Supplementary Information (SI) for ChemComm.

Supporting information

Tube-shaped g-C_3N_4 for enhanced piezocatalytic H_2 evolution

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Experimental section

1. Preparations

g-C_3N_4 microtubes (CNT): A mixture of 7.2 g of melamine and 4.8 g of urea was dissolved/dispersed in 60 mL of deionized water by sonication. After stirring for 1 h, the mixture was transferred to a Teflon-lined autoclave and hydrothermally treated at 180 ^{o}C for 12 h. The resulting product was washed with deionized water and ethanol, and then dried at 60 ^{o}C for 3 h. The dried precursor was placed in a covered crucible and heated to 550 ^{o}C at a rate of 5 $^{o}C\cdot min^{-1}$ in a muffle furnace, followed by calcination at this temperature for 4 h. The obtained microtube g-C_3N_4 was denoted as CNT, corresponding to a precursor containing 60 wt% melamine. For CNT samples with different melamine contents, the same procedure was applied using a total precursor mass of 12 g with varied melamine ratios.

g-C_3N_4 nanosheets (CNS): 10 g of urea was placed in a covered crucible and heated to 550 ^{o}C at a rate of 5 $^{o}C\cdot min^{-1}$ in a muffle furnace, followed by calcination at this temperature for 4 h. The resulting g-C_3N_4 nanosheets were denoted as CNS.

2. Characterizations

Crystalline structures were examined by X-ray diffraction using a Shimadzu Lab XRD-6100 diffractometer equipped with Cu Kα radiation ($\lambda = 0.1541$ nm). Textural properties were evaluated from N_2 adsorption–desorption measurements collected at 77 K on an ASAP 2460 instrument; the specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) model, while pore size distributions were derived using the Barrett-Joyner-Halenda (BJH) approach. Surface chemical states were analyzed by X-ray photoelectron spectroscopy on a Shimadzu/Kratos AXIS SUPRA+ system. Morphological features were observed using a HITACHI SU-8010 scanning electron microscope. Optical absorption characteristics were investigated by ultraviolet-visible diffuse reflectance spectroscopy on a Shimadzu UV-3101 spectrophotometer, employing $BaSO_4$ as the reference material. Fourier-transform infrared spectra were recorded with a Nicolet iS10 spectrometer. Elemental compositions were determined using a Thermo Scientific FLASH 2000 elemental analyzer.

3. Electrochemical test

Electrochemical tests were carried out on a CHI660E electrochemical workstation using a conventional three-electrode setup with 0.5 M Na_2SO_4 as the supporting electrolyte. A platinum wire and a saturated Ag/AgCl electrode were employed as the counter and reference electrodes, respectively. To prepare the working electrode, 10 mg of the catalyst was dispersed in 5 mL of ethanol containing 80 μL of 5 wt.% Nafion binder, followed by ultrasonication for 30 min to obtain a homogeneous suspension. An aliquot of 10 μL of the catalyst ink was drop-coated onto a cleaned FTO substrate (1×1 cm^2) and dried at 80 ^oC for 2 h. Piezoelectric current responses were evaluated by placing the electrochemical cell in a 160 W ultrasonic bath, and the corresponding current-time (i-t) curves were collected under alternating on/off ultrasound irradiation. Electrochemical impedance spectroscopy measurements were conducted at an applied overpotential of 600 mV over a frequency range from 0.01 Hz to 100 kHz with a sinusoidal perturbation of 5 mV. Mott-Schottky plots were recorded within a potential window of -1 to 1 V (vs Ag/AgCl) at frequencies of 1.7 and 2.7 kHz. All measured potentials were converted to the reversible hydrogen electrode (RHE) scale according to the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times pH$$

where $E_{Ag/AgCl}$ is the measured potential versus the Ag/AgCl reference electrode.

