Supplementary Information

Solar thermal-driven capacitance enhancement of supercapacitors

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Note S1. Calculation of the solar thermal conversion efficiency.

The solar thermal conversion efficiency is defined as the ratio of thermal energy originated from solar irradiation per unit time \( (\dot{Q}_{in}) \) to the intensity of irradiation per unit time \( (\dot{q}_0) \):

\[
\eta_{st} = \frac{\dot{Q}_{in}}{\dot{q}_0} \quad (S1)
\]

The solar thermal conversion of the supercapacitor was measured by illuminating the supercapacitor sample that was put on a thermal insulating foam. The energy balance of the entire system can be described as\(^1\)-\(^3\)

\[
\sum m_i C_{p,i} \frac{dT}{dt} = \dot{Q}_{in} - \dot{Q}_{surr,\text{out}} \quad (S2)
\]

where \( m_i \) and \( C_{p,i} \) are the mass and specific heat capacity of the supercapacitor components respectively.

For our supercapacitor sample,

\[
\sum m_i C_{p,i} = (m_{\text{graphene}} C_{p,\text{graphene}} + m_{\text{PEDOT}} C_{p,\text{PEDOT}} + m_{\text{electrolyte}} C_{p,\text{electrolyte}}) \quad (S3)
\]

and the heat dissipation term, \( \dot{Q}_{surr,\text{out}} \), is depicted as

\[
\dot{Q}_{surr,\text{out}} = hA (T - T_{surr}) \quad (S4)
\]

where \( T_{surr} \) is the surrounding temperature, \( h \) is a heat-transfer coefficient, and \( A \) is the surface area of the supercapacitor for heat dissipation.

When the surface temperature of the supercapacitor increases to the equilibrium value by solar illumination, the solar-induced energy input equals to the energy transferred out of the system:

\[
\dot{Q}_{in} = \dot{Q}_{surr,\text{out}} = hA (T_{\text{max}} - T_{surr}) \quad (S5)
\]

Substituting equation (S5) into equation (S1) yields:
\[
\eta_{st} = \frac{hA(T_{\text{max}}-T_{\text{sur}})}{q_0}
\]  

(S6)

A system time constant \(\tau_s\) is introduced as

\[
\tau_s = \frac{\sum m_iC_{p,i}}{hA}
\]

(S7)

The temperature that increases as a function of time during the solar irradiation can be expressed as

\[
\frac{T_{\text{sur}} - T}{T_{\text{sur}} - T_{\text{max}}} = 1 - \exp\left(-\frac{t}{\tau_s}\right)
\]

(S8)

and therefore \(\tau_s\) can be obtained by fitting the photothermal curve data in Figure 2d.

Take the supercapacitor under solar illumination at a power density of 1 kW m\(^{-2}\) as an example, \(\tau_s\) is \(~38.43\) s from the photothermal curve and the value of \(hA\) can be obtained from equation (S7):

\[
hA = \frac{m_{\text{graphene}}C_{p,\text{graphene}} + m_{\text{PEDOT}}C_{p,\text{PEDOT}} + m_{\text{electrolyte}}C_{p,\text{electrolyte}}}{\tau_s}
\]

\[
= \frac{0.006 \text{ g} \times 1.34 \text{ J kg}^{-1} \text{ K}^{-1} + 0.008 \text{ g} \times 1.34 \text{ J kg}^{-1} \text{ K}^{-1} + 0.3528 \text{ g} \times 5 \text{ J kg}^{-1} \text{ K}^{-1}}{38.43 \text{ s}}
\]

\[
= 0.0464 \text{ mW K}^{-1}
\]

The \(T_{\text{max}}\) and \(T_{\text{sur}}\) are \(~337.15\) K (64 °C) and \(~298.15\) K (25 °C) respectively. The area of the illuminated supercapacitor is \(~1\) cm\(^2\). Thus the solar thermal conversion efficiency of the supercapacitor is calculated to be \(~18.56\)% under solar illumination at a power density of 1 kW m\(^{-2}\).
Note S2. Faradaic reaction of the PEDOT:PSS in the pseudocapacitor.

The PEDOT:PSS acts as the active material for the pseudo-type supercapacitor, which provides the faradaic activity through the following doping/dedoping reaction. Note that in the reaction, $A^-$ represents the negative ions including $PSS^-$, $H_2PO_4^-$, etc.
Note S3. Calculation processes of the volumetric specific capacitance.

The volumetric specific capacitances obtained from the cyclic voltammetry (CV) curves and galvanostatic charge/discharge (GCD) curves were calculated from equation (S9) and equation (S10) respectively:

\[
C = \frac{I \, \Delta E}{V \, \Delta t} \quad \text{(S9)}
\]

where \( I \) is the response current, \( \Delta E \) is the potential window, \( V \) is the volume of the supercapacitor.

\[
C = \frac{i \, \Delta t}{V \, \Delta E} \quad \text{(S10)}
\]

where \( i \) is the current applied for the charge/discharge, and \( \Delta t \) is the time elapsed for the discharge.
Note S4. Detailed explanation for the lower cyclic stability under 1 solar illumination.

