

## Supporting Information

### **Integration of hydrogel with functional nanoparticles using hydrophobic comb-like polymers as an adhesive layer**

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## 1. Materials and general methods

All of the following chemical reagents were used as received from Sigma-Aldrich [dimethyl amino proyl acrylamide (DMAPAAM), acrylic acid (AA), N, N'-Methylenebisacrylamide (BIS), dimethyl acrylamide (DMAAM), n-bromosuccinimide (NBC), 2,2'-azobis-(isobutyronitrile) (AIBN), potassium persulfate, N, N, N', N'-tetramethyl ethylene diamine (TEMED), Methyl styrene (MS), Lauryl methacrylate (LMA)], clay nanosheets (Laponite XLS, Rockwood), The superhydrophobic nanoparticles were used as received (DEGUSSA), Sinopharm Chemical Reagents [dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), 1,2-dichloroethane, methanol, ethanol, toluene, carbon tetrachloride ( $\text{CCl}_4$ ), acetone, sodium hydroxide], deionized water was obtained via Milli-Q. All photo images in the current work were taken by the camera (Canon 70D). Planetary centrifugal Mixer (THIKY Mixer, ARE-310) was used to obtain the transparent and homogeneous precursor of hydrogel. All contact angles on sample surfaces were measured using the contact angle measuring system (OCA20, Dataphysics). The thickness of modified layer was characterized by laser scanning confocal microscope (LSM 780, Zeiss). The adhesion force of water droplet upon hydrogel was measured by using a high-sensitivity microelectromechanical balance system (Dataphysics DCAT 11, Germany). The mechanical stability of surface modification was characterized by Universal Mechanical Tester (UMT-1, Bruker). The microscopic images were taken by environmental scanning electron microscope (QUANTA 250 FEG). The adhesion force of hydrogel upon various substrates was characterized by dynamometer (M5 series, mark-10).

## 2. Preparation of hydrogel

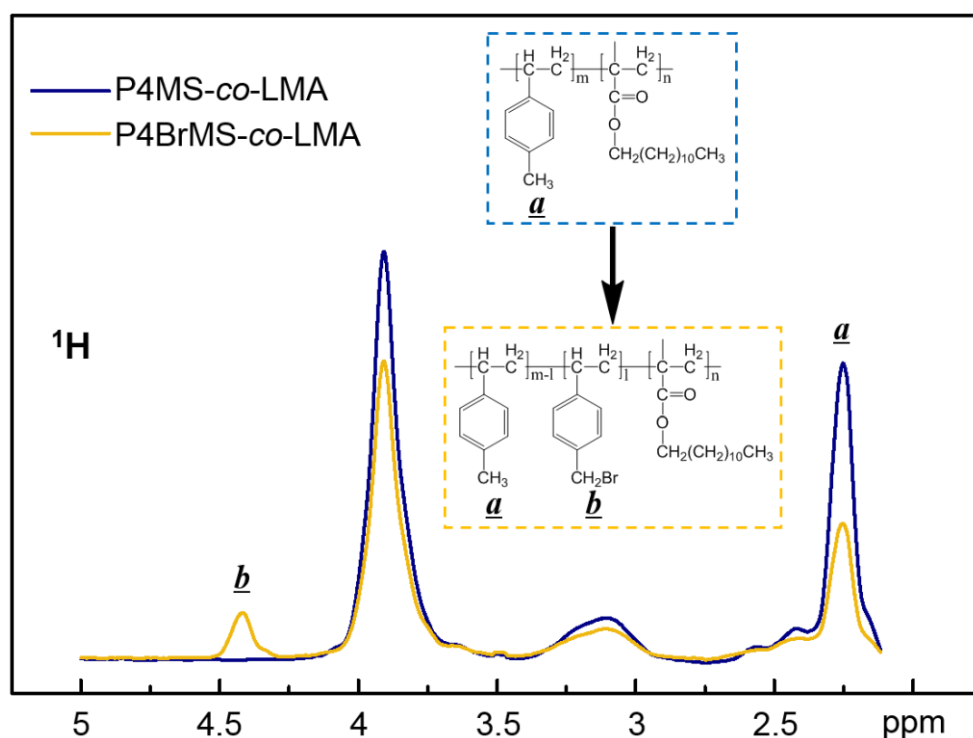
Hydrogel was polymerized by using KPS as initiator and clay nanosheets as crosslinker. Generally, DMAPAAM and DMAAM (anchoring monomer and regular monomers, respectively, with the ratio of 10:1) was first dissolved in water (for the purpose of protecting the tertiary amine groups on anchor monomers, NaOH was used to obtain an alkaline solution

