



Electrochemically building three-dimensional supramolecular polymer hydrogel for flexible solid-state micro-supercapacitors

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ABSTRACT

Conducting polymer hydrogels (CPHs) advantageously synergize the features of both hydrogels and conducting polymers and have gained ground in various applications such as energy storage devices, catalysis and sensors. Conventional synthesis of CPHs usually couples with introducing of non-conductive polymer frameworks or chemical oxidative initiators, which will inevitably lead to degraded electrochemical performance and long rinse time. Here, we report an electrochemical polymerization method free of frameworks and initiators to build three-dimensional (3D) polyaniline/phytic acid supramolecular hydrogel. This CPH provides high conductivity of 0.43 S cm^{-1} and improved electrode interfaces between electronic transporting phase and ionic transporting phase. As a result, the CPHs exhibit large areal capacitance of 561.6 mF cm^{-2} and specific capacitance of 311.3 F g^{-1} . Flexible solid-state micro-supercapacitors (MSCs) based on this CPHs deliver high areal capacitance of 135.9 mF cm^{-2} and considerable integratable potential via tandem and parallel connection. Cyclic stability is demonstrated by 10,000 galvanostatic charge/discharge cycles with 76% capacitance retention. Besides, electrochemical performance of this device can be maintained under different mechanical loadings such as bending and twisting, which makes it a promising power supply candidate for future wearable electronics and on-chip integrated circuit.

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1. Introduction

Twistable and deformable power supplies (batteries and supercapacitors) have long been researched attributed to the explosive proliferation of next generation flexible and wearable electronics [1–3]. Flexible solid-state supercapacitors (FSSCs) represent a novel class of power supply candidate free of electrolyte leakage problem and can work under consecutive bending, rolling, twisting and even stretching without electrochemical performance

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degradation, which have garnered intense interests recently [4–9]. Since electrochemical performance of FSSCs is mainly determined by electrode materials of devices, the majority of current researches shed much light on the preparation of advanced electrode materials featuring both extraordinary electrochemical performance and favourable flexibility [10–13]. As an important family member of supercapacitor electrode materials, conducting polymers is attracting tremendous attention in the fabrication of FSSCs by virtue of considerable softness and high intrinsic pseudocapacitance [14–18]. However, most of current researches tend to design conducting polymers with unique nanostructures [5,15,19] or reveal the synergistic effect between them with other materials [6,20–22] (e.g. carbonaceous materials and transition metal oxides), investigation on derivatives of conducting polymers still remains a virgin land to researchers.

Conducting polymer hydrogels (CPHs), one of the derivatives of conducting polymers, is made up of three-dimensional polymeric

networks and large amounts of water medium. CPHs generally synergize the advantageous features of hydrogels and organic conductors and have gained ground in energy related systems, catalysis, actuators and sensors [23–27]. Different from solid electrode materials, CPHs consist of continuous interconnected electronic and ionic transfer phase, in which the solid state electronic transfer phase is completely surrounded by aqueous ionic transfer phase, resulting in full utilization of electrochemical active materials. Additionally, CPHs can reach contact with the electrolyte solution at the molecular level due to the swelling behavior of polymer with water and ions, thus efficient electrochemical process of supercapacitors can be anticipated [28]. In other word, CPHs provide significantly improved electrode interfaces, between electronic transporting phase and ionic transporting phase as well as between soft and hard materials, which makes them an ideal electrode candidate for the fabrication of FSSCs.

Generally, there are two typical routes to synthesize CPHs: i) polymerizing aromatic monomers in existing nanostructured hydrogel which basically serve as physical frameworks and templates [29–31], this route usually suffers from weak electrochemical activities and specific capacitance due to the introducing of non-conductive hydrogel matrix; ii) adding crosslinkers into monomers of conducting polymers thus chain growth and crosslinking of polymer chains occur simultaneously while initiator is added into the blends of monomers and crosslinkers [32,33]. Compared with the former one, this latter method can effectively avoid the using of non-conductive hydrogel matrix and finally leads to hydrogels with higher conductivity. Nevertheless, chemical oxidative initiator [31,32,34,35] (such as ammonium persulfate) or strong acid [36] (concentrated H_2SO_4) treatment is usually necessary for this route. Besides, the inevitable sequential time-consuming rinse process for removing of by products and excess ions is unfavorable for rapid production. In this regard, electrochemical polymerization can be a relatively ideal route to synthesize CPHs since it is free of non-conductive hydrogel frameworks as well as chemical oxidative initiators.

In this study, electrochemical polymerization was adopted to develop a novel method free of frameworks and initiators for the preparation of CPHs, which could be sequentially utilized in high performance FSSCs. Phytic acid is employed as both crosslinker and dopant to interact with polyaniline (PANI) molecular chains to form three-dimensional (3D) supramolecular CPHs. Due to the high conductivity (0.43 S cm^{-1} at room temperature) and improved electrode interfaces between electronic transporting phase and ionic transporting phase, this CPHs deliver large areal capacitance of 561.6 mF cm^{-2} at 1 mA cm^{-1} and specific capacitance of 311.3 F g^{-1} at 1 A g^{-1} . To further demonstrate the application potential of this CPHs, flexible solid-state micro-supercapacitor (MSC) was developed with considerable energy density of $49.9 \mu\text{Wh cm}^{-2}$ at 0.4 mW cm^{-2} . Even at a high power density of 4 mW cm^{-2} , the device still shows high energy density of $33.7 \mu\text{Wh cm}^{-2}$. Besides, this MSCs can maintain 76% of its initial capacitance after 10,000 charge/discharge cycles. More importantly, this MSC shows excellent flexibility and deformability, the device can be bended and twisted easily without sacrificing its electrochemical performance. The MSC presented here is unambiguously a promising power supply candidate for future wearable electronics and on-chip integrated circuit.

