Air-Stable Conductive Polymer Ink for Printed Wearable Micro-Supercapacitors

Xiang Chu, Guorui Chen, Xiao Xiao, Zixing Wang, Tao Yang, Zhong Xu, Haichao Huang, Yihan Wang, Cheng Yan, Ningjun Chen, Haitao Zhang,* Weiqing Yang,* and Jun Chen*

Printed electronics are expected to facilitate the widespread distributed wearable electronics in the era of the Internet of things. However, developing cheap and stable electrode inks remains a significant challenge in the printed electronics industry and academic community. Here, overcoming the weak hydrophilicity of polyaniline, a low-cost, easy-fabricating, and air-stable conducting polymer (CP) ink is devised through a facile assemble-disperse strategy delivering a high conductivity in the order of $10^{-2}$ S cm$^{-1}$ along with a remarkable specific capacitance of 386.9 F g$^{-1}$ at 0.5 A g$^{-1}$ (dehydrated state). The additive-free CP ink is directly employed to print wearable micro-supercapacitors (MSCs) via the spray-coating method, which deliver a high areal capacitance (96.6 mF cm$^{-2}$) and volumetric capacitance (26.0 F cm$^{-3}$), outperforming most state-of-the-art CP-based supercapacitors. This work paves a new approach for achieving scalable MSCs, thus rendering a cost-effective, environmentally friendly, and pervasive energy solution for next-generation distributed electronics.

1. Introduction

Stepping into the Internet of Things (IoT) era, widely-distributed electronics with connected mobility are changing our living way in personalized healthcare, seamless communication, smart society, and many others.[3-5] In that case, the number of distributed electronics is booming at a skyrocketing rate.[6-11] To drive these distributed electronics, a pervasive power supply system featuring low-cost and environmentally friendly candidates of the pervasive power supply system, possessing miniaturized volume, high power density, and considerable cycling stability, can be directly used as ideal power sources of distributed electronics, especially in cases of high power delivery.[18,19] However, it is a formidable challenge to push MSCs towards mature commercial applications because scalable electrode materials for mass fabrication of MSCs remain a bottleneck.[20,21]

Ink printing is regarded as a practical approach for scalable fabrication of MSCs electrodes. Nevertheless, the manufacture of cost-efficient and stable electrode inks has emerged as a critical unmet scientific challenge.[22,23] In the past decades, a wide variety of electrode inks, e.g., graphene inks and MXene inks, have been successfully devised for printing electronics.[24,25] Among them, graphene inks have long been explored to apply flexible electronics, including supercapacitors, sensors, and batteries. Yet, they to date still suffer from several downsides. 1) Conventional graphene preparation methods, such as mechanical exfoliation[26] and chemical vapor deposition[27] are not suitable for synthesizing scalable inks due to the low yields. 2) Graphene oxide reduction is considered to be a promising strategy for preparing scalable graphene ink.[28] But the homogeneity and structural integrity of graphene cannot be effectively achieved because fierce oxidation of graphite will destroy the intrinsic structure of graphene layers. 3) Other methods, such as electrochemical exfoliation[22] and intercalation of graphite,[29] usually couple with organic solvents and spacers, which are unfriendly to the environment. Recently, 2D MXene emerges as an unexceptional alternative and complement of graphene.[30-33] However, the development of this fast-growing interdisciplinary research field is primarily shadowed by harsh etching conditions and intrinsic poor air stability. Therefore, it remains a great challenge for researchers and practitioners to fabricate scalable electrode inks featuring facile synthesis and considerable stability.