pH ~ 11), The total amount of monomers was 20 wt% (to water) in this experiment. Then clay nanosheets (Laponite XLS) (5 wt% ~15 wt% of water amount) was added and the whole mixture was mixed with Planetary centrifugal Mixer until fully transparent solution was obtained. The solutions were placed in a water bath, at about 5 °C for 10 minutes (to prevent the occurrence of implosion), The polymerization were initiated by KPS (0.005 mol/L) and catalytic by TEMED (0.013 mol/L). The resultant hydrogels were rinsed by ample water to remove residual monomers. For further experiment usage, the as-prepared hydrogel was chopped into hydrogel dices ( $1 \times 1 \times 0.5 \text{ cm}^3$ ).

### **3. Synthesis of Poly(4-bromomethyl styrene-*co*-lauryl methacrylate)**

At first, the copolymer poly(4-methyl styrene-*co*-lauryl methacrylate) (P4MS-*co*-LMA) was synthesized according to literature [1]. Typically, methyl styrene (MS) and lauryl methacrylate (LMA) were dissolved in toluene (the mole ratio of MS and LMA was 4:1), 2,2'-azobis-(isobutyronitrile) (AIBN) was used as initiator. Then the solution was refluxed at 80°C for 12 h under nitrogen flow. The resulting waxy copolymer P4MS-*co*-LMA was purified through precipitation by cold methanol (three times) to remove the unreacted monomers.

Further, the poly(4-bromomethyl styrene-*co*-lauryl methacrylate) (P4BrMS-*co*-LMA) was synthesized according to literature [2]. P4MS-*co*-LMA and n-bromosuccinimide (NBC), 2,2'-azobis-(isobutyronitrile) (AIBN) were mixed in stoichiometric quantity and dissolved in carbon tetrachloride (CCl<sub>4</sub>). Then the solution was refluxed at 80°C for 1 h. Succinimide was filtered and the solvent (CCl<sub>4</sub>) was removed from the brown solution by rotary evaporation. Finally, the waxy product was dissolved in dichloromethane and precipitated (three times) by methanol to remove the unreacted components.



**Figure S1.**  $^1\text{H}$ -NMR spectrometry of P4MS-*co*-LMA and P4BrMS-*co*-LMA. The peak at point *a* representing the chemical shift of  $-\text{CH}_3$ , the peak at point *b* representing the chemical shift of  $\text{CH}_2\text{-Br}$ . As show in the spectrometry, the relative peak value for P4BrMS-*co*-LMA was decreased at point *a*, while the peak at point *b* was observed. This result indicates that P4BrMS-*co*-LMA was achieved using the current synthetic route and bromide substitution on benzyl position was realized.

As shown in **Figure S1**, the formation of P4BrMS-*co*-LMA was verified by  $^1\text{H}$ -NMR spectrometry. The peak value at point *b* (4.42 ppm, corresponding to the benzyl bromide's chemical shift) was observed in  $^1\text{H}$ -NMR spectrometry of P4BrMS-*co*-LMA, which indicates that benzyl bromide moieties were produced.

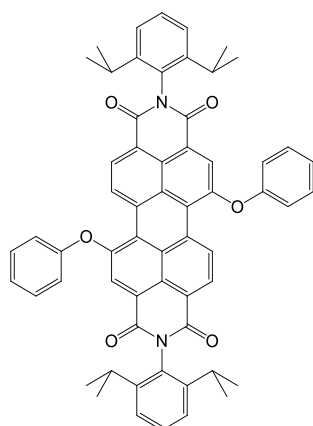
#### 4. Surface modification of hydrogel.