2. Experimental section

2.1. Preparation of CPHs

Aniline, phytic acid solution (50 wt% in H_2O), H_2SO_4 of analytical grade were purchased from Aladdin and were used without

additional purification. Commercial polyethylene terephthalate (PET) film with thickness of $250 \mu\text{m}$ was cut into the size of $20 \times 30 \text{ mm}$ and rinsed with deionized water and acetone for several times to remove contaminants. Gold thin film was sequentially deposited onto the surface of PET film using magnetron sputtering equipment (SKY Technology Development Co., Ltd) with a sputtering power of 40 W for 20 min. To prepare CPHs hydrogel precursor, 1.105 mL (1.2 mmol) phytic acid solution (50 wt %) and 0.550 mL aniline (6 mmol) were added into 60 mL 1 M H_2SO_4 solution under vigorous stir to form clear solution, the molar ratio between aniline and phytic acid is 5:1. To point it out, before we choose the molar ratio of 5:1, we have generally prepared a series of precursor solutions in which the ratio of aniline versus phytic acid varies from 1:1 to 10:1. It seems that in the precursor solution of 5:1, a moderate polymerization speed can be obtained (Fig. S1). So we finally chose 5:1 precursor solution for electrochemical polymerization. For a typical fabrication of CPHs, gold evaporated PET was integrated into three-electrode configuration as working electrode, in which platinum foils and saturated calomel electrode (SCE) were used as counter and reference electrodes. A fixed potential of 0.8 V vs SCE (This parameter is commonly chosen for electrochemical polymerization of conducting polymers in many studies) was then applied on the working electrode and CPHs gradually come into formation with time.

2.2. Preparation of flexible supercapacitors

PVA/ H_2SO_4 gel electrolyte was employed to assemble flexible supercapacitors. For a typical fabrication of PVA/ H_2SO_4 gel electrolyte, 10 g PVA (with the polymerization degree of 1799) and 10 g H_2SO_4 were mixed with 100 mL deionized water in beaker under vigorous stir at an elevated temperature of 85°C to form clear sticky solution.

To assemble flexible solid-state supercapacitor, CPHs were firstly synthesized onto gold interdigital pattern on PET film. PVA/ H_2SO_4 gel electrolyte was then uniformly coated onto interdigital pattern through a facile drop-casting method. A blade was often used in this procedure to remove excess gel electrolyte. Sequentially, the electrolyte coated device was natural dried for 2–4 h to make it lose the majority of its fluidity. Polydimethylsiloxane (PDMS) was finally coated onto the whole device in the same way as encapsulating layer. As a result, the PVA/ H_2SO_4 electrolyte and PDMS layer was measured to be 60 and $100 \mu\text{m}$, respectively.

2.3. Characterization of materials

The morphology and topography of as-prepared samples were characterized using a JSM-7800F prime scanning electron microscope in the high-vacuum mode with an accelerating voltage of 1–5 kV and energy dispersive spectrometer (EDS) elementary mapping was conducted with a high accelerating voltage of 15 kV. Fourier transformed infrared (FTIR) spectra with a resolution of 2 cm^{-1} were recorded on a Nicolet 6700 spectrometer (Thermo Fisher Scientific, US). X-ray diffraction (XRD) of the samples was carried out with PANalytical X'Pert Powder diffractometer with $\text{Cu K}\alpha$ radiation between 5° and 90° . X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo Scientific ESCA-LAB 250Xi.

2.4. Electrochemical testing

Electrochemical tests of CPHs electrode are carried out in a three-electrode configuration, in which platinum foils and saturated calomel electrode (SCE) were used as counter and reference electrodes in 1 M H_2SO_4 aqueous electrolyte. Electrochemical tests

of encapsulated device are carried out in two-electrode system.

2.5. Data processing

To evaluate the intrinsic electrochemical performance of CPHs, specific capacitance was calculated from both the CV curves and discharge curves according to the following equations:

Specific capacitance derived from discharge curves:

$$C = It/m\Delta V$$

where I (A) is the current used for the charge/discharge, t (s) is the discharge time, m (g) is the loading mass of electrochemical active material and ΔV (V) is the voltage interval of the discharge. Specific capacitance derived from CV curves:

$$C = \frac{1}{v \cdot m \cdot \Delta V} \int_{V_0}^{V_0 + \Delta V} i dV$$

where v is the scan rate (V/s), m is the loading mass (g) of electrochemical material, V_0 and ΔV are initial potential and potential window of CV curves (V), i (A) is the voltammetric discharge current.

The areal capacitance can be obtained through replacing loading mass in the above mentioned equations with effective loading area (cm^2) of electrochemical active materials.

The energy density (E) and average power density (P) of as prepared flexible solid-state supercapacitors can be expressed as:

$$E = \frac{CU^2}{2S}$$

$$P = \frac{E}{\Delta t}$$

where C (F) is capacitance of entire device, U (V) is cell voltage, S is effective area (cm^2) of electrochemical active materials and Δt is discharge time.

3. Results and discussion

For a typical fabrication of CPHs, gold thin film patterned commercial PET film (250 μm) realized by magnetron sputtering technology are served as current collector prior to integrating it into three-electrode configuration (Fig. S2). The three-electrode configuration is then dipped into CPHs precursor solution consisting of aniline monomer and phytic acid, which were mixed according to a predetermined molar ratio. Chemically crosslinked CPHs are sequentially synthesized onto gold patterns through electrochemical polymerization, in which a fixed potential of 0.8 V vs SCE is applied onto the gold patterns to motivate polymerization and crosslinking. The gelation mechanism of CPHs can be generally illustrated in Fig. 1a, phytic acid was employed as both dopant and crosslinker by pronating the nitrogen groups on PANI. Since each phytic acid molecule possesses six phosphate groups, it can react with more than one PANI chain, thus a mesh-like hydrogel network comes into formation. With the polymerization of PANI, we observed a change in the color of the surface of current collector from golden (color of gold current collector) to light green (color of thin CPHs film) and finally become dark green (color of thick CPHs film) (shown in Fig. S3). SEM reveals the 3D porous foam morphology of the dehydrated CPHs, which is constructed by numerous interconnected globular particles (Fig. 1b). Conductivity of this CPHs was demonstrated to be 0.43 S cm^{-1} by four-point

probe method and solid content was measured to be 6.6% either by lyophilization and heat drying. As shown in Fig. 1c, this CPHs are generally composed of two distinct phases: electronic transfer phase and ionic transfer phase, in which solid electron transfer phase is completely surrounded by aqueous ion transfer phase, thus full utilization of CPHs can be anticipated. To demonstrate the practical application potential of this CPHs, a flexible solid-state MSC was assembled (Fig. 1d). The MSC based on polyaniline/phytic acid CPHs shows promising electrochemical performance and could be applied into practical applications (Fig. 1e).