The lower cyclic stability of the supercapacitor under 1 solar illumination than that in dark may be mainly due to two reasons. The first reason is the degradation of the solid-state PVA/H₃PO₄ electrolyte at the higher temperature by 1 solar illumination. It has been found that the supercapacitors (both with and without PEDOT:PSS) suffer from capacitance loss even if they stay under 1 solar illumination or heated at 62 °C for 2.5 h without continuous electrochemical tests (about 8~10% capacitance loss) (Fig. S7). Note that the color of the solid-state PVA/H₃PO₄ changes from clear to light brown after kept at 62 °C for 2.5 h (Fig. S8a-b). Therefore the electrolyte may account for the declined capacitance. To further examine this, the SEM and fourier transform infrared spectrometer (FTIR) characterization, as well as the dielectric constant measurement of the electrolyte have been conducted. The SEM images of the supercapacitor electrode filled with solid-state PVA/H₃PO₄ electrolyte before and after 2000 continuous cycles of GCD test under 1 solar illumination or heated at 63 °C (note: both cyclic tests last about 4 h) show that the electrolyte fully filled the electrode, and no change has been found in the SEM mophology after the GCD cyclic test under 1 solar illumination or heated at 63 °C (Fig. S8c-e). The FTIR spectra of the supercapacitor electrode filled with solid-state PVA/H₃PO₄ electrolyte before and after the GCD cyclic test under 1 solar illumination or heated at 63 °C show that three peaks have noticeable changes, which are peaks around 980 cm⁻¹, 828 cm⁻¹ and 1090 cm⁻¹ (Fig. S8f). The peak around 980 cm⁻¹ can be assigned to the P-O stretch in alkyl phosphates and phosphites; the peak around 828 cm⁻¹ can be assigned to the P-O-C linkage; and the peak around 1090 cm⁻¹ can be assigned to the C-O stretch and O-H bend.⁵-⁸ The decreases in these three peaks indicate a loss of phosphate groups that relate to ion exchange⁹-¹¹ and intro- or intermolecular dehydration,⁵,¹²,¹³ which could result in decreased capacitance. Also, it is found that there is a decrease in the dielectric constant of the solid-state PVA/H₃PO₄ electrolyte after it keeps staying under 1 solar illumination or heated at 62 °C for...
2.5 h (Fig. S9), which could also lead to decrease in capacitance. The second reason for the lower cyclic stability is that the reaction rates of side reactions increase at the increased temperature by 1 solar illumination, which could contribute to reduced capacitance.
Note S5. Details for the modeling and simulation of the mechanism for the photothermal effect enhanced capacitance of the pseudo-type supercapacitor.

For the simulation of the pseudo-type supercapacitor, a 3D mathematical model was established. In the model, the supercapacitor has the same structure as that in the experiment, which consists of two identical 3D-h graphene porous electrodes (size of each electrode: 6 mm \( \times \) 2.6 mm \( \times \) 0.14 mm) in parallel, separated by a gap of 0.14 mm. The PEDOT:PSS acts as the active material and has a thickness of 5 nm, which is assumed to be evenly coated on the porous electrode. The PVA/H_3PO_4 electrolyte is treated as a liquid phase in the model, with a concentration of 1 mol/L. The diffusion coefficient in the electrode and electrolyte phase, as well as the transference number are assumed to be independent of the electrolyte concentration. The entire surface area contributes to the electric double-layer capacitance. All side reactions are neglected.

The conductivity and diffusion coefficient are modified in the electrode area considering the porosity:

\[
D_{1,\text{ef}} = \varepsilon_1^{1.5} D_1, \quad \sigma_{1,\text{ef}} = \varepsilon_1^{1.5} \sigma_1, \quad \sigma_{2,\text{ef}} = \varepsilon_2^{1.5} \sigma_2
\]  

(S11)

where \( D_{1,\text{ef}} \), \( \sigma_{1,\text{ef}} \), and \( \sigma_{2,\text{ef}} \) are the effective diffusion coefficient of the electrolyte, the effective conductivity in the electrolyte phase, and the effective conductivity in the electrode phase, respectively. \( D_1, \sigma_1, \) and \( \sigma_2 \) are their corresponding original values. \( \varepsilon_1 \) and \( \varepsilon_2 \) are the volume fractions of the electrolyte phase and the electrode phase respectively.

The total surface current density (\( I_{SC} \)) (unit: A m\(^{-2}\)) that remains constant during the galvanostatic charge/discharge (GCD) process is the sum of the surface current density in the electrolyte phase (\( i_1 \)) and the surface current density in the electrode phase (\( i_2 \)):

\[
I_{SC} = i_1 + i_2
\]  

(S12)

For every position in the model, the conservation of charge leads to:

\[
0 = \frac{\partial i_1}{\partial x} + \frac{\partial i_2}{\partial x}
\]  

(S13)
The movement of current in the electrode phase reflects the movement of electrons and the potential in the electrode phase $\phi_2$ is correlated to $i_2$ by Ohm’s law:

$$i_2 = -\sigma_{2,ef} \frac{\partial \phi_2}{\partial x} \tag{S14}$$

The movement of current in the electrolyte phase reflects the movement of ions, which are originated from the faradaic redox reaction and the double-layer charge. Both the faradaic current $i_{v,f}$ and the double-layer current $i_{v,dl}$ contribute to the current of the supercapacitor (note that $i_{v,f}$ and $i_{v,dl}$ are the volume current densities that have the unit of A m$^{-3}$):

$$i_{v,f} = S_f j_f \tag{S15}$$

$$i_{v,dl} = S_d C_{dl} \frac{\partial (\phi_2 - \phi_1)}{\partial t} \tag{S16}$$

Therefore:

$$\frac{\partial i_1}{\partial x} = S_f j_f + S_d C_{dl} \frac{\partial (\phi_2 - \phi_1)}{\partial t} \tag{S17}$$

where $S_f$ and $S_d$ represent the specific surface area for the pseudocapacitance and double-layer capacitance per unit electrode volume, respectively. $j_f$ is the faradaic transfer current density. $C_{dl}$ represents the double-layer capacitance. $\phi_2$ and $\phi_1$ are the potential in the electrode phase and in the electrolyte phase, respectively.