A hydrogel cube was immersed in the dichloromethane, in which a certain concentration of modifiers was dissolved (0.5 mg/mL). The hydrogel dices were immersed for a certain time about 6 ~ 12 hours, which turn out was the optimized condition for the surface modification. For further experiment usage, the as-prepared hydrogels were rinsed with excessive  $\text{CH}_2\text{Cl}_2$  in order to remove physically attached modifiers, then dried by nitrogen flow. The as-prepared gel

pieces were stored at low temperature (2 ~ 8°C, to slow down the dehydration of hydrogel) in the dark.

## 5. Characterization of the thickness of the modified layer

The thickness of the modified layer on hydrogel was characterized by laser scanning confocal microscope. A fluorescent label was used as shown in **Figure S2**. The fluorescent label was dispersed in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) to reach a concentration about 10<sup>-6</sup> mol/L. Then the post-modulated hydrogel were immersed in the solution mentioned above for about 1 h. After that, the sample was rinsed with adequate CH<sub>2</sub>Cl<sub>2</sub> and dried under nitrogen flow before used.



**Figure S2.** N, N'- Bis(2,6-diisopropylphenyl)-1,7-diphenoxy-perylene-3,4,9,10-tetracarboxydiimide.

## 6. Contact angle measurements

Contact angles (CAs) were measured on an OCA20 system (Dataphysics, Germany) at room temperature (25 °C), for water contact angle measurement, 2 μL droplet of water was syringed out and carefully dropped onto the underlying surfaces in air. The average CA values were obtained by measuring at least five different positions on the same sample.

## 7. Water droplet adhesion force measurements

The adhesion force was measured by using a high-sensitivity microelectromechanical balance system in air environment (Dataphysics DCAT 11, Germany). A water droplet about 10  $\mu\text{L}$  was suspended by a copper cap, and a hydrogel sample (1 by 1 by 0.5  $\text{cm}^3$ ) was placed on the balance table, the table moved upward at a constant speed of 0.005  $\text{mm s}^{-1}$ , until the underlying surface contacted the water droplet. Then the table was moved down. Adhesion forces were obtained from the force-distance curves. For each sample, the average adhesion force was obtained from five repeats.

### **8. The preparation of hydrogel electrolyte**

Acrylic acid and DMAPAAm were used as common monomer and anchor monomer, respectively. Clay nanosheets was replaced by BIS due to the easily gelation of clay in salt solution. Hydrogel was polymerized by using KPS (0.004 mol/L) as initiator. The total amount of monomers (with the ratio AA : DMAPAAm = 2 : 3) was 20 wt% to water in this experiment. The surface modification of electrolyte hydrogel was the same as the above-mentioned strategy (1 mol/L KOH and 4 mol/L NaCl were added to prepare hydrogel electrolytes).

### **9. The preparation of polyaniline nanawires coated carbon nanotube papers (PANI-CNTP)**

Polyaniline coated carbon nanotube papers were prepared by electrochemical polymerizing aniline onto carbon nanotube papers (CNTP). The electrochemical polymerization was carried out in a three-electrode system, with CNTP as working electrode, platinum wire as reference electrode and Ag/AgCl electrode as counter electrode. The electrolyte contained 0.2 M aniline and 1 M HCl. After the equipment was setup, the electrochemical polymerization was started immediately. Constant voltage (0.85 V) was used to polymerize aniline onto CNTP. The content of PANI was controlled by the polymerization time (120 s), and estimated by the weight

increase of the as-prepared PANI-CNTP. After deposition, the electrode was immersed in 1 M HCl to remove aniline monomer [3].

## 10. Calculation

### Areal capacitance of the PANI-CNTP electrode:

The areal capacitance ( $C_{\text{cell-GCD}}$ ) ( $\text{mF cm}^{-2}$ ) of PANI-CNTP based electrodes was calculated from their GCD curves and derived from the equation (1):

$$C_{\text{cell-GCD}} = \frac{I \times t}{S \times \Delta V} \quad (1)$$

where  $I$  is the discharge current;  $t$  is the discharge time (s);  $S$  is the surface area of PANI-CNTP electrode; and  $\Delta V$  is the voltage change upon discharging.