4. Piezocatalytic tests

For piezocatalytic measurements, 10 mg of catalyst was suspended in 20 mL of an aqueous glucose solution (1.4 $mol \cdot L^{-1}$) within a 60 mL glass reaction vessel. A calculated volume of H_2PtCl_6 solution was introduced to yield a Pt cocatalyst loading of 2 wt.% relative to the catalyst. The resulting mixture was bubbled with high-purity argon (99.999%) for 30 min to eliminate dissolved oxygen and then hermetically sealed using a silicone septum. The suspension was first exposed to a 300 W xenon lamp under continuous magnetic stirring for 1 h. Subsequently, the stir bar was removed, and the system was purged again with argon. The sealed reactor was then positioned at the center of an ultrasonic bath operating at 40 kHz with an output power of 160 W. To suppress temperature rise during sonication, the bath water was replaced every 15 min, ensuring that the reaction temperature remained below 30 ^oC. Gas aliquots (100 μL) were withdrawn at 1 h intervals using a gastight syringe, and the evolved hydrogen was quantified by gas chromatography (s·sun GC-9860) equipped with a thermal conductivity detector.

5. Simulations

Finite element method (FEM) simulations were performed using the Piezoelectric Devices (pze) Multiphysics interface to analyze the stress distribution and the induced piezoelectric potential. Two representative geometries were considered: a nanosheet with dimensions of 300 nm × 300 nm × 2 nm, and a hexagonal microtube with an outer side length of 5 μm, an inner side length of 4 μm, and a height of 20 μm. A compressive stress of 1×10^8 Pa was applied to the surface of the nanosheet or to one face of the microtube, while a tensile stress of the same magnitude was imposed on the thin edge surfaces of both models. Due to the lack of reliable piezoelectric parameters for $g\text{-}C_3N_4$, ZnO and several other representative piezoelectric materials ($BaTiO_3$, PVDF, CdS, GaAs, Rochelle salt and AlN) with well-established material properties available in the COMSOL database were used as substitutes in the simulations.

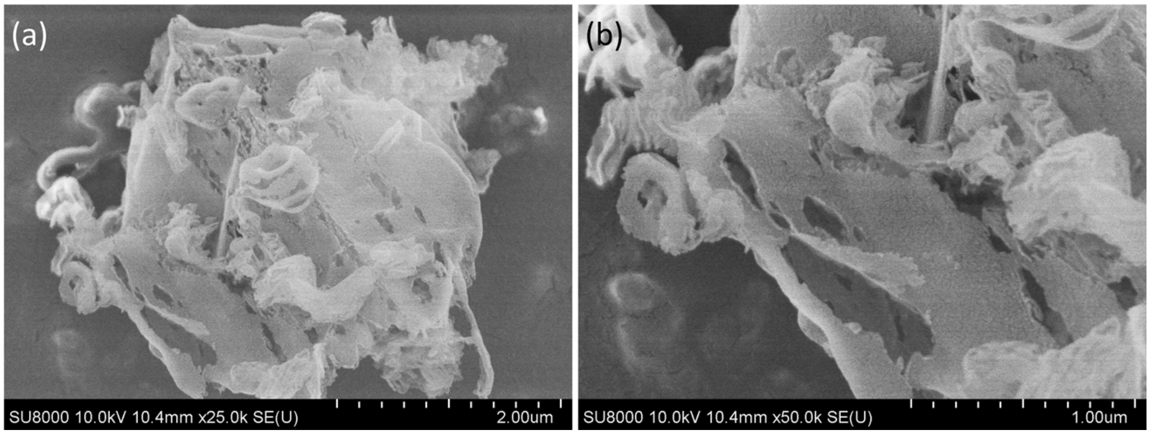

Fig. S1 SEM images of 2D CNS.

Table. S1 Surface elemental compositions of CNS and CNT determined by XPS analysis.

