Supporting Information

Mineralized Soft and Elastic Polymer Dots-Hydrogel for Flexible Self-Powered Electronic Skin Sensor

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Determination of crosslinking density:

The crosslinking density measurement based on the equilibrium swelling of polymer in solvent was performed using the Flory-Rehner equation:

\[-[\ln(1 - V_r) + V_r + \chi V_r^2] = N V_s (V_r^{\frac{1}{3}} - \frac{V_r}{2}) \]

(S1)

Where \(V_r\) is the volume fraction of PAA in equilibrium swollen sample, \(\chi\) is Flory-Huggins polymer-solvent interaction parameter, \(N\) is the crosslinking density and \(V_s\) is the molar volume of the solvent. The PCLA hydrogel showed a higher crosslinking density of \(2.1 \times 10^{-4}\) mol cm\(^{-3}\) compared to that of PCL hydrogel \(1.3 \times 10^{-5}\) mol cm\(^{-3}\).

Characterization of the devices:

Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) cycles and electrochemical impedance spectra (EIS) at open circuit potential in the frequency range of 0.01 Hz to 100 kHz were carried out in two-electrode configuration and measured by using CorrTest CS350 electrochemical workstation.

The ionic conductivity of the hydrogel films was determined from EIS using equation S2

\[\sigma = \frac{L}{R \times S} \]  

(S2)

\(L\), \(S\) and \(R\) are the thickness, area and resistance obtained from EIS, respectively, of the hydrogel film.

Table S1: Conductivity measurement parameters of the PCL and PCLA hydrogel.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (cm)</th>
<th>Area (cm(^2))</th>
<th>Resistance (Ω)</th>
<th>Conductivity (S cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>0.31</td>
<td>3.19</td>
<td>3.60</td>
<td>0.027</td>
</tr>
<tr>
<td>PCLA</td>
<td>0.30</td>
<td>2.25</td>
<td>2.26</td>
<td>0.059</td>
</tr>
</tbody>
</table>
The areal capacitance \( (C_A, \text{ mF cm}^{-2}) \), energy density \( (E_A, \text{ µWh cm}^{-2}) \) and power density \( (P_A, \text{ µW cm}^{-2}) \) of the supercapacitor are evaluated from the GCD curve according to the following equations respectively:

\[
C_A = \frac{I \times t}{S \times V} \quad (\text{S3})
\]

\[
E_A = \frac{C_A \times V^2}{2 \times 3.6} \quad (\text{S4})
\]

\[
P_A = \frac{E_A \times 3600}{t} \quad (\text{S5})
\]

where \( I, t, S \) and \( V \) are the current density, discharge time from GCD curves, electrode area and potential range, respectively.

The overall photon to electrical conversion and storage efficiency (OPECSE) was calculated using the equation:

\[
OPECSE = \frac{\frac{1}{2} \times C_A \times V^2}{P_{in} \times t \times S} \quad (\text{S6})
\]

Here \( C_A \) is the average capacitance evaluated from the integrated device during the discharge phase, \( V \) is the device voltage, \( P_{in} \) is the intensity of the incident light (100 mW cm\(^{-2}\)), \( t \) is the photo charging time and \( S \) is the active surface area of the solar cell.

The photovoltaic performance of the device was evaluated using the current density vs. voltage (J-V) characteristics measured with a Keithley 2450 source meter unit under AM 1.5G illumination of 100 mWcm\(^{-2}\) using a solar simulator.

**Pressure and motion sensor fabrication and testing:**

The PCLA hydrogel sandwiched between two integrated PANI electrode itself acts as a capacitive pressure and strain sensor. The PANI electrodes are connected with copper wire to the detector. The capacitive sensor was sealed with VHB tapes to prevent evaporation. The
capacitive sensing measurements were obtained using a Wayne Kerr 4100 LCR meter at an AC voltage of 1 V and a sweeping frequency of 1 kHz.

