## **Supporting Information**

## High stretchable, transparent cellulose/PVA composite hydrogel for multiple sensing and triboelectric nanogenerator

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## **Experimental Section**

*Materials*: Cellulose (cotton linter pulps) with a certain viscosity–average molecular weight of  $10.8 \times 10^4$  g mol<sup>-1</sup> containing  $\alpha$ -cellulose content of no less than 95 % supplied by Hubei Chemical Fiber Co., Ltd. (Xiangfan, China) was vacuum-dried at 60 °C for 48 h to remove any moisture before use. BzMe<sub>3</sub>NOH (40 wt% aqueous solution) was purchased from Sigma-Aldrich Co. PVA with an average degree of polymerization of 1750±50 and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., and were used without further purification.

Fabrication of Cellulose/PVA Composite Hydrogel (CPH): The PVA sample was dispersed in BzMe<sub>3</sub>NOH aqueous solution (1.88 mol L<sup>-1</sup>) at room temperature, and the mixture was heated to 74 °C for 15 min with stirring, during which PVA was dissolved and a transparent solution was obtained. The resultant solution was cooled to room temperature followed by dispersing the cellulose sample, and the mixture was then stored in a refrigerator (-24 °C) for 3 h to freeze. The solid was then thawed with stirring at room temperature, to obtain the blend solution. The blend solution with the cellulose concentration of 4 wt% and PVA concentration of 4 wt% was kept at 5 °C by soaking in an ice-water bath, and epichlorohydrin (ECH) was injected dropwise via a syringe into the mixture solution with the volume ratio of 1:75. The resultant mixture was stirred constantly at 5 °C for another 20 min, and centrifuged with a speed of 6000 rpm for 10 min at 5 °C to remove the air bubbles. The transparent and viscous cellulose/PVA solution with ECH was then poured into a rectangular silica gel mold (40 mm width, 100 mm length, 20 mm height) for the preparation of composite hydrogel with rectangular shape. The cellulose/PVA solution in the mold was placed with no cover at 25 °C, 45 % relative humidity for 12 h, to control the water evaporation rate during chemical cross-linking. Afterwards, the cellulose/PVA hydrogels were directly obtained by removing from the mold, and used directly as the conductive cellulose/PVA hydrogel without further treatment, marked as CPH. For comparison, CPHs with different volume ratio of ECH to mixture solution of 1:150, 1:50, 2:75, 1:30 were also tested.

*Assembly of Devices:* Four kind of devices were presented herein: CPH-based temperature sensor, CPH-based strain sensor, CPH-based pressure sensor, and CPH-based triboelectric nanogenerator (CPH-TENG). For CPH-based temperature sensor, CPH-based strain sensor and CPH-TENG, a piece of CPH was sandwiched by two layers of VHB (VHB 4905, 3M). While for the CPH-based pressure sensor, the transparent VHB layer was sandwiched between two layers of CPHs, and extra two layers of VHB were attached to the top and bottom of the sensor to insulate the sensor and prevent evaporation, following the structure of capacitive sensor designed by previous researchers.<sup>1, 2</sup> The surfaces of the CPH samples were dried with N<sub>2</sub> gas for 1 min before assembling. Copper foil tape was used as electrode to ensure a good contact, and each device was connected to tester by insulated copper wires.

*Characterization*: Mechanical tests of CPH at ambient temperature were performed using Instron 5967 universal testing machine (Instron Ltd., America) with a 500 N load cell. CPH sample with a rectangular shape was trimmed to dumbbell-shaped specimens for the tensile test, and tests were terminated when fracture occurred. For the compression tests of CPH-based pressure sensor, pre-experiment showed that no obvious fracture happened before 100 % strain, thus the compression tests were terminated at 50 % strain. Deformation rate of the dumbbellshaped samples in tensile tests and CPH-based pressure sensor in compression tests were both 5 mm min<sup>-1</sup>. All the tests were repeated at least 8 times. The optical transmittances of CPH were measured using a Shimadzu UV-160A UV-vis spectrophotometer. Microscope images of CPH and freeze-dried CPH were taken by a XY-P polarized microscope (Sunny Optical Technology (Group) Co., Ltd.).

Rheological tests of the CPH samples (cylinders, 40 mm in diameter and 2 mm in height) were carried out by using a TA Discovery HR-2 Hybrid Rheometer (TA Instruments Ltd, USA) with a parallel plate geometry (40 mm in diameter) at the temperature arrange from 0 to 100

°C. The rheometer was equipped with a Julabo FS18 cooling/heating bath that was calibrated to maintain the temperature of the sample chamber within a  $\pm 0.5$  °C difference of the set value. The storage modulus (*G*') and loss moduli (*G*'') of CPH were measured with angular frequency ( $\omega$ ) of 10 rad s<sup>-1</sup> at a constant strain ( $\gamma$ ) of 0.1 %.