The $j_f$ can be expressed in a kinetic form using the Butler-Volmer equation:

$$j_f = i_0 \left\{ \exp \left[ \alpha_a \frac{nF}{RT} (\phi_2 - \phi_1 - U_1) \right] - \exp \left[ -\alpha_c \frac{nF}{RT} (\phi_2 - \phi_1 - U_1) \right] \right\} \tag{S18}$$

where $i_0$ is the exchange current density, $\alpha_a$ is the anodic transfer coefficient (set as 0.5), $\alpha_c$ is the cathodic transfer coefficient (set as 0.5), $n$ is the number of electrons involved in the faradaic reaction (set as 1), $F$ is Faraday’s constant, $R$ is the universal gas constant, $T$ is the absolute temperature, and $U_1$ is the equilibrium potential for the faradaic reaction.

The exchange current density can be expressed as follows:

$$i_0 = Fk(c_{2,\text{max}} - c_2)^{\alpha_a} (c_2)^{\alpha_c} (c_1)^{\alpha_a} \tag{S19}$$
where \( k \) is the standard rate constant, \( c_2 \) is the electrode phase concentration at the surface and \( c_1 \) is the electrolyte concentration.

\( U_1 \) can be evaluated as a function of the state of charge \( \delta \), and \( U_1 \) of the anode is evaluated as:

\[
U_1 = 0.5(1 + \delta)
\]  
(S20)

\( U_1 \) of the cathode is evaluated as:

\[
U_1 = 0.5\delta
\]  
(S21)

The \( \delta \) represents the degree of faradaic reaction, which can be expressed as:

\[
\delta = \frac{c_2}{c_{2,\text{max}}}
\]  
(S22)

Assuming that the transport of ions can take place on the surface and in the bulk of the active material. If considering the PEDOT:PSS film as a group of densely packed spherical particle, then a material balance inside the particles can be given by:

\[
\frac{\partial c_z}{\partial t} = D_z \left[ \frac{\partial^2 c_z}{\partial r^2} + \frac{2 \partial c_z}{r \partial r} \right] \quad 0 \leq r \leq r_p
\]  
(S23)

where \( r \) is the radial coordinate, \( r_p \) is the particle radius (equals to half of the film thickness), and \( D_z \) is the diffusion coefficient of the reaction ion in the particle.

In the electrolyte phase, Ohm’s law is modified considering the porosity of the electrode:

\[
i_1 = -\sigma_{1,\text{ef}} \frac{\partial \phi_1}{\partial x} - \frac{2 \sigma_{1,\text{ef}} RT}{F} \left( 1 - t_- \right) \frac{\partial (\ln c_1)}{\partial x}
\]  
(S24)

where \( t_- \) is the transport number. The electrolyte concentration \( c_1 \) correlates with the faradaic redox reaction and double-layer reaction via a material balance on the electrolyte using concentrated solution theory:

\[
\varepsilon_1 \frac{\partial c_1}{\partial t} + \nabla \cdot \left( -D_{1,\text{ef}} \nabla c_1 + \frac{i_1 t_-}{F} \right) = \frac{i_{\text{ion}} + i_{\text{elec}}}{F}
\]  
(S25)

In the separator, the porous electrode theory is not applicable, and equation (S24) and (S25) can be simplified as:

\[
i_1 = -\sigma_{1,\text{ef}} \frac{\partial \phi_1}{\partial x}
\]  
(S26)
\[
\frac{\partial c_1}{\partial t} + \nabla \cdot \left( -D_1 \nabla c_1 + \frac{i_{1t}}{\mathcal{F}} \right) = 0
\]  
(S27)

The boundary conditions of the model are as follows:

at \( x=0 \)

\[
\frac{\partial c_1}{\partial x} = 0, \quad i_1 = 0, \quad L_{sc} = i_2
\]  
(S28)

at \( x=L_+ = L_+ + L_2 \)

\[
i_2 = 0, \quad \frac{\partial i_1}{\partial x} = 0
\]  
(S29)

where \( L \) is the thickness of the electrode,

at \( x=L_+ + L_2 + L_- \)

\[
\frac{\partial c_1}{\partial x} = 0, \quad i_1 = 0, \quad L_{sc} = i_2, \quad \phi_2 = 0
\]  
(S30)

inside the PEDOT:PSS layer

\[
\frac{\partial c_2}{\partial r} \bigg|_{r=0} = 0, \quad \frac{\partial c_2}{\partial r} \bigg|_{r=r_p} = -\frac{i_{v,f}}{D_2 F a_\phi}
\]  
(S31)

The initial conditions are as follows:

at \( t=0 \)

\[
c_1 = c_0, \quad c_2 = c_{20}, \quad \phi_2 \big|_{x=0} = 0
\]  
(S32)

where \( c_0 \) is the initial electrolyte concentration and \( c_{20} \) is the initial electrode phase concentration.

In the model, the supercapacitor has an initial potential of 0 V and is set to be fully charged to 0.7 V and then discharged completely back to 0 V. The GCD current density is set as 35.7 A/m\(^2\) (6.7 mA cm\(^{-2}\)). The equations of the model are solved by using the COMSOL Multiphysics software.