Fig. 2a shows the cross-section SEM image of as-prepared CPHs (corresponding to a polymerization time of 120 s). Obviously a three-layer architecture can be observed, in which the bottom layer is PET substrate, the middle layer is gold current collector with average thickness of 380 nm (Fig. S4) and the top layer is 3D interconnected CPHs nanostructures with the thickness of 7.5–8.9 μm . Surface morphology of dehydrated CPHs is depicted in Fig. 2b, it can be clearly seen that this CPHs possess 3D porous foam morphology. The foam-like nanostructures are constructed with globular particles with an average diameter of $\sim 320 \text{ nm}$. Investigation at lower magnification reveals that the CPHs form a continuous network, in which abundant macropores are distributed in (Fig. S5). As a result, interconnected particles naturally form continuous conductive path within the CPH networks, the interconnected macropores among solid networks naturally form unblocked channels favoring molecule and ion transport. Compared with other solid state materials, this kind of structure leads to full utilization of materials and high speed of electrochemical process. Energy dispersive spectroscopy (EDS) was carried out to probe the elementary composition of CPHs, uniform distribution of carbon, nitrogen and phosphorus can be clearly seen in Fig. 2c, confirming the chemical composition of this CPHs. The chemical structure of the hydrogel was analyzed by Fourier-transform infrared spectroscopy (FTIR) spectroscopy. The FTIR spectrum of the CPHs suggests two typical characteristic peaks of PANI located at 1579 and 1489 cm^{-1} corresponding to the $\text{C}=\text{N}$ and $\text{C}=\text{C}$ stretching vibration of the quinoid ring and benzenoid ring, respectively [37]. The band at 1303 cm^{-1} is assigned to the $\text{C}-\text{N}$ stretching of the benzenoid unit while the band at 1143 cm^{-1} is due to the $\text{C}=\text{N}$ bond stretching of doped quinonoid unit [19]. The broad peak near 3440 cm^{-1} is attributed to either $-\text{OH}$ groups in phytic acid or $\text{N}-\text{H}$ stretching of PANI and the peak at 823 cm^{-1} is associated with the vibration of $\text{C}-\text{H}$ stretching (Fig. 2d). XRD spectrum of CPHs shows a typical peak of PANI located at 25.2° and the peak of 43.4° can be attributed to the intercalation of phytic acid molecules between PANI chains and consequently leading to larger interspace between PANI molecules [31,34] (Fig. 2e). The surface chemical composition analysis of CPHs film was determined utilizing X-ray photoelectron spectroscopy (XPS) [38,39]. The XPS survey scan of CPH sample shows the presence of oxygen ($\text{O}(1s)$ $\sim 531 \text{ eV}$), nitrogen ($\text{N}(1s)$ $\sim 399 \text{ eV}$), carbon ($\text{C}(1s)$ $\sim 284 \text{ eV}$) as well as phosphorus ($\text{P}(2s)$ $\sim 190 \text{ eV}$, $\text{P}(2p)$ $\sim 133 \text{ eV}$). The quantitative analysis of relative concentrations of C, N, O and P in the CPHs, calculated from the corresponding photoelectron peak area are listed in Table S1. In general, the C/N ratio is 6 for aniline units in PANI. However, in case of our sample the ratio of total carbon to nitrogen is higher than the theoretical formula $(\text{C}_6\text{H}_5\text{N})_n$, this can be attributed to the introducing of phytic acid, which contains abundant carbon. The presence of 26.3% oxygen can be originated from either introducing of phytic acid or partial oxidation of the film's surface. The nitrogen 1s XPS core level spectra is shown in Fig. 2g, the peaks corresponding to quinoid di-imine nitrogen and benzenoid diamine nitrogen are centered at 398.8 eV and 399.6 eV , respectively. The surface of CPHs films contains $\sim 17\%$ imine nitrogen and $\sim 83\%$ amine nitrogen (Table S2), which corresponds to an