**Characterization of the materials:**

Field emission scanning electron microscopy (FE-SEM) images of the freeze-dried PCLA hydrogel was recorded using a JEOL, JSM-6700F instrument. FTIR was carried out in transmittance mode with a Nicolet iS10 spectrometer with a KBr palette. Raman spectroscopic measurements were performed using JASCO NRS-3200 Laser Raman Spectrometer. The rheological performance of the mineralized hydrogel was studied by a HAAKE MARS modular advanced rheometer using 25 mm parallel-plate geometry. Dynamic frequency sweep was evaluated from 0.01 to 100 Hz at 20 °C in the oscillation mode with a fixed oscillatory strain of 1%. The recovery of strength of the mineralized hydrogel was evaluated by the recovery of storage modulus (G') with performing strain sweeps from 1% to 300% and back to 1% at the frequency of 1 Hz. All of the compression tests were performed on a tensile machine (Instron 5583, USA) at a deformation rate of 1 mm min⁻¹ at 22 °C. The tensile test was performed at a speed of 10 mm min⁻¹ using a universal tensile machine (Instron 5583, USA) with a 100 N load cell. The hydrogel was sized into 15 mm width × 32 mm length × 2 mm rectangular shapes prior to testing. The UV-Vis absorption spectra of the P3TAA and N-CD were recorded from their solid films on quartz plate using, Optizen 2120 UV spectrophotometer. The PL spectra of the solid films of P3TAA and P3TAA/N-CD mixture on a quartz plate was examined with a Scinco FS2 Fluorescence spectrophotometer at the excitation wavelength of 403 nm.
Synthesis of carbon dot (N-CD):

\[
\begin{align*}
\text{[OH-OH-\text{NH}_2]}_n & \quad \text{50 ml 2\% acetic acid,} \\
& \quad \text{Hydrothermal carbonization} \\
& \quad 180 \, ^\circ\text{C, 8 hr}
\end{align*}
\]

Synthesis of P3TAA:

\[
\begin{align*}
\text{\text{COOH}} & \quad \text{CH}_3\text{OH, 50 ml} \\
& \quad \text{Catalytic amount} \\
& \quad \text{H}_2\text{SO}_4 \\
& \quad \text{Reflux, 24 h} \\
\text{\text{COOCH}_3} & \quad \text{FeCl}_3 \\
& \quad \text{Dry CHCl}_3, 0 \, ^\circ\text{C} \\
\text{\text{COONa}} & \quad \text{2M aq.NaOH,} \\
& \quad 100 \, ^\circ\text{C, 72 h} \\
\text{\text{COOH}} & \quad \text{Dilute HCl}
\end{align*}
\]

Scheme S1. Synthesis of amino-functionalized carbon dot (N-CD) and synthesis of P3TAA.
Figure S1. DLS spectra of A-PD showing an average particle size of 288 nm.
**Figure S2.** TEM images of a) A-PD, b) N-CD. Inset is the corresponding HRTEM images.
Figure S3. FTIR Spectra of PAA, Laponite, A-PD, PCL hydrogel and PCLA hydrogel.
Figure S4. Raman spectra of PCL and PCLA hydrogel.
Figure S5. a) An image of 4 mL of 2 wt% PAA (left) and A-PD (right) aqueous solutions, and b) that of the two solutions upon the addition of 0.5 mL of 0.1 M CaCl₂ aqueous solution. After 30 min, the A-PD solution formed a hydrogel, while the PAA sample remained fluid.
Figure S6. Frequency dependencies of the storage ($G'$) and loss ($G''$) moduli of the PCL and PCLA.
Figure S7. The compression stress-strain curves of the PCLA hydrogel in the strain ranges of 0-93%.
Figure S8. The tensile stress-strain curves of the PCL and PCLA hydrogel in the strain ranges of 0-120% showing the tensile modulus of 4.57 kPa for PCL and 5.86 kPa for PCLA hydrogel.
Figure S9. GCD curves of the supercapacitors based on the various concentrations of PANI films at 0.5 mA cm$^{-2}$. 
Figure S10. Electrochemical characterization of PCL hydrogel based supercapacitor: a) cyclic voltammograms of the supercapacitor device, b) galvanostatic charge/discharge curves at different current density, c) GCD curves of the supercapacitor at 0.5 mA cm$^{-2}$ with various bending angles: inset is the definition of the bending angle, d) stability of the supercapacitor devices after various bending cycles, e) Nyquist plot of the supercapacitor, f) normal cyclic stability of the supercapacitor.
Figure S11. The capacitance-pressure curve of the hydrogel pressure sensor in the range of 0–4 kPa.