	CNS	CNT
C1s	49.78 %	40.62 %
N1s	45.45 %	57.8 %
O1s	4.77 %	1.58 %

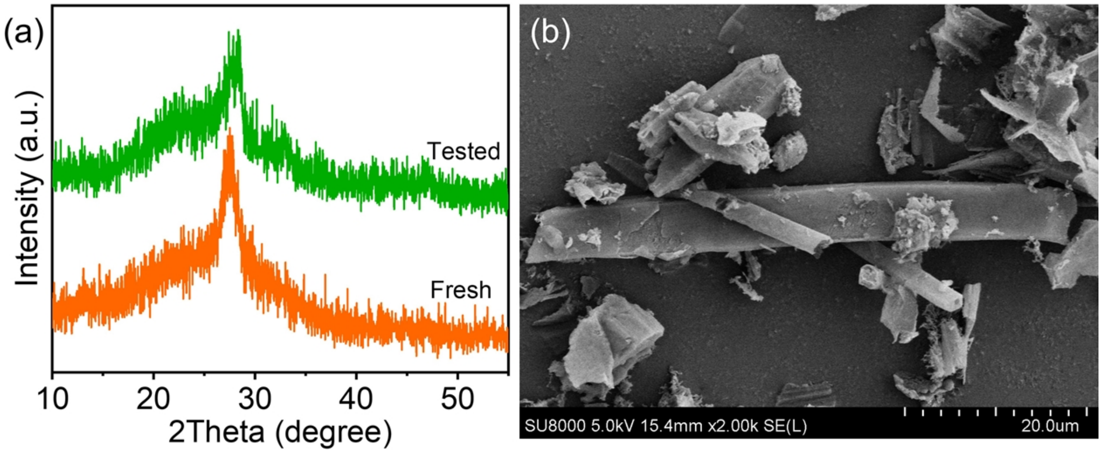

Fig. S2 (a) XRD patterns of CNT before and after the recyclability tests; (b) SEM image of CNT following the recyclability tests.

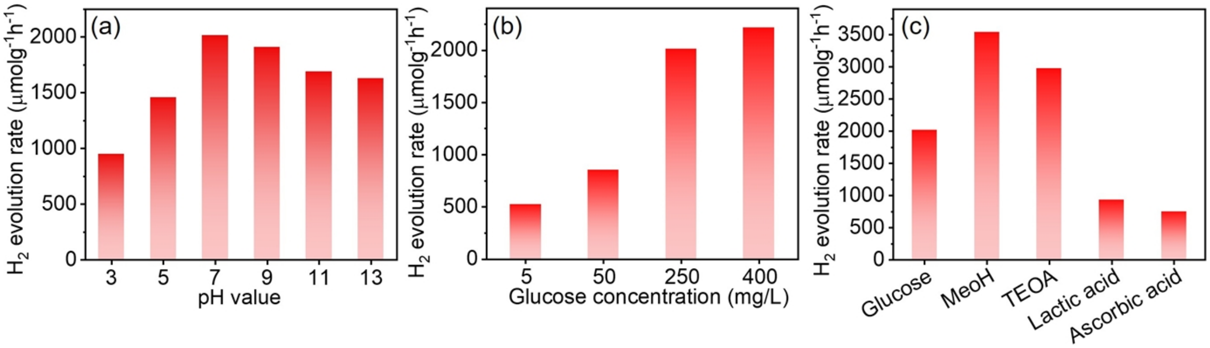

Fig. S3 Evaluation of CNT activity at varying (a) pH values, (b) glucose concentrations, and (c) using different sacrificial reagents.

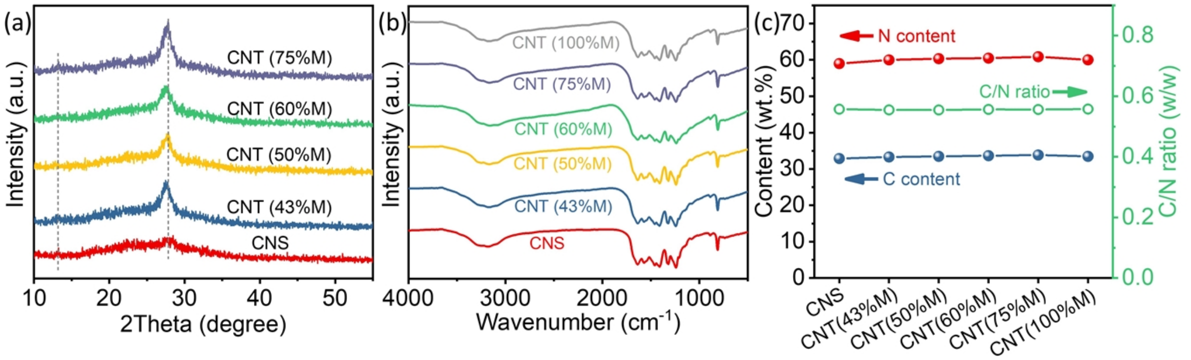

Fig. S4 (a) FTIR spectra, (b) XRD patterns, and (c) elemental compositions of various g-C_3N_4 samples.