*Characterization and Performances of CPH Based Sensors*: Electric resistance change of the CPH-based temperature sensor and the CPH strain sensor were measured by a UC2684A Insulation Resistance Tester (UCE Technologies., Ltd, China) and recorded by software under 1 V, which could eliminate the electrochemical reaction during the functioning of conductive hydrogels. For the CPH-based temperature sensor, the cooling-heating cyclic tests were performed by using a Peltier temperature controller system. The CPH-based\* temperature sensor was placed on the 80 mm Standard Peltier Plate and the temperature were elevated from 0 to 64 °C and then back to 0 °C, for 10 cycles, at a ramp rate of 5 °C min<sup>-1</sup>. The temperature coefficient of resistance (TCR) was calculated by Equation 1:<sup>3</sup>

$$TCR = (dR/dT)/R \tag{1}$$

where *R* is resistance-temperature function, dR/dT is the differentiation of resistancetemperature function. CPH-based pressure sensor was connected to the electrodes of a capacitance meter (LCR/ESR meter, Model 885, BK Precision). A sinusoidal measurement signal with a maximum voltage of 1 V was set and a frequency of 10000 Hz was applied. The change of capacitance with repeated pressure and release at ambient temperature was recorded, with each pressure or release was hold for about 36 seconds.

Characterization and Performances of CPH-TENG: Open circuit voltage ( $V_{OC}$ ), short-circuit charge quantity ( $Q_{SC}$ ) and short-circuit current ( $I_{SC}$ ) were recorded by a Keithley electrometer 6514. The contact-separation motion was controlled by placement and removal of a certain weight on and off CPH-TENG which was fixed on an insulation plane, to provide certain pressures with frequency about 0.5 Hz. The weight was wrapped with nylon, which has larger difference in the ability of losing/gaining electrons compared with VHB among the available

materials, thus the more electrostatic charges generated at the interface and the higher  $V_{OC}$  was obtained.<sup>4</sup> For the dehydration test, CPH and CPH-TENG were stored in a constant temperature oven with desiccants, and the temperature and relative humidity (RH) were monitored by a commercial HTC-1 Digital Electronic Thermohygrometer (Zhengzhou Boyang Instrument And Meter Co., Ltd, China) to be 25 °C and 30 RH%, respectively, and the weights of the samples were recorded every day. For the measurement of  $V_{OC}$  at different temperatures, CPH-TENG was fixed on Standard Peltier Plate and the temperatures were controlled by computer system. For the measurement of CPH-TENG at different RH, various constant RH conditions were achieved by airtight boxes containing saturated solutions of different metal salts. LiCl, MgCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, CuCl<sub>2</sub> and KCl were sealed in boxes at 25 °C to obtain RH conditions of 11 %, 32 %, 43 %, 68 % and 85 %, respectively.<sup>5</sup> The real value of RH were measured by a commercial HTC-1 Digital Electronic Thermohygrometer (Zhengzhou Boyang Instrument And Meter Co., Ltd, China).



**Fig. S1** The preparation of cellulose/PVA/BzMe<sub>3</sub>NOH solution. (a) 1.88 mol L<sup>-1</sup> BzMe<sub>3</sub>NOH aqueous solution. (b) PVA was added to the BzMe<sub>3</sub>NOH aqueous solution. (c) After being heated to 74 °C for 15 min with stirring, PVA was dissolved. (d) Cellulose sample was dispersed in the resultant solution after being cooled to room temperature. (e) The mixture was stored in a refrigerator (-24 °C) for 3 h to freeze and thawed at room temperature with stirring, to obtain cellulose/PVA/BzMe<sub>3</sub>NOH solution.



**Fig. S2** CPHs prepared with different volume ratio of ECH to mixture solution. The ratio 1:150 was too low to construct a chemically cross-linked hydrogel.



**Fig. S3** The photographs of columnar CPH gel before (a), during (b), and immediately after compressed to 50% (c).



**Fig. S4** SEM images of freeze-dried CPH: (a) cross section, (b) surface and (c) detailed surface, magnifications were  $250\times$ ,  $700\times$  and  $1750\times$ , accordingly.



**Fig. S5** (a) Resistive response of CPH-based temperature sensor is insensitive to compressive strain at 25 °C. (b) The capacitive response of CPH-based pressure sensor is insensitive to the temperature variation.



**Fig. S6** Relative resistance variation  $(\Delta R/R_0)$  and gauge factor (GF) of the CPH strain sensor as function of strain, blue line is the linear fitting result.



Fig. S7 Weight change of CPH and CPH-TENG in dry air (30 RH%, 55 °C).