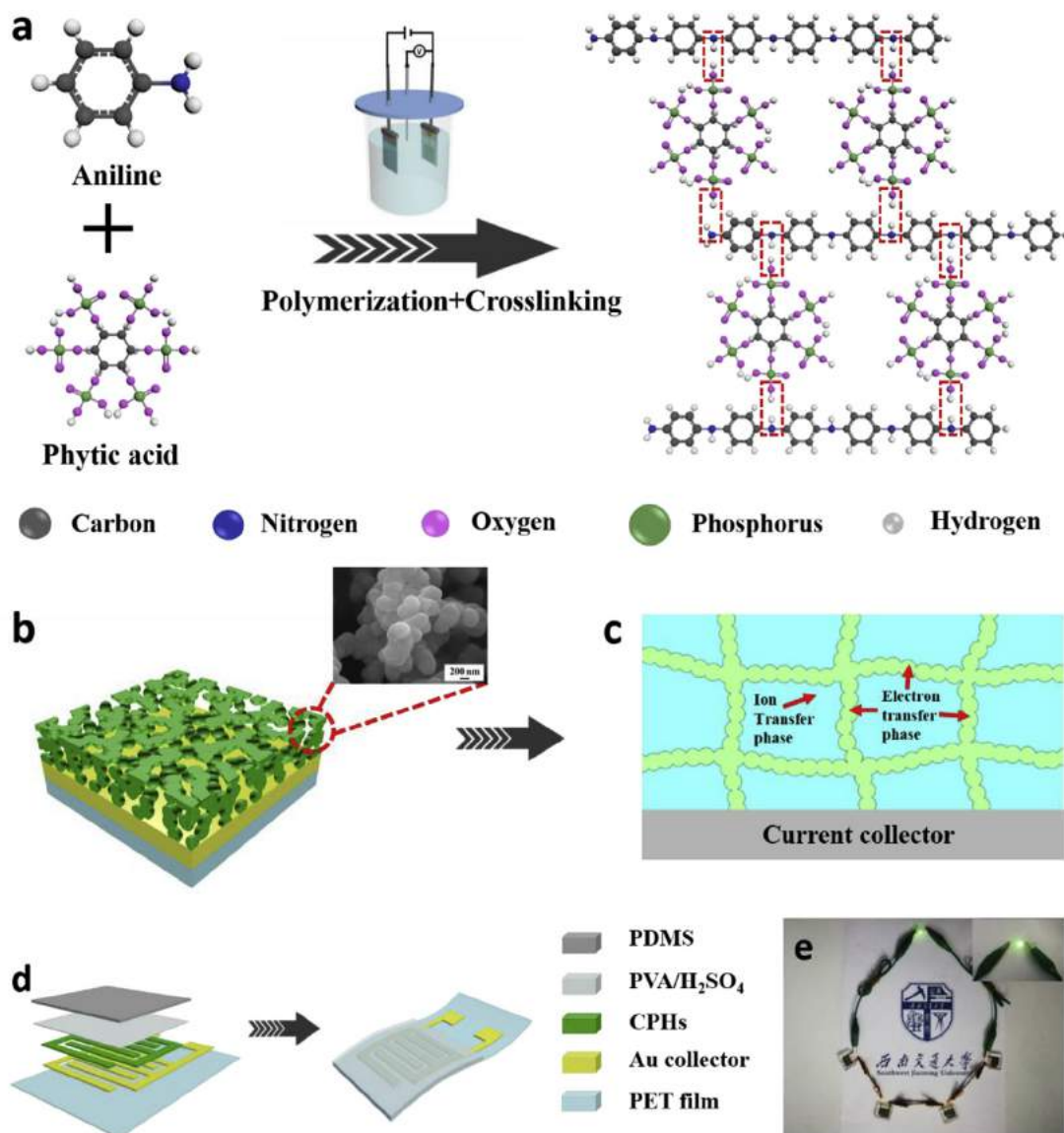


Fig. 1. Flexible solid-state MSC based on electrochemical synthesized polyaniline/phytic acid CPHs. (a) Schematic illustration for fabrication of CPHs. The red rectangular in short dash line indicates the protonation interaction between PANI and phytic acid. (b) Structure diagram of as-prepared CPHs. (c) Interconnected dual phases of CPHs. (d) Schematic illustration of flexible solid-state MSC. (e) A blue LED can be lighted by tandem MSCs. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

oxidation state close to that of protoemeraldine base [40]. Besides, the N^+/N ratio of CPHs is 45.6%, indicating a relatively high doping level of PANI. The C(1s) core level spectra with binding energies spanning the range from ~287 eV to 284 eV is depicted in Fig. 2h. The C1s core level spectra can be deconvoluted in four peaks: C–C/C–H at 284.1 eV, C–N/C=N at 285 eV, C–N⁺/C=N⁺ at 285.8 eV and C–O/C=O at 286.8 eV. Fig. 2i reports that the spectra of P 2p at 133.2 eV corresponds to PO_4^{3-} . Peaks of P 2p located at 134.2 and 134.32 eV corresponds to HPO_4^{2-} [41]. These results clearly confirm the chemical composition and high doping level of as-prepared CPHs.

To evaluate electrochemical performance of as-prepared CPHs, we firstly estimated the performance of flexible electrode based on CPHs in three-electrode configuration. The CPH electrode was characterized by utilizing cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) methods with 1 M H₂SO₄ solution serves as electrolyte. It

should be noted that we have pre-designed the gold current collector pattern into 1 cm × 1 cm square so that the loading area of CPHs can be correspondingly controlled into 1 cm². Since electrochemical performance of electrode is strictly dependent on the loading mass of active material [42], we have primarily inquired the relationship between polymerization time and loading mass of CPHs. As expected, the loading mass of CPHs increases proportionally with the increase of polymerization time from 120 s to 720 s (Fig. 3a), which means the loading mass of electrochemical active materials can be precisely controlled through varying polymerization time.

As shown in Fig. 3b, the specific capacitance of CPH electrode shows decrease trend while the areal capacitance shows a reversed one with increased loading mass. The highest specific capacitance is obtained with 0.07 mg cm^{−2} CPHs loading, reaching 311.3 F g^{−1} based on the mass of dehydrated CPH (specific capacitance of hydrated CPHs was calculated to be 20.6 F g^{−1} at the current density of