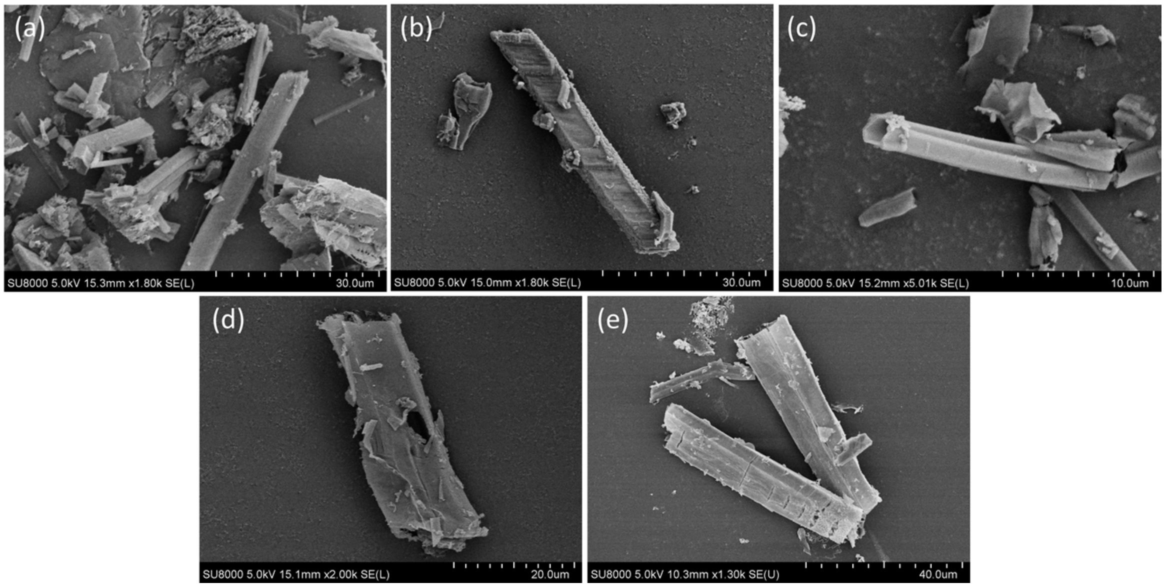

Fig. S5 SEM images of CNT prepared with (a) 43%, (b) 50%, (c) 60%, (d) 75%, and (e) 100% melamine.