**Fig. S8** Comparison of (a) open circuit voltage ( $V_{OC}$ ), (b) short-circuit charge quantity ( $Q_{SC}$ ) and (c) short-circuit current ( $I_{SC}$ ) of CPH-TENG before and after storing in the dry environment (30 RH%, 25 °C) for 30 days.



**Fig. S9** (a)  $V_{OC}$ , (b)  $Q_{SC}$  and (c)  $I_{SC}$  of the CPH-TENG that lasted for ~4800 cycles of contact-separation motions (about 3 hours).



**Fig. S10** (a)  $V_{OC}$  of CPH-TENG with contact-separation motion measured at five different relative humidity. (b) The summarized  $V_{OC}$  of CPH-TENG with contact-separation motion measured at different relative humidity (from 11.3 % to 85.1 %).



Fig. S11  $V_{OC}$  of CPH-TENG with contact-separation motion measured at five different temperatures.

Table S1 Mechanical property and transparency of CPH at different temperatures.  $\sigma_b$  and  $\varepsilon_b$ 

are tensile strength and elongation at break, respectively.

Temperature [°C]	$\sigma_{ m b}$ [kPa]	$\mathcal{E}_{\mathrm{b}}\left[\% ight]$	Transparency at 550 nm [%]
-10	36.95±0.59	743.65±2.25	81.65
0	36.41±0.53	741.51±1.74	81.47
10	$36.72 \pm 0.65$	744.12±1.64	80.44
25	36.67±0.76	737.04±2.68	80.42
40	35.85±0.62	741.29±1.85	80.63
50	$36.82 \pm 0.94$	743.23±2.58	81.17
60	36.16±0.82	748.88±2.24	80.82

**Table S2** Temperature coefficient of resistance (TCR) of the reported flexible resistance-temperature sensors.

Mate	erials	TCR [°C-1]	Reference

AgNW/CPI <sup>a)</sup>	0.0033	3
CCH <sup>b)</sup>	-0.0508	6
Ag/Kapton HN <sup>c)</sup>	0.00223	7
GNWs/PDMS <sup>d)</sup>	0.214	8
p-3C–SiC <sup>e)</sup>	-0.0055	9
GOP <sup>f)</sup>	-0.0044	10
BCTS <sup>g)</sup>	-0.002778	11
OFETs array-device	0.044	12
DN Hydrogelh)	0.026	13
DN Hydrogel <sup>i)</sup>	0.094	14
CPH <sup>j)</sup>	-0.03	This work

<sup>a)</sup>(AgNWs embedded on the flexible colorless polyimide film); <sup>b)</sup>(Conductive cellulose hydrogel based dual functional sensor); <sup>c)</sup>(Thermistor composed silver deposited on a Polyimide substrate); <sup>d)</sup>(Combination of graphene nanowalls with polydimethylsiloxane); <sup>e)</sup>(P-type single crystalline 3C–SiC); <sup>f)</sup>(Graphite on paper); <sup>g)</sup>(Biocompatible temperature sensor); <sup>h)</sup>(Polyacrylamide/carrageenan double network hydrogel); <sup>i)</sup>(Muti-wall carbon nanotubes composite polyacrylamide/Fe<sup>3+</sup>-polyacrylic acid double network hydrogel); <sup>j)</sup>(Cellulose/PVA hydrogel).

**Table S3** Comparison of the sensitivity (S) and gauge factor (GF) of the reported flexible pressure sensors.

Materials	S [kPa⁻¹]	GF	Detection Limit [Pa]	Device	Transparent	Ref.
СРН	0.76~13.91	9.70	<36	Capacitive	Yes	This work
Salt/PEG hydrogel ionic circuits	0.00111~0.005	/	1	Resistive	Yes	15
NaCl/SA/PAM DN ionic gel	0.02~1.45	2.66	100	Resistive	Yes	16
PAM-PVA conductive hydrogel	0.02~0.05	1	1	Current	Yes	17
ACC/PAA/alginate hydrogel- based ionic skin sensor	0.17	1.19	1	Capacitive	No	18
PAAm/PEO/LiCl ionic conducting hydrogels	0.67~1	/	<250	Resistive	No	19
Carbonized silk nanofiber membranes	1.16~34.47	1	0.8	Current	Yes	20
PMAA-co-DMAPS	0.09	1	/	Capacitive	Yes	2
lonic skin	0.00925	1	/	Capacitive	Yes	21
CC/PDMS composites	2.2~6.04	1	/	Resistive	No	22
Flexible piezocapacitive pressure sensor	0.077~0.601	/	0.16	Capacitive	No	23
Wireless pressure sensor	5.09~9.32	/	25	Capacitive	No	24
Pressure sensitive transistor	0.38~8.4	/	20	Current	No	25

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