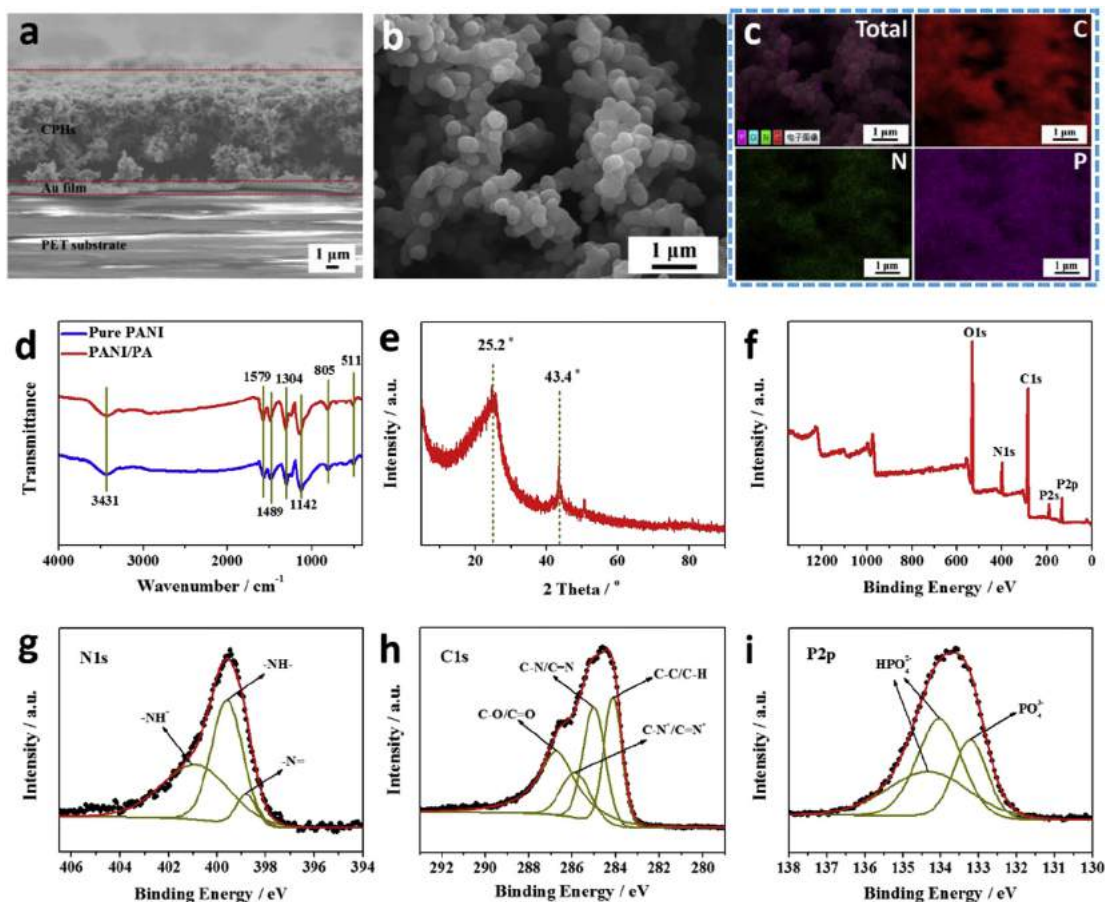


Fig. 2. Morphology and chemical composition of CPHs. (a) Cross-section and (b) surface morphology of as-prepared CPH electrode. (c) EDS mapping of CPHs. (d) FTIR spectrum and (e) XRD spectrum of CPHs. (f) XPS wide scan of CPHs. The (g) N 1s, (h) C 1s and (i) P 2p deconvoluted spectra of CPHs.

1 A g^{-1} , which can be clearly seen in Fig. S6). The maximum areal capacitance is obtained with 1.79 mg cm^{-2} CPHs loading, reaching 508.8 mF cm^{-2} . At around 1.11 mg cm^{-2} CPHs loading, the requests for both high specific capacitance and high areal capacitance are balanced. However, people often put more emphasis on areal capacitance than specific capacitance since it is very important for practical application to storage as much energy as possible in limited area. Therefore, the CPHs loading of electrode and devices was fixed at around 1.79 mg cm^{-2} for the following tests, which corresponds to highest areal capacitance.

To show the detailed capacitive behavior, CV and GCD curves of flexible electrode with 1.79 mg cm^{-2} loading are exhibited in Fig. 3c and d. Two distinct couples of characteristic redox peaks of PANI can be observed on the CV curves, originating from the transformation among the leucoemeraldine base (LB), the emeraldine salt (ES), and the pernigraniline base (PB) [29,43]. With the scan rate increases from 5 mV s^{-1} to 100 mV s^{-1} , the redox peaks can still be detected. GCD curves of CPHs exhibit the typical triangle-shape profile, indicating highly reversible charge-discharge behavior [44]. Areal capacitance of CPHs derived from CV and GCD curves are 561.6 mF cm^{-2} (with the scan rate of 80 mV s^{-1}) and 561.7 mF cm^{-2} (with the current density of 1 mA cm^{-2}), respectively. This is a promising value compared with many state-of-the-art polymer based materials (Table S3). The CPH electrode also shows a moderate rate performance (Fig. 3e), with 67.5% capacitance retention when current density is increased from 1 mA cm^{-2} (561.7 mF cm^{-2}) to 10 mA cm^{-2} (379.4 mF cm^{-2}). The electrochemical kinetics and ionic resistance were studied by EIS (Fig. 3f). The slope of the EIS

plot in the low frequency region is close to 90° , indicating a relatively good capacitive behavior. In the high frequency region, the interception on the real impedance axis in the Nyquist plot manifests small series resistance $1.71 \Omega \text{ cm}^{-2}$. The semicircle on the EIS plot shows a small charge-transfer resistance ($0.04 \Omega \text{ cm}^{-2}$), indicating a favourable charge-transfer kinetics of the CPH electrode [45].