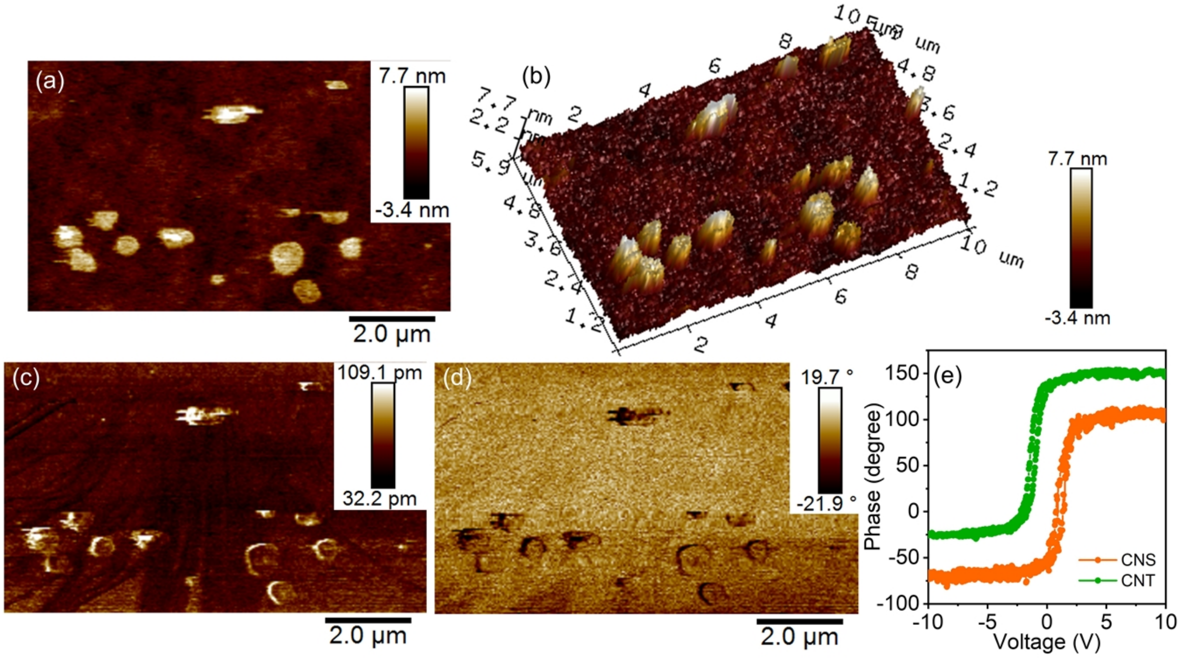

Fig. S6 (a,b) AFM images of CNS. (c) PFM amplitude and (d) phase images of CNS. (e) Phase hysteresis loops of CNS and CNT.