Herein, we present a facile assemble-disperse strategy achieving a low-cost, easy-fabricating, and air-stable conducting polymer (CP) ink for scalable printing wearable MSCs. Firstly, the polyaniline (PANI) chains are effectively cross-linked enabled by citric acid (CA) via supramolecular interactions,
and consequently, assemble into uniform nanosheets. These nanosheets are then interconnected to form hydrogel due to multiple active groups in the edge of nanosheets. After that, the interactions among nanosheets can be easily broken through vigorous stirring or ultrasonic treatment. The PANI/CA nanosheets can thus be stably distributed in the water to form CP ink. Owing to the high doping level of PANI, such ink exhibits a high conductivity in the order of $10^{-2}$ S cm$^{-1}$ along with a remarkable specific capacitance of 386.9 F g$^{-1}$ at 0.5 A g$^{-1}$ (dehydrated state). The printable MSC derived from as-prepared CP ink delivers high areal capacitance of 96.6 mF cm$^{-2}$, large volumetric capacitance of 26.0 F cm$^{-3}$ as well as considerable energy density of 2.4 mWh cm$^{-3}$ at 238.3 mW cm$^{-3}$, surpassing the majority of state-of-the-art MSCs derived from pseudocapacitive materials.$^{[34–37]}$ We envision that the printed MSC provides a cost-effective, environmentally friendly, and pervasive energy solution that underpins wearable and portable electronics in the IoT era.

2. Results and Discussion

Figure 1a shows the digital photograph of a 5 × 4 wearable MSCs array printed on a PET thin film with the size of 10 cm × 10 cm, which is highly flexible and lightweight. To this end, such MSCs can give rise to wearable bioelectronics where flexible and foldable power supplies are highly needed. The fabrication procedure and configuration of this MSC are illustrated in Figure 1b. Patterned interdigital current collector is sputtered onto PET thin film through mask-assisted magnetron sputtering, after which interdigital electrode pattern is printed onto current collector using CP ink. To assemble an encapsulated MSC, PVA/H$_2$SO$_4$ gel and PDMS are drop-casted onto the interdigital electrode pattern in sequence, serving as the electrolyte and encapsulating layer (See details in Experimental Section). Due to the unique nanosheet structure of the CP electrode, high-performance MSC with fast ion transfer dynamics can be easily assembled (Figure 1c). To point it out, we propose an assemble and disperse strategy containing two different stages labeled assemble and disperse for the scalable fabrication of CP ink. In the assemble stage, aniline and CA dispersed in the precursor solution can be spontaneously assembled into PANI/CA hydrogel. While in the disperse stage, the weak interactions between PANI/CA nanosheets can be effectively broken, and consequently, CP ink is successfully fabricated (Figure 1d).

Specifically, in the former stage (assemble stage), aniline and CA were mixed as precursor solution according to a fixed molar ratio of 5:1. The other solution containing oxidative initiator ammonium persulfate (APS) was sequentially added into the precursor solution to trigger polymerization and cross-linking. With the polymerization and cross-linking progressing, aniline and CA can spontaneously assemble into PANI/CA nanosheets and consequently interconnect to form three-dimensional PANI/CA hydrogel. As shown in Figure S1 in the Supporting Information, the color of mixed solution changed from clear to dark green during the reaction procedure. It indicates the formation of polyaniline in emeraldine salt.$^{[38]}$ Besides, the mixed solution typically gelates and loses its fluidic properties in approximately 15 min, suggesting that PANI polymeric chains are efficiently cross-linked by CA molecules. The average solid content of PANI/CA hydrogel was tested by thermal drying and lyophilization to be ≈2.2% (wt/wt). Generally, the reaction system was kept at 0–4 °C for 6 h to ensure thorough polymerization and cross-linking (Movie S1, Supporting Information). In the latter stage (disperse stage), the supramolecular interactions between each nanosheet are broken through vigorous stirring or ultrasonic treatment. The PANI/CA nanosheets can thus be stably dispersed in water to form CP ink. To figure it out, we have conducted a series of experiments with different aniline verses CA molar ratios ranging from 50:1 to 1:1 with fixed aniline concentration. We found that precursor solutions with all the above-mentioned molar ratios can be effectively gelled after adding APS initiator. However, the dark green hydrogel can only be observed with the aniline:CA molar ratios of 5:1, 3:1, and 1:1, which indicates the formation of highly conductive PANI in emeraldine salt. Other hydrogels show colors of brown or light brown, which tend to be oligomers or byproducts. It thus indicates that the assemble and disperse strategy is feasible with aniline versus CA molar ratios of 5:1, 3:1, and 1:1 (Figure S2, Supporting Information).