The pressure sensitivity was calculated from the slope of the capacitance–pressure curve, as:

\[
\frac{\delta (\frac{\Delta C}{C_0})}{\delta p}
\]
Figure S12. Capacitive change of PCL hydrogel-based supercapacitor in response to object motion (4 cycles) on its surface along a) x-direction, b) y-direction and c) 45° angle along x-direction repeatedly.
Figure S13. Characteristic capacitance response of handwriting characters: a) “B,” b) “Q,” c) “R,” and d) “G.”
Figure S14. Capacitance change under cyclic a) pressing experiment, b) finger bending and c) handwriting of letter K repeatedly for 2000 times.
Figure S15. Schematic representation of the integrated device.
**Figure S16.** a) FTIR spectra of the CD, P3TAA and P3TAA+N-CD mixture. b) Possible interaction between the N-CDs and P3TAA.
Figure S17. a) UV-Vis spectra of the CD and P3TAA, b) PL Spectra of P3TAA and P3TAA+N-CD mixture.
**Figure S18.** Photocurrent density-voltage (J-V) characteristics and the photovoltaic parameters of the P3TAA/N-CD based solar cells.
Figure S19. J-V characteristics and photovoltaic parameters of the solar cells after attaching with the sensing device.
**Figure S20.** Relative energy diagram illustrating the charge transfer within the solar cell.
Figure S21. a) CV curve of N-CD and b) CV curve of Fc/Fc⁺. c) Tauc’s plot of N-CD.
Figure S22. The dynamic voltage curve of the PCL based integrated device during photocharging and galvanostatic discharging process at a constant current density of 0.5 mA cm$^{-2}$. 
Figure S23. OPECSE retention of the integrated device for 100 consecutive cycles.
Figure S24. Handwriting test of letter “K” continuously under a) solar stimulator and b) outdoor sunlight.
Figure S25. Stability test of the integrated device under constant illumination and the respective capacitance change during continuous pressing for 3 hr.
**Portable power pack application:**

The integrated devices after photo charging when connected with three devices, can supply power to light a 1.8 V light-emitting diode (Figure S26). Thus, the device can also act as a portable power source for supply power to other flexible devices.

**Figure S26.** Digital photographs of three supercapacitors connected in series to power a light-emitting diode (LED).
Wireless sensing application of the integrated device:

As the PCLA hydrogel-based integrated device exhibits characteristic electronic response during pressure sensing, bending-stretching motion sensing, and handwriting movement sensing, we further investigate to detect the signals by using real-time monitoring systems by wireless Bluetooth connection to a smartphone. The wireless detection system was established by connecting the supercapacitor part of the device with a customized circuit board attached with a Bluetooth module and microcontroller interfaced with a smartphone using the AppGosuV2 application. The change in electrical response was collected by the customized circuit and transmitted through the Bluetooth to the smartphone. Interestingly, the Bluetooth response shows a similar signal pattern as demonstrated by the capacitance detection (Figure S27 and S28) upon bending-stretching of finger, pressing-releasing and handwriting response. This phenomenon suggests the successful use of the PCLA hydrogel-based integrated device into a wearable health monitoring system and wireless safety communication system.
Figure S27. Wireless response during a) bending and b) pressing the device.
Figure S28. Handwriting wireless response of the letter “K”, “N”, “U” and “T”.