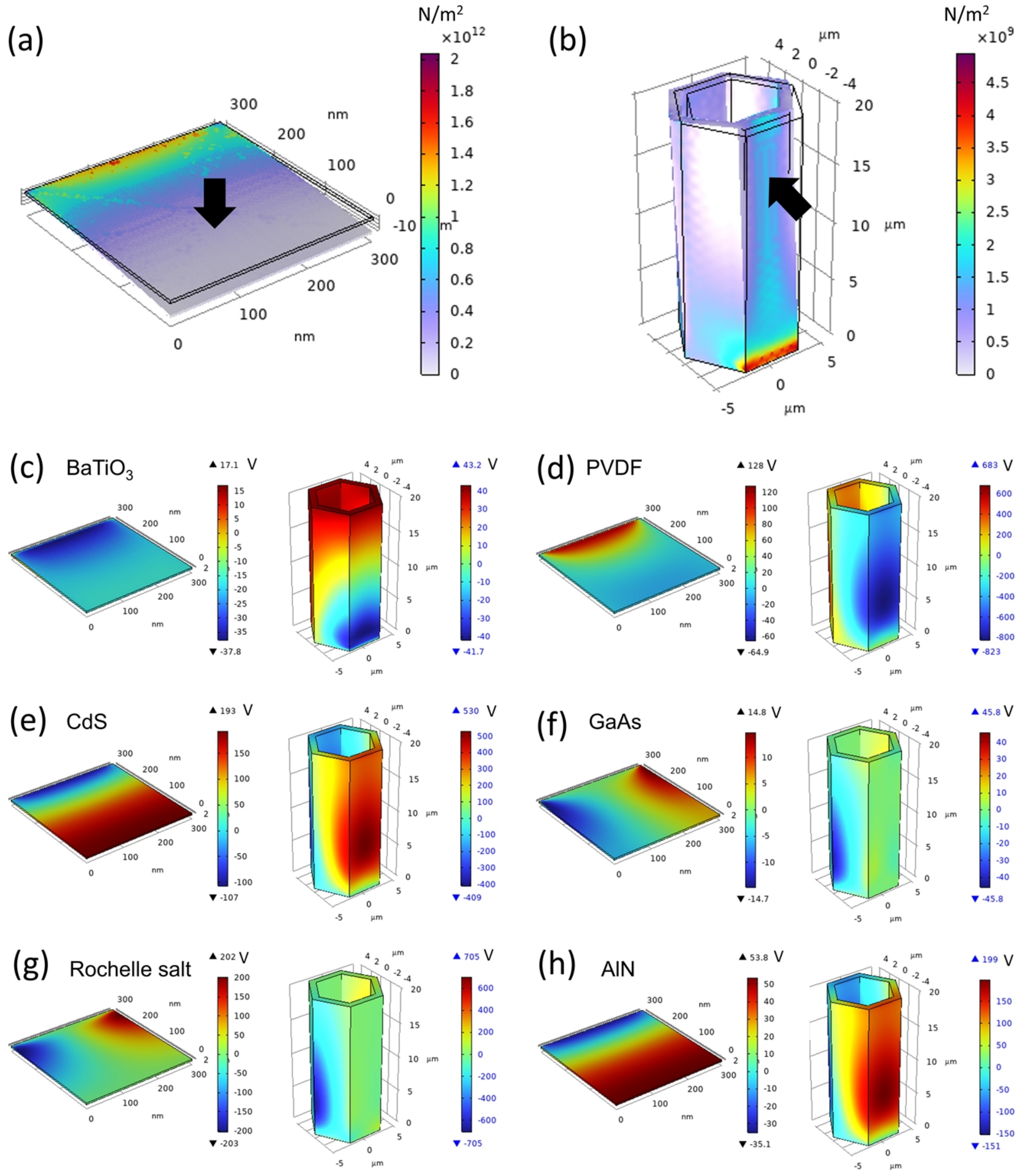

Fig. S7 COMSOL Multiphysics-simulated strain distributions of ZnO (a) nanosheets and (b) hexagonal microtubes under an external pressure of 10^8 Pa applied to the nanosheet surface or to one face of the microtube. COMSOL Multiphysics-simulated piezoelectric potential distributions of nanosheet and hexagonal microtube geometries under the same pressure (10^8 Pa), using different piezoelectric materials: (c) $BaTiO_3$, (d) PVDF, (e) CdS, (f) GaAs, (g) Rochelle salt, and (h) AlN. The microtube geometry generates a much larger maximum voltage difference than the nanosheet for all materials examined.