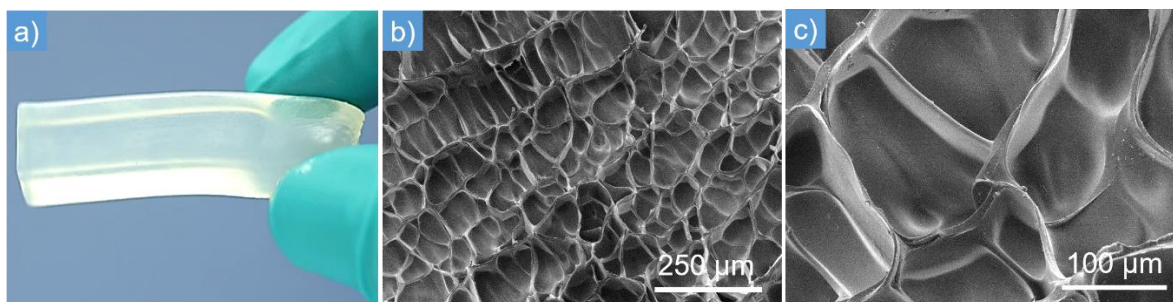
### Energy density and power density of the supercapacitor:

The energy density ( $E_{\text{cell-GCD}}$ ) ( $\mu\text{Wh cm}^{-2}$ ) and power density ( $P_{\text{cell-GCD}}$ ) ( $\mu\text{W cm}^{-2}$ ) of the supercapacitor were obtained based on Equations (2) and (3), respectively:

$$E_{\text{cell-GCD}} = \frac{1}{2} C_{\text{cell-GCD}} \times (\Delta V)^2 \quad (2)$$

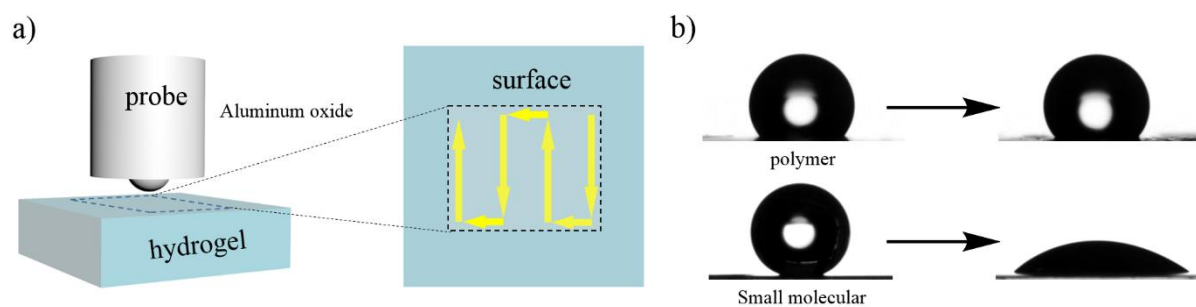
$$P_{\text{cell-GCD}} = \frac{E_{\text{cell-GCD}}}{t} \quad (3)$$

where  $E_{\text{cell-GCD}}$ ,  $C_{\text{cell-GCD}}$ ,  $\Delta V$ ,  $P_{\text{cell-GCD}}$  and  $t$  are the energy density, cell specific capacitance, voltage change upon discharging, power density and discharge time, respectively [4].