The parameters used in the simulation for the supercapacitor in dark (~25 °C) are listed in Table S1.
Table S1. List of parameters in the simulation model for the supercapacitor in dark (298.35 K).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Physical meaning</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{\text{SC}}$</td>
<td>Charge/discharge current density</td>
<td>35.7 A/m$^2$</td>
<td>Measured</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperature</td>
<td>298.35 K</td>
<td>Measured</td>
</tr>
<tr>
<td>$c_{2\text{max}}$</td>
<td>Maximum concentration of active material</td>
<td>9.36 mol/L</td>
<td>Estimated</td>
</tr>
<tr>
<td>$c_{20}$</td>
<td>Initial concentration of active material</td>
<td>0 mol/L</td>
<td>Assumed</td>
</tr>
<tr>
<td>k</td>
<td>Reaction rate constant</td>
<td>$2.30 \times 10^{-10}$ m/s</td>
<td>Estimated</td>
</tr>
<tr>
<td>$\alpha_a$</td>
<td>Anodic transfer coefficient of faradaic reaction</td>
<td>0.5</td>
<td>Assumed</td>
</tr>
<tr>
<td>$\alpha_c$</td>
<td>Cathodic transfer coefficient of faradaic reaction</td>
<td>0.5</td>
<td>Assumed</td>
</tr>
<tr>
<td>$\tau_-$</td>
<td>Transport number</td>
<td>0.363</td>
<td>Assumed</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>Conductivity in the electrolyte phase</td>
<td>66.3 S/m</td>
<td>Estimated</td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>Conductivity in the electrode phase</td>
<td>674.4 S/m</td>
<td>Estimated</td>
</tr>
<tr>
<td>$D_1$</td>
<td>Diffusion coefficient of reaction ion in the electrolyte phase</td>
<td>$1.18 \times 10^{-10}$ m$^2$/s</td>
<td>Estimated</td>
</tr>
<tr>
<td>$D_2$</td>
<td>Diffusion coefficient of reaction ion in the electrode phase</td>
<td>$1.18 \times 10^{-10}$ m$^2$/s</td>
<td>Estimated</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Thickness of active material</td>
<td>$5 \times 10^{-9}$ m</td>
<td>Estimated</td>
</tr>
<tr>
<td>$S_f$</td>
<td>Specific surface area for the pseudocapacitance per unit electrode volume</td>
<td>$5.6 \times 10^3$ m$^2$/m$^3$</td>
<td>Estimated</td>
</tr>
<tr>
<td>$S_d$</td>
<td>Specific surface area for the double-layer capacitance per unit electrode volume</td>
<td>$5.6 \times 10^3$ m$^2$/m$^3$</td>
<td>Estimated</td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>Electric double-layer capacitance</td>
<td>2.1 F/m$^2$</td>
<td>Measured</td>
</tr>
<tr>
<td>$c_1$</td>
<td>Concentration of electrolyte</td>
<td>1 mol/L</td>
<td>Estimated</td>
</tr>
<tr>
<td>$\varepsilon_1$</td>
<td>Volume fraction of the electrolyte phase</td>
<td>0.75</td>
<td>Estimated</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>Volume fraction of the electrode phase</td>
<td>0.25</td>
<td>Estimated</td>
</tr>
<tr>
<td>$L_e$</td>
<td>Gap between the two electrodes</td>
<td>$1.4 \times 10^{-4}$ m</td>
<td>Measured</td>
</tr>
<tr>
<td>L</td>
<td>Thickness of electrode</td>
<td>$1.4 \times 10^{-4}$ m</td>
<td>Measured</td>
</tr>
<tr>
<td>$E_{\text{size}}$</td>
<td>Size of electrode</td>
<td>6 mm $\times$ 2.6 mm $\times$ 0.14 mm</td>
<td>Measured</td>
</tr>
</tbody>
</table>

Note that the maximum electrode phase concentration ($c_{2,\text{max}}$) is the maximum amount of ions the active material can combine through faradaic reaction per unit volume. For our pseudo-type supercapacitor, it is the concentration when each monomer (EDOT) of PEDOT is doped with a negative ion, which can be estimated as:
\[ c_{z,\text{max}} = \frac{\rho}{M} \quad (S33) \]

where \(\rho\) is the mass density of EDOT (\(\sim 1.331 \text{g cm}^{-3}\)) and \(M\) is the molar mass of EDOT (142.18 g mol\(^{-1}\)). Thus \(c_{z,\text{max}}\) is \(\sim 9.36\) mol L\(^{-1}\).

Supposing that there is no temperature difference inside the supercapacitor, then the main variables in the model induced by the increasing temperature under solar illumination are the temperature \(T\), the conductivities of the electrolyte \(\sigma_1\) and the electrode \(\sigma_2\), the electric double-layer capacitance \(C_{dl}\), the diffusion coefficient \(D\), and the reaction rate constant \(k\).

The resistance of the electrolyte is estimated by subtracting the resistances of the two electrodes from the equivalent series resistance obtained from the electrochemical impedance spectroscopy (EIS) curve.

The electric double-layer capacitances in dark and under solar illumination are measured from the electric double-layer capacitor (EDLC) that has the same structure as the pseudo-type supercapacitor but only without the PEDOT:PSS active material.

The diffusion coefficient in the electrode phase is estimated from the cyclic voltammetry (CV) curves. During the CV process, the total current response at a fixed potential \((i(V))\) can be divided into the adsorption-controlled capacitive effects (proportional to the scan rate \(\nu\)) and diffusion-controlled faradaic reactions (proportional to \(\nu^{1/2}\)):\(^{30-32}\)

\[ I(V) = I_c(V) + I_f(V) = \eta_c \nu + \eta_f \nu^{1/2} \quad (S34) \]

The values of \(\eta_c\) and \(\eta_f\) can be obtained by plotting \(I_{(V=0.7)\text{V}/\nu^{1/2}}\) against \(\nu^{1/2}\) (Fig. S23).

The peak current of the diffusion-controlled faradaic reactions \((I_{f,\text{peak}})\) can be described by the Randles-Sevcik equation:\(^{33,34}\)

\[ I_{f,\text{peak}} = 0.4463 \nu^{1/2} nF \left( \frac{nF}{RT} \right)^{1/2} A_s c_{2f} D_s^{1/2} \quad (S35) \]

where \(\nu\) is the scan rate, \(F\) is Faraday’s constant, \(R\) is the universal gas constant, \(n\) is the number of exchanged electron during the redox process (set as 1), \(A_s\) is the geometry area of
the electrode (set as 6 mm × 2.6 mm), \(c_{2f}\) is the concentration of reaction ions in the electrode (set as 1 mol/L).

