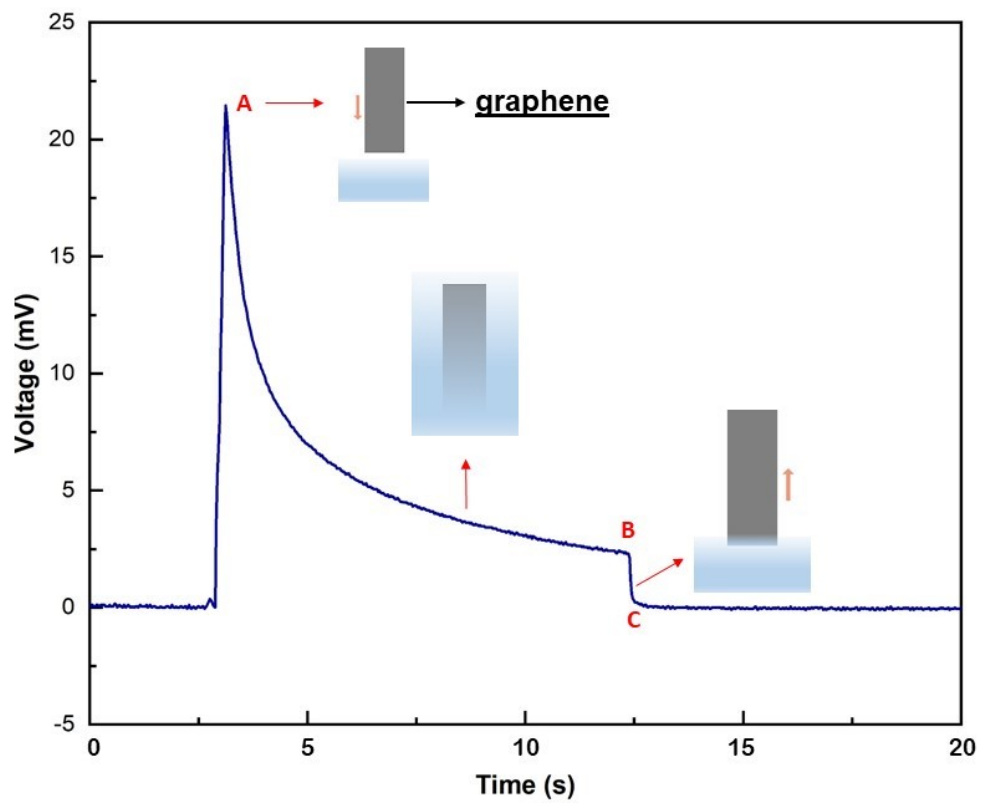


Figure S5 Voltage signal during the entire course of the immersion of the graphene/TiO₂ sample. A: The sample was first inserted into the salt solution. A-B: The sample was immersed in the solution without any movement. B-C: The sample was pulled out of the solution.