To examine the practical application potential of CPHs, a flexible solid-state MSC was fabricated. To point it out, here we employ the coplanar interdigital electrode configuration because it is separator-free and preferable for integration with microelectronic systems and enables further miniaturization of portable and wearable devices [46]. As shown in Fig. 4a, PET film possessing considerable flexibility is utilized as substrate for deposition of interdigital gold electrode patterns. CPHs with 3D interconnected frameworks were sequentially polymerized onto gold collector. PVA/ H_2SO_4 gel system was employed as quasi solid-state electrolyte and the device was finally encapsulated with PDMS elastomer after PVA/ H_2SO_4 gel electrolyte losing the majority of its fluidity. Particularly, here we employed a relatively large inter-space of interdigital fingers for a value of 0.8 mm (Fig. 4b) to avoid short circuit of device because the inter-space of interdigital fingers can be slightly shorten due to the random growth of CPHs. The photograph of as-prepared device is shown in Fig. 4c, it can be clearly observed that this device possesses considerable flexibility as well as thin bulk layer. Electrochemical performance of as-prepared MSC is tested in two-electrode system using CV, GCD and EIS techniques. As shown in Fig. 4d, the characteristic redox

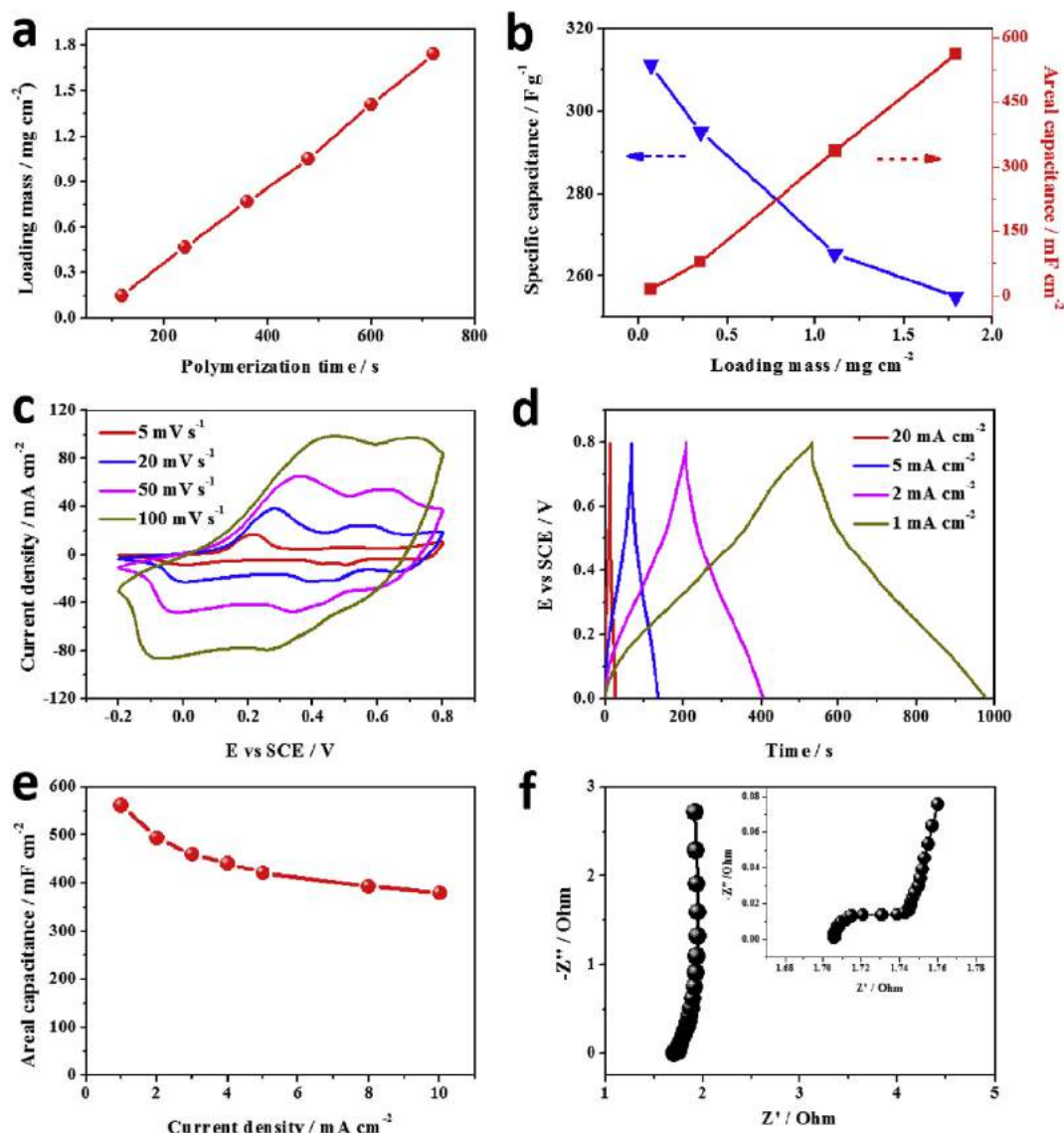


Fig. 3. Electrochemical performance of CPHs based electrodes. (a) Loading mass of CPHs with different polymerization time. (b) Specific capacitance (obtained in 1 A g^{-1}) and areal capacitance (obtained in 1 mA cm^{-2}) of CPHs electrodes with different loading mass of CPHs. Data in (c)–(f) are based on a CPH electrode with 1.79 mg cm^{-2} CPH loading. (c) CV diagrams at scan rates of 5–100 mV s^{-1} . (d) GCD curves at current density of 1–20 mA cm^{-2} . (e) Areal capacitance of CPH electrode derived from GCD curves. (f) Impedance plot in the frequency range of 10 mHz–100 kHz.

peaks of PANI can still be traced in CV diagrams at different scan rates and the profile of CV curves can be well maintained with increasing scan rate, suggesting good capacitive behavior of this supercapacitor [47]. GCD curves (Fig. 4e) show a typical charge-discharge pattern for PANI-based supercapacitors with negligible IR drop, owing to good conductivity of CPHs and gold current collector. The areal capacitance of this supercapacitor was calculated from GCD curves based on the total areal covered with CPHs (Fig. 4f). This supercapacitor demonstrates a high areal capacitance of 135.9 mF cm^{-2} at the current density of 0.5 mA cm^{-2} and a high specific capacitance of 77.6 F g^{-1} at the current density of 0.5 A g^{-1} (Fig. S7). Besides, this supercapacitor also shows good rate performance, with 72% capacitance retention when the current density was increased from 0.5 A g^{-1} (135.9 mF cm^{-2}) to 5 A g^{-1} (98.1 mF cm^{-2}). These results convincingly manifest that this CPHs can be utilized in high performance MSCs.