Note that there are no obvious redox peaks in the measured CV curves, which is common for supercapacitors with PEDOT:PSS as the active material because of the broad redox activity of PEDOT.\(^{35,36}\) The maximum value in the CV curve (\(I_{V=0.7V}\)) can be taken as the \(I_{\text{f,peak}}\), and then the diffusion coefficient can be calculated as:

\[
D_2 = \frac{\left(\frac{I_{\text{f,peak}}}{0.4463^2n^3F^2A_c^2c_{2f}}\right)^2RT}{0.4463^2n^3F^2A_s^2c_{2f}^2} = \frac{\eta_f^2RT}{0.4463^2n^3F^2A_s^2c_{2f}^2} \tag{S36}
\]

The diffusion coefficient in the electrode phase in dark is calculated to be \(1.18 \times 10^{-15} \text{ m}^2/\text{s}\). The diffusion coefficient in the electrolyte phase is set as the same as that in the electrode phase. It is found that the electrolyte concentration gradient increases with the charging potential and reaches the maximum value when the supercapacitor is fully charged (Fig. S18a). When changing the diffusion coefficient from \(1.18 \times 10^{-15} \text{ m}^2/\text{s}\) to \(1.18 \times 10^{-11} \text{ m}^2/\text{s}\) while other parameters maintained the same, the electrolyte concentration becomes more evenly distributed but the capacitance is nearly unchanged (Fig. S18).

The reaction rate constants in dark (\(\sim 25^\circ\text{C}\)) is estimated by using the following simplified equation:\(^{37,38}\)

\[
k = \frac{RT}{F^2 n^2 A_r c_{1f} R_{ct}} \tag{S37}
\]

where \(A_r\) is the reaction area of the electrode, \(c_{1f}\) is the concentration of reaction ion in the electrolyte phase, \(R_{ct}\) is the charge transfer resistance. Considering that the accurate \(A_r\) and \(c_{1f}\) are hard to be acquired due to the complicated kinetic process, \(R_{ct}\) is inconspicuous in the EIS curve and this equation is simplified, an adjustment coefficient \(\xi\) is introduced as:

\[
n^2 R_{ct} A c_{1f} = \xi n^2 R_{ct}' A' c_{1f}' \tag{S38}
\]
where $\xi$ is $7.5 \times 10^2$ and $A'$ is the geometry area of the electrode (6 mm $\times$ 2.6 mm), $n$ is set as 1, $c'_{1f}$ is set as 1 mol/L. $R'_{ct}$ is set as 100 $\Omega$ at 298.35 K (in dark). The calculated $k$ at ~25 °C (in dark) is ~2.30$\times$10$^{-10}$ m/s.

Since the temperature of the supercapacitor from in dark to under 1 solar illumination is within a common range (25–65 °C), van’t Hoff’s rule is employed to estimate the reaction rate constants at the elevated temperatures under solar illumination. According to van’t Hoff’s rule of the temperature effect on the equilibrium constant for a chemical reaction, the reaction rate constant increases twice to three times for every increase of 10 °C. Assuming that there is a twofold increase in the reaction rate constant for every increase of 10 °C within the temperature range of 25–65 °C, the reaction rate constants under solar illumination are estimated as:

$$k_{\text{solar}} = 2^\left(\frac{\left(T_{\text{solar}} - T_{\text{dark}}\right)}{10}\right) k_{\text{dark}}$$  \hfill (S39)

As is mentioned above, the $k$ in dark is estimated to be ~2.3$\times$10$^{-10}$ m/s. Then the $k$ under solar illumination intensities of 0.41 kW m$^{-2}$ (~40°C), 0.72 kW m$^{-2}$ (~52°C) and 1 kW m$^{-2}$ (~64°C) are calculated to be ~6.51$\times$10$^{-10}$ m/s, ~1.49$\times$10$^{-9}$ m/s and ~3.43$\times$10$^{-9}$ m/s, respectively.

Note that the estimated $k$ values fit well with the Arrhenius equation (Fig. S19c):

$$k = Ae^{-E_A/RT}$$  \hfill (S40)

where $R$ is the universal gas constant, $A$ is the frequency factor (~17.123) and $E_A$ is the actication energy (~61.534 kJ mol$^{-1}$).

The changed parameters for the supercapacitor under 1 solar illumination are listed in Table S2. The simulated GCD curve under 1 solar illumination has a discharging time ~1.7 times longer than that in dark, which is close to the experimental data (~1.5 times) (Fig. S20a).

Table S2. List of changed parameters in the simulation model for the supercapacitor at the photothermal temperature of 337.55 K (Solar 64°C).
To further investigate the contribution of each variable parameter to the increasing capacitance by the photothermal effect, the GCD curves were simulated by only changing an individual variable parameter and the temperature to those under 1 solar illumination based on the parameters in dark. The simulated GCD curves (Fig. S20b) show that increase in the conductivity, reaction rate constant and electric double-layer capacitance all contribute to the enhanced capacitance.

The changed parameters in the model for the supercapacitor under solar illumination intensities of 0.41 kW m⁻² (~40°C) and 0.72 kW m⁻² (~52°C) are shown in Table S3 and S4, respectively. The simulated GCD curves show a increasing discharging time with the increasing solar power density (Fig. S20a), which agrees with the experimental results.