The morphology of PANI/CA nanosheets is definitely demonstrated by several morphological characterization methods, including TEM, SEM, and AFM. As shown in Figure 2a, stacked nanosheets with crumpled structure and mean lateral size of several micrometers can be observed in the TEM image, indicating considerable flexibility of PANI/CA nanosheets. SEM image shows the dehydrated CP ink with uniform nanosheet morphology. Commonly, the secondary growth of PANI on the surface of the as-formed nanosheets makes the surface scratchy, therefore nanosheets with both smooth and scratchy surfaces appear in the SEM images (Figure S3, Supporting Information). These results explicitly demonstrate the ultrathin 2D nanosheet structure of CP ink. On one hand, this kind of 2D structure can stack in a layer by layer manner on a smooth substrate to form continuous and dense electrode film, which gives rise to efficient inter-layer mass/ion transportation and large volumetric capacitance. On the other hand, this kind of flexible 2D structure holds great promise for flexible devices because applied stress can be easily transferred and dissipated through the shrinkage and stretching process of individual nanosheet.

The gelation mechanism of PANI/CA hydrogel is explicitly depicted in Figure 2b. Through electrostatic interaction and hydrogen bonding between CA molecules and PANI macromolecular chains, effective cross-linking is achieved. Since every CA molecule possesses three functional groups, it can interact with more than one PANI polymer chain and consequently cross-link multiple PANI chains. Finally, PANI chains and CA molecules aggregated into nanosheets in a self-sorting manner. To further investigate the formation mechanism of PANI/CA nanosheets, the morphologies of products of different reaction times are characterized in Figure S5 in the Supporting Information. At the initial state, aniline and CA tend to form a
granular micelle.\(^{[39]}\) With the polymerization and cross-linking proceeding, the micelle collapse and discrete sheets come into formation. Finally, these discrete sheets aggregate spontaneously to form continuous nanosheets. To probe the chemical composition of PANI/CA nanosheets, FT-IR characterization was employed (Figure S6, Supporting Information). In the FT-IR spectrum of dehydrated PANI/CA nanosheets, the broad peak located at around 3448 cm\(^{-1}\) is attributed to the N-H vibration of PANI and O-H vibration of CA. The peaks located at 1570 cm\(^{-1}\) and 1493 cm\(^{-1}\) arise from the C=\(\equiv\)C stretching vibration of the quinoid ring and the benzenoid ring of PANI backbone. These absorption peaks indicate the existence of amine and imine nitrogen unites in PANI polymer molecular chains.\(^{[40]}\) The band at 1302 cm\(^{-1}\) is assigned to the C\(\equiv\)N stretching of the benzenoid unit while the band at 1144 cm\(^{-1}\) arise from the C = C stretching vibration of the quinoid ring and the benzenoid ring of PANI backbone. These absorption peaks indicate the existence of amine and imine nitrogen unites in PANI polymer molecular chains.\(^{[40]}\) The band at 1302 cm\(^{-1}\) is assigned to the C\(\equiv\)N stretching of the benzenoid unit while the band at 1144 cm\(^{-1}\) is ascribed to the doped quinoid unit.\(^{[43]}\) In particular, the absorption at 1041 and 509 cm\(^{-1}\) come from the -COOH group stretching are observed, indicating the as-prepared PANI was doped with CA.\(^{[42]}\)