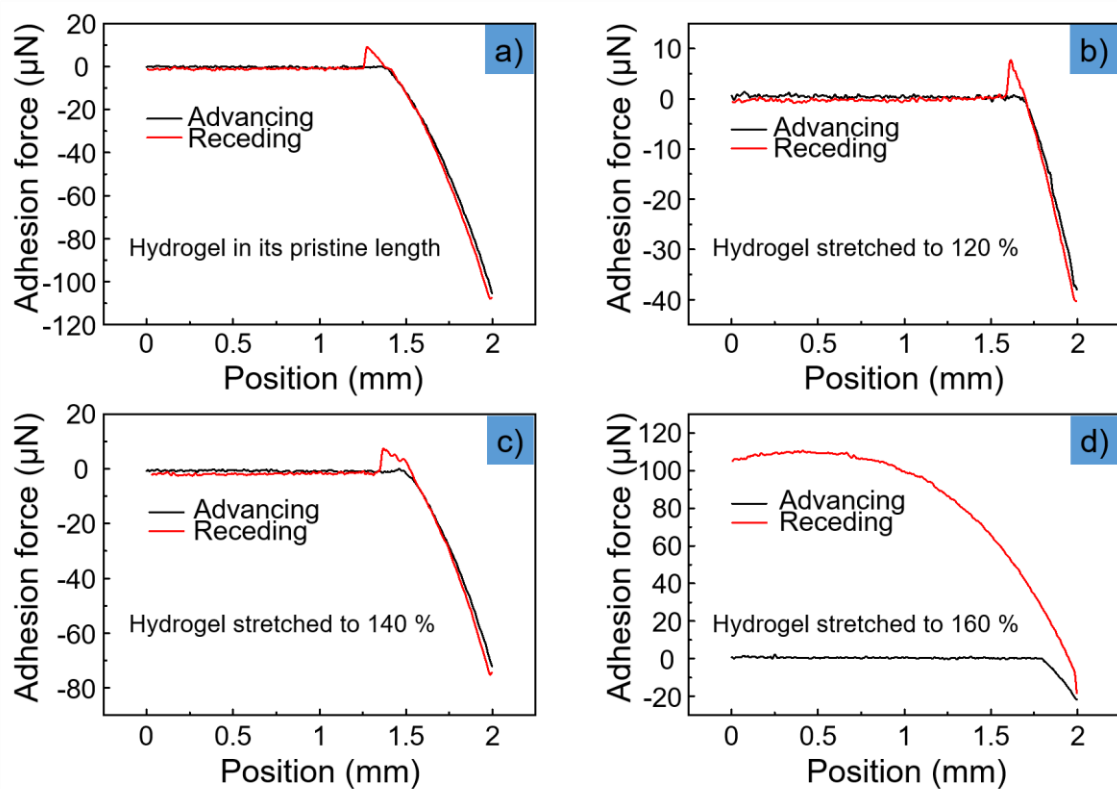


**Figure S3.** a) Photograph of DMAPAAm/DMAA hydrogel in wet gel state. b) and c) Pore structures of DMAPAAm/DMAA copolymerized hydrogel in different magnification.