EIS was used to study the charge transport process of the device (Fig. 4g). The high frequency intercept on the real impedance axis

represents the cell resistance, which is around 5.3Ω for all supercapacitor prototypes. In the low frequency region, the slope is nearly vertical, suggesting considerable capacitive behavior [48]. Cycling life of supercapacitor was investigated by consecutive GCD cycles at a current density of 2 mA cm^{-2} . As shown in Fig. S8, this supercapacitor provides a good cycling stability with 76% capacitance retention over 10,000 cycles. The specific energy and specific power of the as-fabricated MSC are calculated and compared with recently reported works, as shown in the Ragone plots (Fig. 4h). As a result, our FSSC demonstrates a high energy density, reaching $49.9 \mu\text{Wh cm}^{-2}$ at a power density of 0.4 mW cm^{-2} and maintaining $33.7 \mu\text{Wh cm}^{-2}$ even at a high power density of 4 mW cm^{-2} , which is enough to power burst communications, sensors, or other micro-devices [49]. These value are indeed promising compared with previously reported $\text{I-Ti}_3\text{C}_2\text{T}_x/\text{I-Ti}_3\text{C}_2\text{T}_x$ [50], CDC/TiC film [51], graphene quantum dots [52] and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate/Ag [53]. The observed outstanding electrochemical performance can be

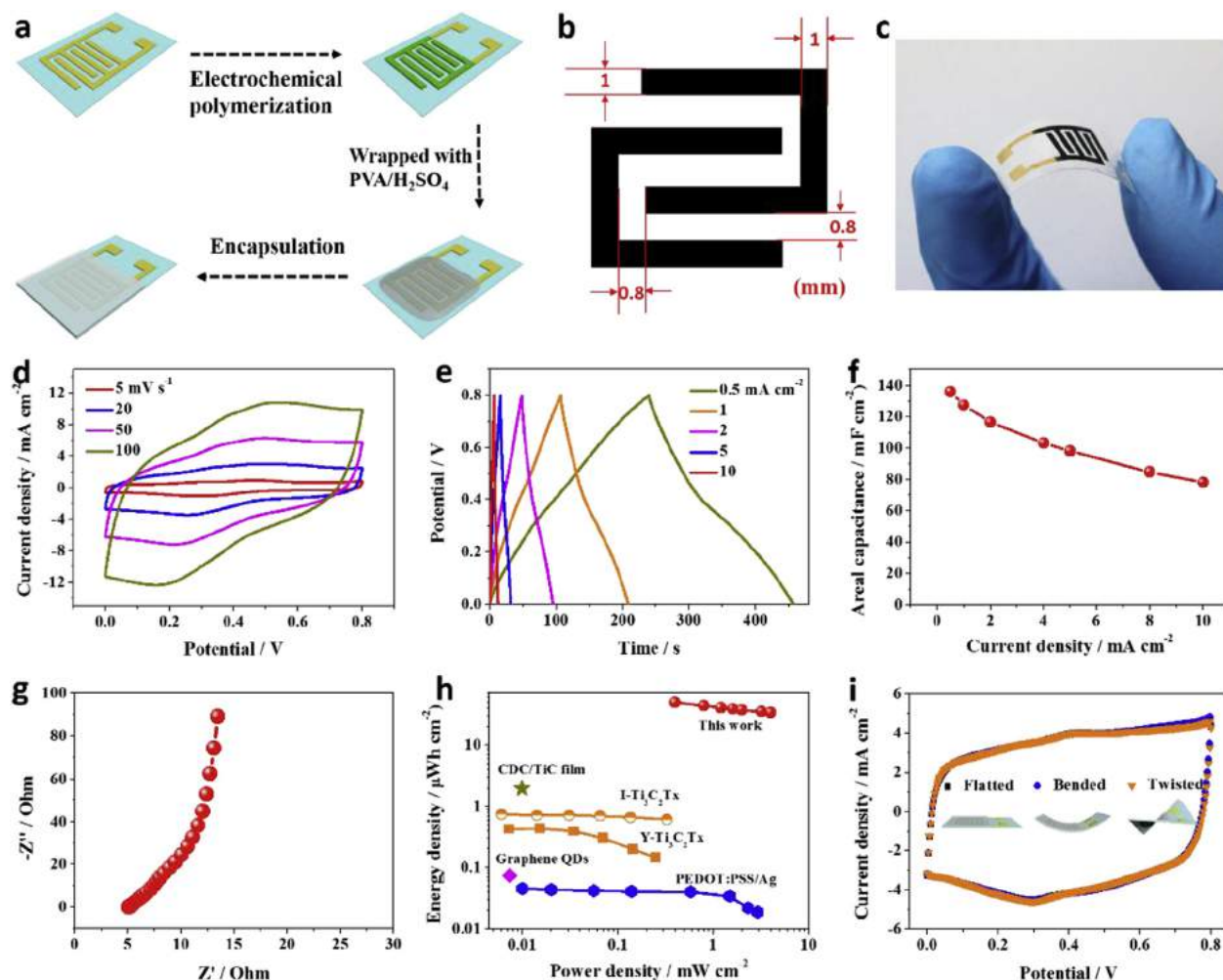


Fig. 4. Electrochemical performance of flexible solid-state MSCs. (a) Schematic diagram of fabrication process of MSCs. (b) The detailed parameters of designed interdigital electrodes. (c) Photograph of as-prepared MSC. (d) CV and (e) GCD curves of the MSC. (f) Areal capacitance of MSC calculated from GCD curves. (g) Nyquist plots of MSC. (h) Ragone plots of recent works compared with this work. (i) CV curves of as-prepared MSC with different mechanical loading.

generally attributed to the following: (i) Large mass loading (up to 1.79 mg cm^{-2}) of CPHs have been achieved through electrochemical polymerization method; (ii) CPHs composed of PANI and phytic acid possess intrinsic high pseudocapacitance, additionally, the interconnected continuous 3D porous structure leads to efficient contact between electrolyte and CPHs; (iii) Additional interface between the PANI chains and the solution phase can be created when it is swollen in water and further facilitates electron transport and easy access of electrolyte ions within the hierarchical 3D structures. Owing to the outstanding mechanical properties of CPHs and PET substrate, this MSC can be deformed easily without sacrificing its electrochemical performance. As depicted in Fig. 4i, the CV curves obtained at flattening, bending and twisting state can maintain its shape, indicating considerable stability under different mechanical loading.