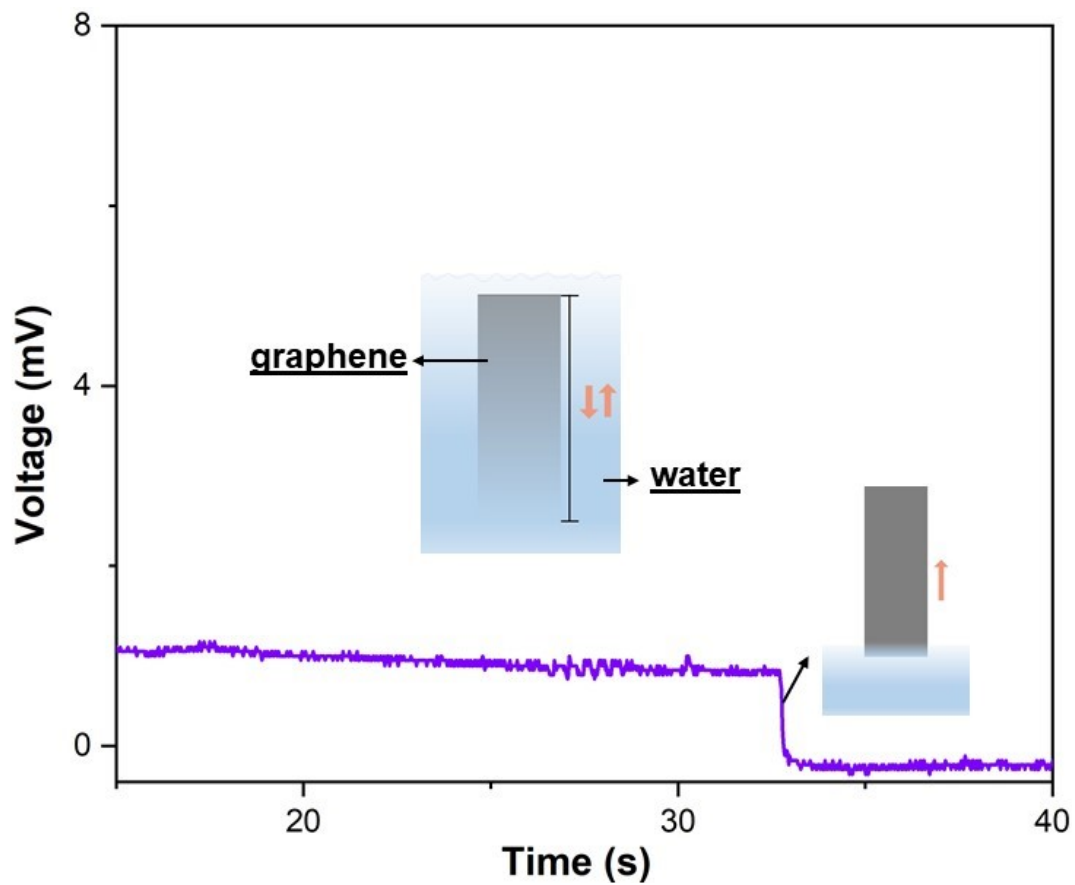


Figure S6 Voltage signal during the multiple inserting/pulling cycles of the graphene/TiO₂ film fully immersed in the saltwater. After reaching the first peak voltage signal, the sample was fully immersed in the water. In spite of multiple inserting/pulling cycles, no more voltage peaks could be observed.

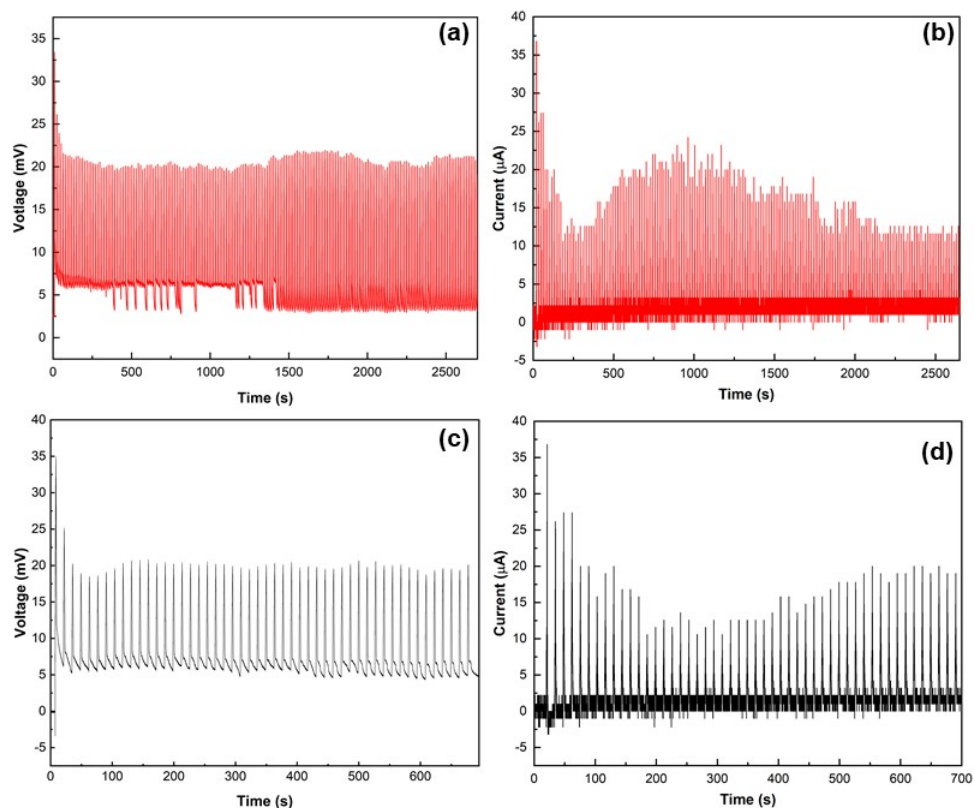


Figure S7 Recorded voltage signals of graphene/TiO₂ film during (a) 200 cycles of movement into and out of 0.6 M NaCl solution. (b) The corresponding current signals generated by graphene/TiO₂ film during 200 cycles of movement. (c and d) The first 50-cycles voltage and current signals from (a) and (b), respectively. All the measurements were conducted at the same velocity of 1 cm/s, the interval time of 10 s, and the inserting depth of 5 cm.