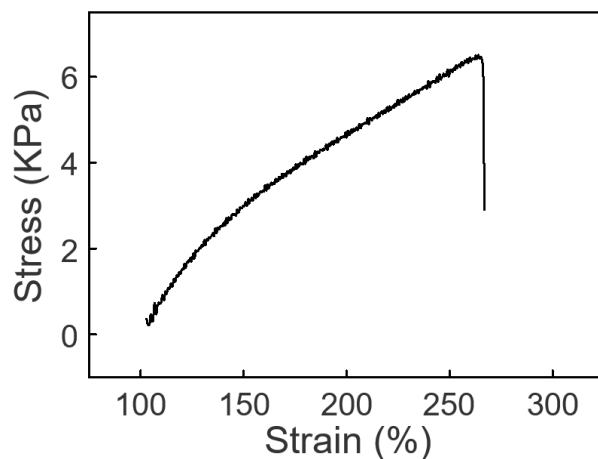




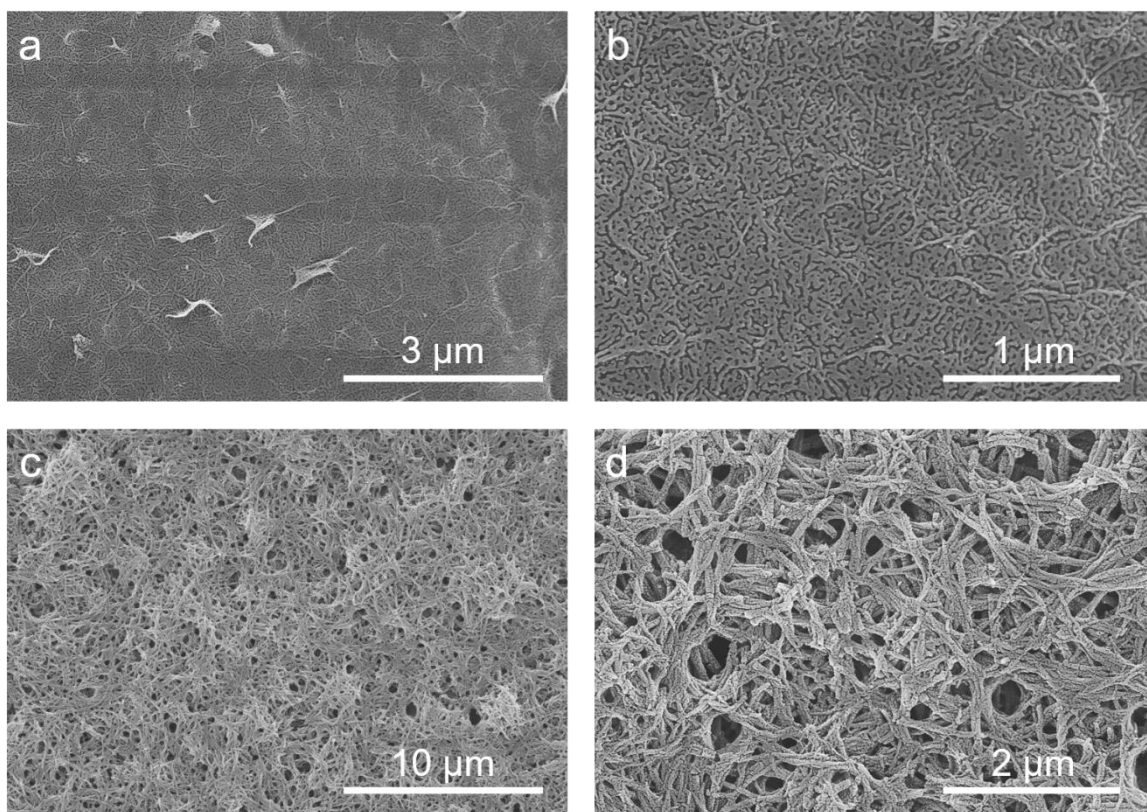
**Figure S4. The stability test of modified layer on hydrogel surface.** (a) Schematic illustration of the friction and wear test of modified layer on hydrogel surface by using universal mechanical tester. The probe is contact with the surface of hydrogel by giving certain normal force (4 mN), and the probe is moving along the path as shown in **a**) (yellow arrow). (b) The water contact angle of polymer-modified hydrogel (left) was barely unchanged after the surface friction treatment (right). While the contact angle of C<sub>16</sub>I-modified hydrogel was obviously decreased after the surface friction treatment. These results indicate that after polymer modification a stable polymeric layer on hydrogel surface was formed, which was contribute to the hydrophobicity of hydrogel.



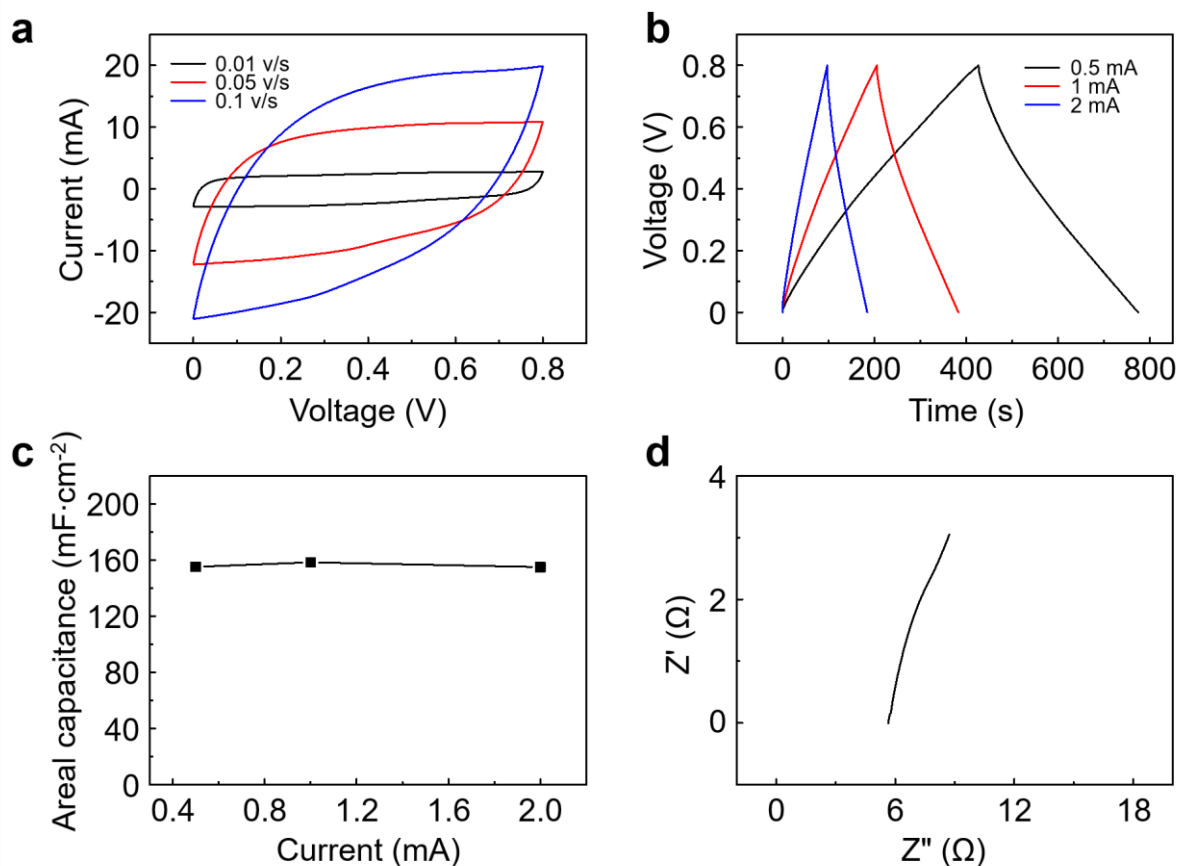
**Figure S5. Force-distance curves corresponding to the water droplet adhesion force measurements in Figure 3.** (a-d) Force-distance curves of water droplet adhesion force upon superhydrophobic nanoparticles coated hydrogel in its pristine length ( $9.5 \pm 0.9 \mu\text{N}$ ), 120 % ( $8.8 \pm 1.3 \mu\text{N}$ ), 140 % ( $8.5 \pm 1.1 \mu\text{N}$ ) and 160 % (the adhesion force is high enough to break the liquid bridge of water), respectively.