Figure S7 in the Supporting Information presents the XRD patterns of a dehydrated hydrogel, showing two typical peaks centered at \(2\theta = 19.0^\circ\) and \(25.6^\circ\), corresponding to the inter-surface distances of 4.67 and 3.47 Å, which can be assigned to (0 2 0) and (2 0 0) reflections of PANI. This data indicates that the PANI/CA hydrogel possesses a partially ordered structure at the nanoscale. TG analysis was employed to investigate the thermal behavior of PANI/CA nanosheets with pure PANI in de-doped state appearing as a reference scan (Figure S8, Supporting Information). For both PANI/CA nanosheets and pure PANI, a mild weight loss below 100 °C related to evaporation of moisture can be clearly observed. The pure PANI shows second weight loss stage at 350–600 °C due to the degradation of polymeric backbones. However, a sharp loss in weight from 200 to 380 °C can be detected in the TG profile of PANI/CA nanosheets, which is attributed to desorption of incorporated water and decomposition of CA molecules. The third mass loss of PANI/CA nanosheets that occurred from 440 to 800 °C was attributed to the decomposition and degradation of polymeric segments. The surface chemical composition of as-prepared CP ink was determined using XPS analysis. The XPS survey scan of dehydrated CP ink shows the presence of carbon (C(1s) \(\approx\) 284 eV), nitrogen (N(1s) \(\approx\) 399 eV) as well as oxygen (O(1s) \(\approx\) 531 eV) (Figure S9, Supporting Information). The quantitative analysis C, N, and O element concentrations in this CPH, derived from the corresponding photoelectron peak area are shown in Table S1 in the Supporting Information. According to the XPS results, the ratio of total carbon to nitrogen in PANI/CA hydrogel is higher (about 9.4) than the theoretical formula \((\text{C}_6\text{H}_5\text{N})_n\) of pure PANI (typical C/N ratio is 6). Such a high C/N ratio is ascribed to the introducing of abundantly carbon-contained citric acid. Similarly, the presence of 16.8% oxygen element is originated from either introducing of citric acid or partial oxidation of the sample surface. The high-resolution nitrogen 1s XPS core level spectra are shown in Figure S10 in the Supporting Information, which can
be deconvoluted into three typical peaks: $\text{NH}^+$ at 400.8 eV, $\text{NH}^-$ at 399.3 eV, and $\text{N}=\text{N}$ at 398.2 eV. It can be calculated that the $N^+/N$ ratio of PANI/CA hydrogel is 27.7%, indicating the PANI backbone is successfully doped by $\text{COOH}$ groups arise from CA molecules, which is consistent with that of FTIR spectrum.\[43\] In the carbon 1s XPS core-level spectra of PANI/CA hydrogel (Figure S11, Supporting Information), the characteristic peaks of CA are located at 286.3 (C-O/C = O) and 288.7 eV (O-C = O), respectively. The typical peak of $\text{C}=\text{N}/\text{C}=\text{N}$ corresponding to PANI centered at about 285.0 eV. As a result, all the above-mentioned characterization results evidently confirmed the chemical composition of CP ink.

Due to the abundant surface carboxyl groups (Figure 2c), the PANI/CA nanosheets exhibit promising hydrophilicity. Figure S12 in the Supporting Information shows the water contact angle of both PANI/CA nanosheets and pure PANI. As a result, the PANI/CA nanosheets exhibit a much smaller water contact angle of 44° than pure PANI (74°), indicating greatly improved hydrophilicity. Therefore, the PANI/CA nanosheets can be stably dispersed in water to form CP ink. To investigate the particle size of as-prepared CP ink, dynamic light scattering (DLS) method is employed for the test of CP ink with a concentration of 0.05 mg mL$^{-1}$. Three peaks of scattering intensity located at 110.1, 470.5, and 5116.0 nm can be observed in the results (Figure S13, Supporting Information). The particle size distribution (PSD) of CP ink is tested to be in the range of 68–5560 nm, which is in good agreement with the TEM and SEM images of PANI/CA nanosheets. A natural sedimentation test further demonstrates the stability of this CP ink. The CP ink can keep its stability at room temperature for one week without trackable sedimentation. At the same time, for the pure PANI powders dispersion, the powders precipitated in the bottom of the
vial within just two days (Figure S14, Supporting Information). Besides, we have demonstrated the versatility of the CP ink through dispersing PANI/CA nanosheets in different organic solvents such as ethanol, acetone, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and N-Methyl-2-pyrrolidone (NMP) for the preparation of stable organic inks (Figure S15, Supporting Information). Due to the easy fabricating routine of this CP ink, it can be prepared in large quantities. Figure 2d shows the aqueous CP ink with a fixed concentration of 5 mg/mL prepared in large quantity (each reagent bottle is 250 mL), which shows promising potential for the fabrication of scalable MSCs. Air stability is a crucial property of electrode inks, which is of great significance in determining commercialized inks’ shelf-life. For comparison, we have prepared aqueous CP ink and MXene (Ti3C2T1) ink with the same concentration and kept them in air atmosphere at 30 °C for 7 days. As a result, the MXene ink is fully oxidized into TiO2 while the CP ink can remain stable (Figure S16, Supporting Information).