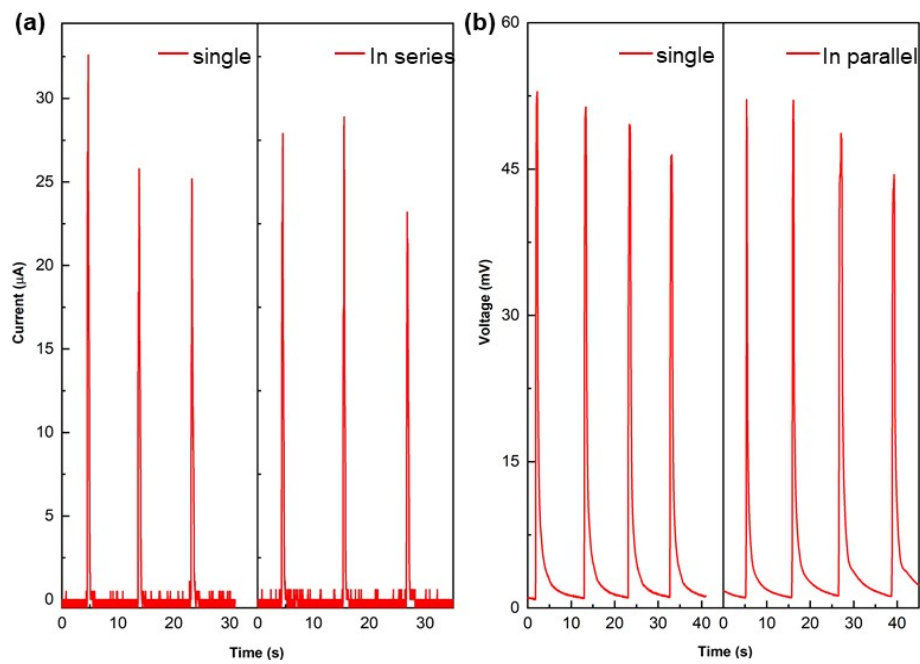


Figure S8 (a) Current signals for single and two series-connected samples; (b) Voltage signals for single and two parallel-connected samples.

Table S1 Comparison of waving potential performance on our graphene/TiO₂ film with other reported generators.

Materials	Flow Type	Preparation	Substrate	Velocity (cm/s)	Potential (mV)	Power (nW)	Refs.
Monolayer graphene/GO	Droplet	Electrophoresis	PET	40-100 mL/h	0,062	0,304	S2
Monolayer graphene	Droplet	CVD	SiO ₂ /Si	2,25	0,15	--	14
rGO	Droplet	Hummers	PET		0,15	0,081	S3
G-CB/PTFE	Droplet	Wet Chemistry	Pt/Pt-Ni	50 mL/h	0,152	0,085	S4
Monolayer graphene	Waving	CVD	PET	100	100	1100	5
				3.1	3	--	
Wrinkled graphene	Waving	CVD	SiO ₂ /Si	80	73,1	633,8	21
ZnO nanofilm	Waving	sputtering	PET	4.2	53	47.7	23
G-CB/PU	Waving	Wet Chemistry	Glass, etc.	--	20	400-500	17
Boron-doped graphene	Waving	HFCVD	Quartz glass	10	40-60	--	19
Graphene nickel foam	Waving	Hummers	--		0,3	--	S5
rGO/MXene	Waving	Hummers	--		260	--	S6
Graphene/TiO ₂ film	Waving	Electrochemical exfoliation	Glass	3.2	75	1800	This work
				1.0	19	430	

PET – polyethylene terephthalate
G-CB – Graphene and carbon black
PTFE – Polytetrafluoroethylene
PU – polyurethane

References

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