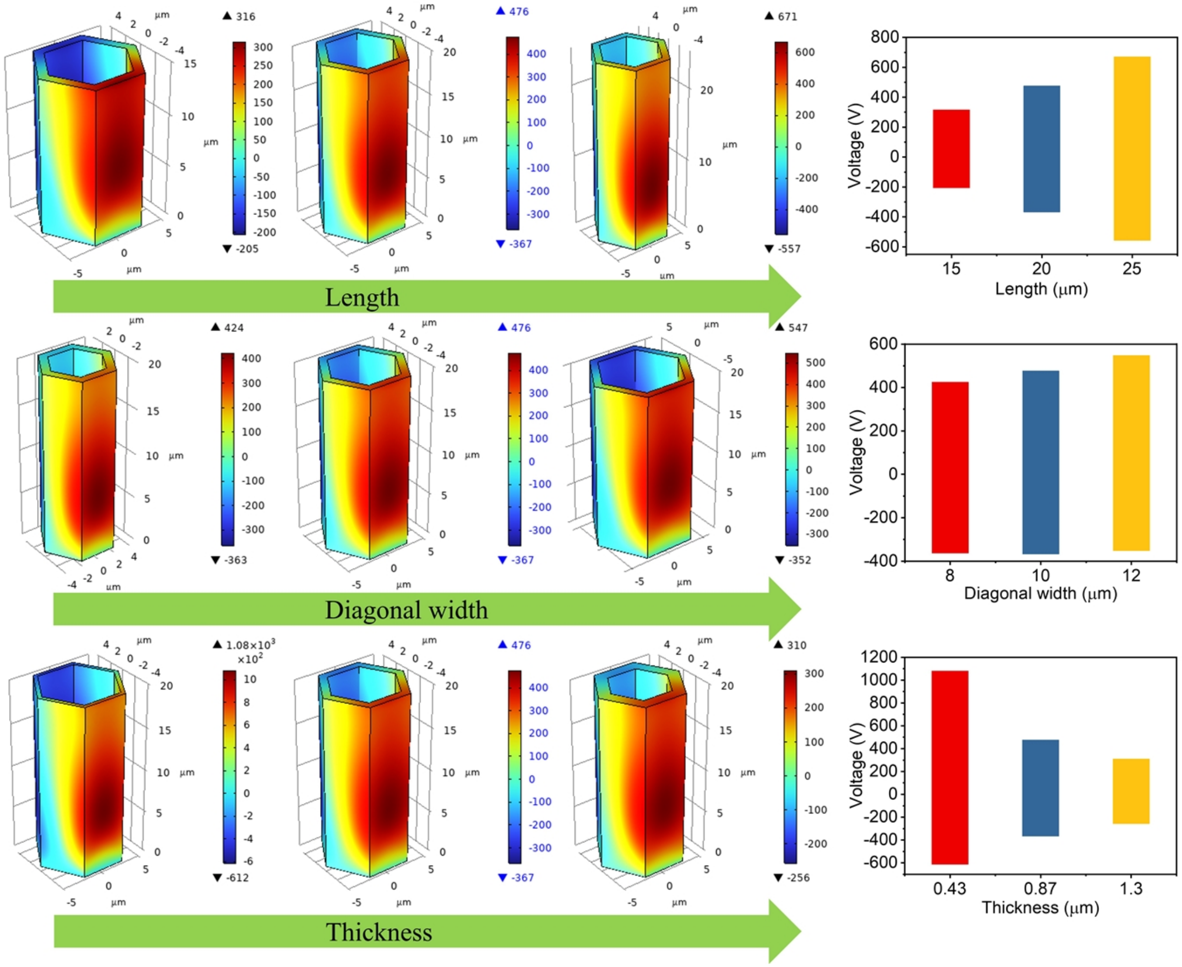

Fig. S8 COMSOL Multiphysics-simulated piezoelectric potential distributions of hexagonal microtubes with different lengths, diagonal widths, and wall thicknesses under the same applied pressure (10^8 Pa). The results show that the piezoelectric potential increases with increasing tube length and diagonal width, or with decreasing wall thickness.

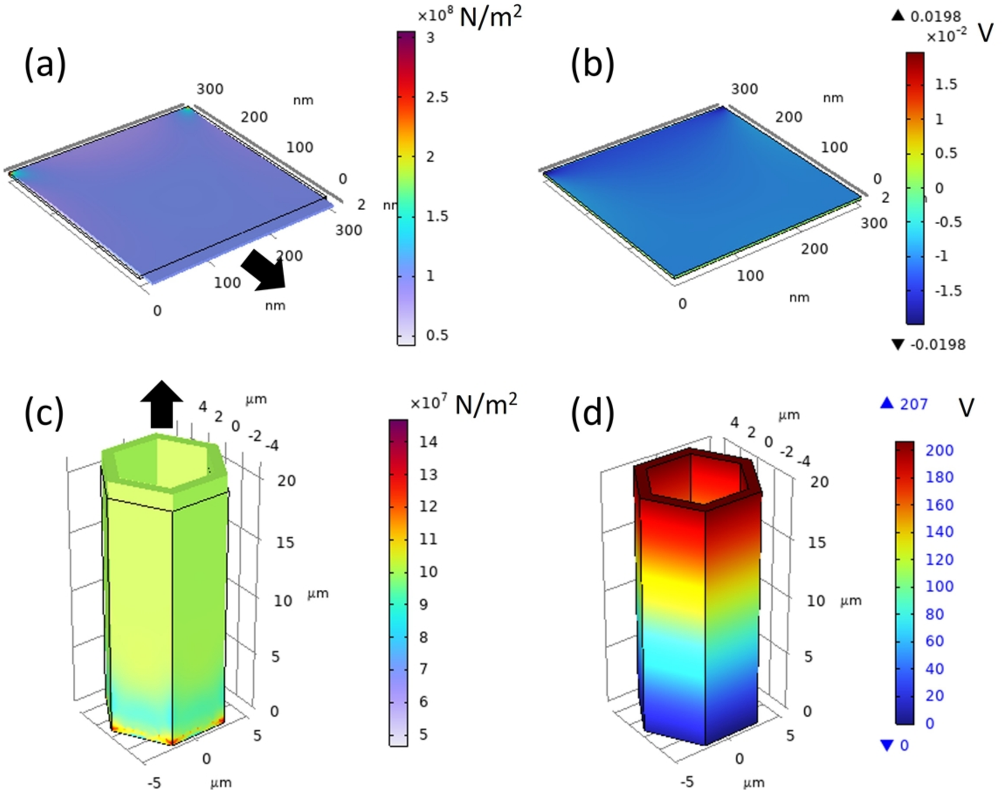

Fig. S9 COMSOL Multiphysics-simulated strain and piezoelectric potential distributions of ZnO (a-b) nanosheet and (c-d) hexagonal microtube under a tensile force of 10^8 Pa applied to the thin edge surfaces.