Table S3. List of changed parameters in the simulation model for the supercapacitor at the photothermal temperature of 313.65 K (Solar 40°C).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Physical meaning</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Absolute temperature</td>
<td>313.65 K</td>
<td>Measured</td>
</tr>
<tr>
<td>k</td>
<td>Reaction rate constant</td>
<td>6.51×10⁻¹⁰ m/s</td>
<td>Estimated</td>
</tr>
<tr>
<td>σ₁</td>
<td>Conductivity in the electrolyte phase</td>
<td>87.8 S/m</td>
<td>Estimated</td>
</tr>
<tr>
<td>σ₂</td>
<td>Conductivity in the electrode phase</td>
<td>678.8 S/m</td>
<td>Estimated</td>
</tr>
<tr>
<td>D₁</td>
<td>Diffusion coefficient of reaction ion in the electrolyte phase</td>
<td>1.87×10⁻¹⁰ m²/s</td>
<td>Estimated</td>
</tr>
<tr>
<td>Cₑd₁</td>
<td>Electric double-layer capacitance</td>
<td>8.6 F/m²</td>
<td>Measured</td>
</tr>
<tr>
<td>Parameter</td>
<td>Physical meaning</td>
<td>Value</td>
<td>Reference</td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------------------------------</td>
<td>---------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>$D_2$</td>
<td>Diffusion coefficient of reaction ion in the electrode phase</td>
<td>$1.87 \times 10^{-15}$ m$^2$/s</td>
<td>Estimated</td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>Electric double-layer capacitance</td>
<td>$4.54$ F/m$^2$</td>
<td>Measured</td>
</tr>
</tbody>
</table>

Table S4. List of changed parameters in the simulation model for the supercapacitor at the photothermal temperature of 325.45 K (Solar 52°C).
Note S6. The modeling and simulation for the mechanism of the photothermal effect enhanced capacitance of the double-layer-type supercapacitor.

To investigate the mechanism for the increasing capacitance of the double-layer-type supercapacitor (EDLC) with the increasing photothermal temperature, a classic EDLC model (for plane electrodes) was applied by treating the stern and diffuse layer capacitances in series. In the model, the total double-layer integral areal capacitance \( C_{dl} \) can be expressed as:

\[
\frac{1}{C_{dl}} = \frac{1}{C_{dl}^{S}} + \frac{1}{C_{dl}^{D}} = \frac{H}{\varepsilon_0 \varepsilon_r} + \frac{\psi_D}{2\varepsilon \varepsilon_0 N_A c_{\infty} \lambda D} \left\{ \nu_p \ln \left[ 1 + 2 \nu_p \sin \frac{h^2}{2k_B T} \right] \right\}^{-1/2}
\]

where \( H \) is the thickness of the Stern layer that is approximately the radius of the solvated ions, \( \varepsilon_r \) is the average dielectric permittivity along electrode surface, \( \varepsilon_0 \) is the free space permittivity, \( T \) is the absolute temperature, \( z \) is the ion valency, \( e \) is the elementary charge, \( N_A \) is the Avogadro constant, \( c_{\infty} \) is the bulk molar concentration of ion species, \( k_B \) is the Boltzmann constant, \( \psi_D \) is the potential at the interface located at \( x = H \). Note that the ion conducting ability of the solid-state PVA/H\(_3\)PO\(_4\) electrolyte is mainly due to the ion exchange properties of the phosphorylated PVA (esterification product of PVA and H\(_3\)PO\(_4\)).

The accurate concentration of the ion-exchange species can not be obtained since it is unable to get the exact degree of the esterification reaction between the PVA and H\(_3\)PO\(_4\). In the simulation model, the ion concentration of the solid-state PVA/H\(_3\)PO\(_4\) electrolyte is set as \( 1 \) mol/L (approximately the concentration of H\(_3\)PO\(_4\) in the mixture of water, H\(_3\)PO\(_4\) and PVA (weight ratio: 10:1:1) when preparing the PVA/H\(_3\)PO\(_4\) electrolyte).

\( \lambda_D \) is the Debye length for symmetric electrolytes that corresponds to an estimated EDLC thickness, \( 37,43 \) which is defined as:

\[
\lambda_D = \sqrt{\varepsilon_0 \varepsilon_r k_B T / 2 z^2 e^2 N_A c_{\infty}}
\]

\( \nu_p \) is the packing number that represents the ratio of the total bulk ion concentration to the maximum ion concentration assuming a simple cubic ion packing, \( 46,47 \) which is defined as:

\[
\nu_p = 16 H^3 N_A c_{\infty}
\]
When the EDLC undergoes a temperature change, the variables in equation (S41) are $T$, $\varepsilon_r$ and $\lambda_D$. The constant and the variable parameters at different photothermal temperatures are listed in Table S5 and S6, respectively.

**Table S5. The constant parameters at different photothermal temperatures in the EDLC model.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_0$</td>
<td>$8.854 \times 10^{-12}$ F/m</td>
<td>H</td>
<td>$0.25 \times 10^{-9}$ m</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>1</td>
<td>$\psi_0$</td>
<td>0.7 V</td>
</tr>
<tr>
<td>$N_a$</td>
<td>$6.022 \times 10^{23}$ mol$^{-1}$</td>
<td>$\epsilon$</td>
<td>$1.602 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>$\nu_p$</td>
<td>$2.409 \times 10^{18}$</td>
<td>$c_\infty$</td>
<td>1000 mol/m$^3$</td>
</tr>
<tr>
<td>$k_b$</td>
<td>$1.381 \times 10^{-23}$ J K$^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table S6. The variable parameters at different photothermal temperatures in the EDLC model.**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\varepsilon_r$</th>
<th>$\lambda_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>68959.00</td>
<td>$9.018 \times 10^8$</td>
</tr>
<tr>
<td>311.15</td>
<td>134702.96</td>
<td>$1.288 \times 10^8$</td>
</tr>
<tr>
<td>324.15</td>
<td>223502.60</td>
<td>$1.693 \times 10^8$</td>
</tr>
<tr>
<td>337.15</td>
<td>612261.17</td>
<td>$2.858 \times 10^8$</td>
</tr>
</tbody>
</table>
**Note S7. Details for the simulation of the temperature distribution along the supercapacitor under solar illumination.**

The solar irradiance contains ~7% of ultraviolet light, ~50% of visible light and ~43% of infrared light. In the visible region, the penetration depth of the light can be estimated as $1/\alpha$, where $\alpha$ is the absorbance coefficient; and $\alpha$ can be simply calculated as $\alpha=a/d$, where $a$ is the absorbance and $d$ is the thickness of the supercapacitor. The absorbance of the supercapacitor is ~2 among the visible light range (Fig. S22a), and therefore the penetration depth of the visible light in the supercapacitor is approximately half of the supercapacitor thickness.