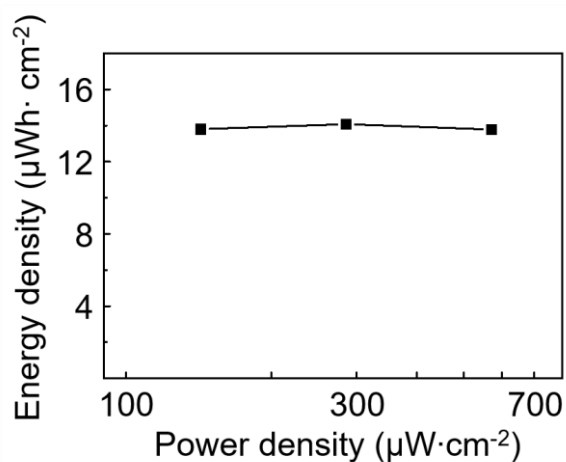
**Figure S6.** Strain stress curve during the adhesion test of PM-hydrogel upon PANI electrode corresponding to the photographs in **Figure 4c**. It is worth noting that the breakpoint during the adhesion test is due to the fracture of hydrogel. Therefore, it was supposed that the adhesion force between hydrogel and PANI electrode is higher than this value (6.52 KPa).



**Figure S7.** Surface topography of the electrodes in Different magnification. a) and b) Surface topography of CNT paper. c) and d) Surface topography of PANI nanowires coated CNT paper (The PANI loading on CNTP is  $0.161 \text{ mg/cm}^2$ ).



**Figure S8.** The electrochemical performances of as-prepared supercapacitor (electrode materials: PANI coated carbon nanotube papers; thickness of hydrogel electrolyte: 1 mm). a) Cyclic voltammetry (CV) curves at various scan rates. b) Galvanostatic charge/discharge (GCD) curves at various currents. c) The specific areal capacitance at different current was calculated based on the GCD curves (158.4 mF·cm<sup>-2</sup>). d) The electrochemical impedance spectroscopy (EIS) of the supercapacitor represents the cell resistance is around 5.64 Ω (4.03 Ω/cm<sup>2</sup>).



**Figure S9.** Ragone plots of a PANI-CNTP based supercapacitor at current densities of 0.36, 0.71 and 1.43 mA cm<sup>-2</sup>.

### References

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