To understand further the properties of as-prepared flexible solid-state MSCs, the parallel and tandem connecting circuit of this supercapacitor were studied and explained in detail. According to Fig. 5a, the potential window can be remarkably broadened through connecting three devices in series (2.4 V, with a scan rate of 20 mV s^{-1}), thus the output of energy can be correspondingly boosted according to the equation $E = 1/2 CV^2$ compared with single device (0.8 V). CV curves of single device and three devices parallel connecting circuit are exhibited in Fig. 5b, it can be clearly observed

that the output of current can be greatly enhanced through parallel connecting. GCD curves of single device, three devices connected in series and parallel are shown in Fig. 5c, the charge/discharge voltage window of the device arrays in serial can be multiplied by the number of single supercapacitors integrated to 2.4 V with similar discharge times while the parallel circuit demonstrate nearly 3 times of charge-discharge time of single device, this result is consistent with the CV curves discussed above. To further demonstrate the application potential and versatility of this MSC, the tandem circuit was used to power various daily electronics. As shown in Fig. 5d, a LCD timer can be motivated by three serial connected supercapacitors, which unambiguously demonstrate the versatility and application potential of as-developed MSCs.

4. Conclusion

In summary, a chemical initiator-free method have been developed to build 3D porous polyaniline/phytic acid CPHs, in which phytic acid serves as both dopant and crosslinker. The resultant hydrogel is consisted of numerous interconnected nanoparticles with abundant continuous macropores distributed in the matrix, with this unique hierarchical structure, efficient electrochemical process can be anticipated. As a result, this CPHs exhibit large areal capacitance of 561.7 mF cm^{-2} and gravimetric

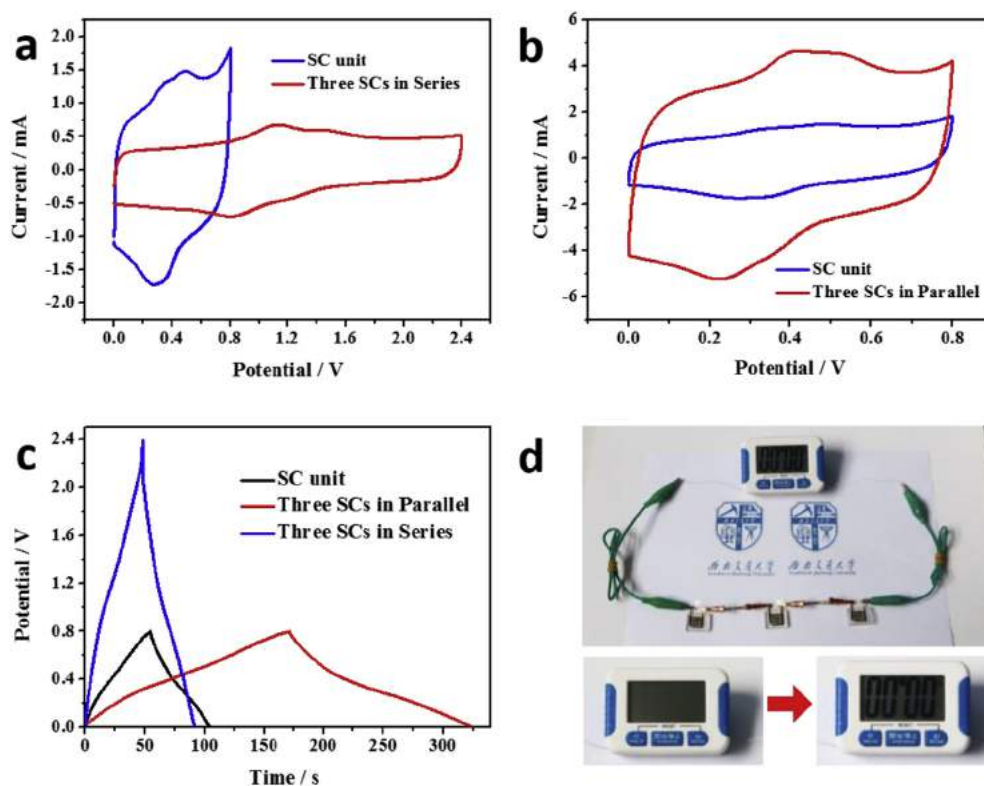


Fig. 5. CV curves of single supercapacitor device and three devices connected (a) in series and (b) in parallel with scan rate of 20 mV s^{-1} . (c) GCD curves of single device, three devices parallel circuit and series circuit at a test current of 1 mA . (d) LCD timer can be successfully powered by three devices series circuit.

capacitance of 311.3 F g^{-1} . Additionally, flexible solid-state MSC based on this CPHs delivers high energy density ($49.9 \mu\text{Wh cm}^{-2}$ at 0.4 mW cm^{-2}), considerable flexibility and good cycling stability (76% capacitance retention over 10000 GCD cycles). These encouraging results presented here unambiguously demonstrate the promising potential of CPHs for the fabrication of high performance MSCs. Additionally, this may pave a way in designing novel supramolecular CPHs for next-generation of flexible solid-state energy storage devices.

Declarations of interest

None.

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Appendix A. Supplementary data

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