Supposing that the penetration depths of light over the entire light source spectrum (340~850 nm, Fig. S4b) are all half of the supercapacitor thickness, a simplified model is established by using the COMSOL Multiphysics software. The supercapacitor can be regarded as being composed of small units of 3D graphene and solid-state PVA/H$_3$PO$_4$ electrolyte. In the model, a typical cuboid material unit contains two parts with the same volume (side length of each square is set as 1 mm). The temperature of the top square part is set as the photothermal temperature induced by solar illumination while the temperature of the bottom square part is set as the temperature without solar illumination (in dark). Also, the bottom side of the bottom square part is set as thermal insulating (corresponding to the thermal insulating foam in the experiment), and the surrounding environment is set as non-circulating air. The photothermal effect induced heat will transfer from the top part to the bottom part and dissipate into the surrounding environment.

The heat transfer in the solid material can be expressed by the following equations:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \mathbf{u} \cdot \nabla T + \nabla \cdot \mathbf{q} = Q \tag{S44}$$

$$\mathbf{q} = -k \nabla T \tag{S45}$$
where \( \rho \) is the material density, \( C_p \) is the material heat capacity at constant pressure, \( k \) is the material thermal conductivity, \( \mathbf{u} \) is the velocity field, and \( Q \) is the heat source.

The temperature distribution is obtained when the heat transfer and heat dissipation reach an equilibrium. The parameters in the model for the heat transfer of the 3D graphene and the solid-state PVA/H\(_3\)PO\(_4\) electrolyte are listed in Table S7.

**Table S7. Parameters used in the simulation model for the temperature distribution along the supercapacitor under 1 solar illumination.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>3D graphene</th>
<th>Solid PVA/H(_3)PO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ) (kg/m(^3))</td>
<td>2.8</td>
<td>1200</td>
</tr>
<tr>
<td>( C_p ) (J/(kg K))</td>
<td>(1.34\times10^3)</td>
<td>(5\times10^3)</td>
</tr>
<tr>
<td>( k ) (W/(m·K))</td>
<td>800</td>
<td>0.2</td>
</tr>
</tbody>
</table>
**Fig. S1** TEM images and Raman spectrum of the 3D-h graphene. (a) Typical HRTEM overview of the graphene nanoplates. (b) Enlarged HRTEM view showing the thickness of a typical graphene nanoplate (~7 layered). (c) Raman spectrum of the 3D-h graphene. Note that the intensity of the 2D peak (~2690 cm$^{-1}$) is ~0.7 times that of the G peak (~1580 cm$^{-1}$).
Fig. S2 SEM images of the PEDOT:PSS coated 3D-h graphene. (a) SEM overview of the 3D-h graphene coated with PEDOT:PSS. (b) Enlarged SEM view showing the thickness of the PEDOT:PSS layer.
**Fig. S3** Light interactions with flat surface and graphene nanoplates anchored surface. (a) Schematic depiction showing the light reflected away from the flat surface. (b) Calculated cross-sectional electric field distribution of the flat surface at light wavelength of 550 nm. (c) Schematic depiction showing the light trapped in the graphene nanoplates anchored surface. (d) Calculated cross-sectional electric field distribution of the graphene nanoplates anchored surface at light wavelength of 550 nm.
Fig. S4 (a) Absorption spectrum of the PEDOT:PSS film. (b) Light spectrum of the light source for the solar illumination in the experiments.
**Fig. S5** Dependence of the IR drop and corresponding internal resistance on the photothermal temperature and heating temperature. (a) Dependence of the IR drop on the photothermal temperature and heating temperature. Note that the galvanostatic charge/discharge (GCD) current density is 3.3 mA cm$^{-2}$. (b) Dependence of the internal resistance obtained from the IR drop on the photothermal temperature and heating temperature.
**Fig. S6** Cycle tests of the supercapacitor in dark and under 1 solar illumination. (a) Retention test of the supercapacitor in dark (~25 °C) via continuous GCD cycling process. The inset shows the GCD curves from the 15080th to the 16000th cycle. (b) Retention test of the supercapacitor under 1 solar illumination via continuous GCD cycling process. The inset shows the GCD curves from the 1080th to the 2000th cycle.
**Fig. S7** (a) The galvanostatic charge/discharge (GCD) curves of the pseudo-type supercapacitor stays under 1 solar illumination before and after 2.5 h. (b) The GCD curves of the pseudo-type supercapacitor stays heated at 62°C before and after 2.5 h. (c) The GCD curves of the double-layer-type supercapacitor stays under 1 solar illumination before and after 2.5 h. (d) The GCD curves of the double-layer-type supercapacitor stays heated at 62°C before and after 2.5 h.
**Fig. S8** (a-b) Photographs showing the solid-state PVA/H$_3$PO$_4$ electrolyte (a) in the original condition and (b) after staying heated at 62 °C for 2.5 h. (c-e) SEM images of the supercapacitor electrode filled with solid-state PVA/H$_3$PO$_4$ electrolyte (c) in the original condition, (d) after 2000 continuous cycles of GCD test under 1 solar illumination and (e) after 2000 continuous cycles of GCD test under heated at 63 °C. (f) FTIR spectra of the supercapacitor electrode filled with solid-state PVA/H$_3$PO$_4$ electrolyte in the original condition; after 2000 continuous cycles of GCD test under 1 solar illumination or heated at 63 °C. (Peak 1: 828 cm$^{-1}$; Peak 2: 980 cm$^{-1}$; Peak 3: 1090 cm$^{-1}$)
**Fig. S9** Dielectric constants of the solid-state PVA/H$_3$PO$_4$ electrolyte at different temperatures before and after staying under 1 solar illumination or heated at 62 °C for 2.5 h.
**Fig. S10** Coulombic efficiencies of the supercapacitor under various light illumination intensities and at various heating temperatures. (a) Coulombic efficiencies of the supercapacitor at different GCD current densities under various light illumination intensities. (b) Coulombic efficiencies of the supercapacitor at different GCD current densities under various heating temperatures.

Note that the coulombic efficiency of the supercapacitor is defined as the ratio of the charge delivered during the discharge to that stored during the charge:

$$\eta = \frac{t_d}{t_c} \times 100\%$$  \hspace{1cm} (S46)

where $t_d$ and $t_c$ are the time required for the discharging and charging processes respectively.
**Fig. S11** The cyclic voltammetry (CV) curves of the supercapacitor upon periodic dark/illumination cycles.
Fig. S12 CV and GCD curves of the supercapacitor under various light illumination intensities. (a-d) The CV curves at a scan rate of (a) 10 mV s\(^{-1}\), (b) 20 mV s\(^{-1}\), (c) 50 mV s\(^{-1}\), and (d) 100 mV s\(^{-1}\) of the supercapacitor under various light illumination intensities. (e-g) The GCD curves at a current density of (e) 6.7 mA cm\(^{-3}\), (f) 12.2 mA cm\(^{-3}\), and (g) 21.1 mA cm\(^{-3}\) of the supercapacitor under various light illumination intensities.
Fig. S13 Dependence of the equivalent series resistance ($R_{esr}$) and ionic resistance on the photothermal temperature and heating temperature. (a) Dependence of the $R_{esr}$ obtained from the EIS curve on the photothermal temperature and heating temperature. (b) Dependence of the ionic resistance obtained from the EIS curve on the photothermal temperature and heating temperature.
Fig. S14 Influences of solar power density on the electrode conductivity and electrolyte conductivity. (a) Relationship between the electrode conductivity and solar power density. (b) Relationship between the electrolyte conductivity and solar power density.
**Fig. S15** Electrochemical properties of the double-layer-type supercapacitor (EDLC) in dark and under 1 solar illumination. (a-b) CV curves at various scan rates for the EDLC (a) in dark and (b) under 1 solar illumination. (c) Comparative CV curves at 5 mV s\(^{-1}\) of the EDLC in dark and under 1 solar illumination. (d-e) GCD curves at various current densities of the EDLC (d) in dark and (e) under 1 solar illumination. (f) Comparative GCD curves at 1.0 mA cm\(^{-3}\) of the EDLC in dark and under 1 solar illumination. (g-h) Volumetric specific capacitances calculated from the (g) CV curves and (h) GCD curves. (i) Coulombic efficiencies of the EDLC in dark and under 1 solar illumination.
**Fig. S16** Dependences of the pseudo-type supercapacitor capacitance and electric double-layer capacitance on the photothermal temperature. (a) Dependence of the pseudo-type supercapacitor capacitance (total capacitance) on the photothermal temperature by solar illumination. (b) Dependence of the double-layer-type supercapacitor capacitance (EDLC capacitance) on the photothermal temperature by solar illumination.
Fig. S17 Influence of the temperature on the dielectric constant of the PVA/H₃PO₄ electrolyte and simulated relationship between the EDLC capacitance and temperature. (a) Influence of the temperature on the dielectric constant of the solid-state PVA/H₃PO₄ electrolyte (frequency: 100 Hz). (b) Simulation results for the relationship between the EDLC capacitance and temperature. Note that the simulation was carried out by a classical EDLC model based on plane electrodes.
**Fig. S18** Simulated electrolyte concentration distributions and GCD curves in dark upon changing the diffusion coefficient. (a) Simulated results for the evolution of electrolyte concentration gradient with the increasing charging potential of the supercapacitor in dark (diffusion coefficient: $1.18 \times 10^{-15}$ m$^2$/s). (b-c) Simulated result for the electrolyte concentration gradient at 0.7 V with a diffusion coefficient of (b) $1.18 \times 10^{-12}$ m$^2$/s and (c) $1.18 \times 10^{-11}$ m$^2$/s. (d) Simulated GCD curves (current density: 6.7 mA cm$^{-3}$) of the supercapacitor in dark with various diffusion coefficients.
Fig. S19 Simulated GCD curves in dark upon changing the reaction rate constant and dependence of the capacitance on the reaction rate constant. (a) Simulated GCD curves (current density: 6.7 mA cm\(^{-3}\)) of the pseudo-type supercapacitor in dark with various reaction rate constants. (b) Simulated results for the relationship between the reaction rate constant and capacitance of the pseudo-type supercapacitor. (c) The values of the reaction rate constant at different photothermal temperatures fitted by the Arrhenius equation.
Fig. S20 (a) Simulated GCD curves (6.7 mA cm$^{-3}$) of the supercapacitor at different photothermal temperatures. (b) Simulated GCD curves showing contributions of variables to the enhanced capacitance.
**Fig. S21** Retention test of the supercapacitor under heated at 63 °C via continuous GCD cycling process. The inset shows the GCD curves from the 1080th to the 2000th cycle.
**Fig. S22** Absorbance spectrum of the supercapacitor in the visible light range and simulated temperature distributions. (a) Absorbance spectrum of the supercapacitor in the visible light range. (b-d) Simulation results showing the temperature difference between the top and bottom surface of the 3D graphene at (b) solar 40.5 °C, (c) solar 52.3 °C, and (d) solar 64.4 °C. (e-g) Simulation results showing the temperature difference between the top and bottom surface of the solid-state PVA/H₃PO₄ electrolyte at (e) solar 40.5 °C, (f) solar 52.3 °C, and (g) solar 64.4 °C.
**Fig. S23** Plots of $I_{V=0.7 \text{ V}}/V^{1/2}$ against $V^{1/2}$ based on the CV curves at different scan rates of the pseudo-type supercapacitor.

**References**