Rheological behavior of the PANI/CA hydrogel is exhibited in Figure S17 (Supporting Information) and Figure 2e. Generally, this hydrogel exhibits a shear-thinning (pseudoplastic) behavior, indicating a non-Newtonian fluid feature. The PANI/CA hydrogel shows an apparent viscosity of 36331 mPa s at a shear rate of 1 s⁻¹ and the viscosity decreases to 67 mPa s at a larger shear rate of 100 s⁻¹ (Figure S17, Supporting Information). The shear-thinning characteristic can on one hand enable printable ink to flow fluently and continuously.[43] On the other hand, it demonstrates that the PANI/CA hydrogel can be easily transformed into CP ink through a facile “breaking” strategy, consistent with the above-mentioned experiment. Figure 2e depicts the storage modulus (G') and loss modulus (G'') of the PANI/CA hydrogel. The storage modulus is much higher than the loss modulus when the strain is smaller than 2%, implying the PANI/CA hydrogel with the characteristic of viscoelastic solid. Increasing the strain beyond 2% leads the loss modulus to be higher than the storage modulus, indicating a transition from solid-like to liquid-like behavior.[44] To demonstrate the versatility of the CP ink, we conducted printing experiment against different substrates using as-prepared CP ink. As a visualized demo, artistic flower pattern can be easily and stably printed onto different substrates including commercialized cellulose paper (Figure 2f), silicon wafer (Figure 2g), Kapton film (Figure 2h), stainless steel plate (Figure 2i), and ITO film (Figure 2j) through a mask-assisted spray-coating method (Movie S2, Supporting Information). The scalable fabrication of CP ink and considerable adhesion against various substrates further reveal the potential of commercialization of the CP ink.

To inspect the electrochemical properties of the CP ink, comprehensive measurements combining GCD, CV, and EIS characterization in a conventional three-electrode system with 1 M H2SO4 solution serving as electrolyte are performed. As results, the CP ink derived from precursor solution with aniline versus CA molar ratio of 5:1 (denoted as CP ink-5) exhibits specific capacitance of 386.9 F g⁻¹ at a discharge current density of 0.5 A g⁻¹ (395.9 F g⁻¹ derived from CV curve with a scan rate of 20 mV s⁻¹) (Figure S18, Supporting Information), which is higher than that of inks derived from precursor solutions with aniline versus CA molar ratios of 3:1 (denoted as CP ink-3) and 1:1 (denoted as CP ink-1). This can be explained that ink-5 holds larger PANI proportion than ink-3 and ink-1, which plays a dominant role in determining specific capacitance. Therefore, we employed CP ink-5 for further study due to its outstanding electrochemical performance. In the CV curves of ink-5, characteristic redox peaks of PANI can be observed originating from the transformation among the leucoemeraldine base (LB), the emeraldine salt (ES), and the perimaraniline base (PB). GCD curves of CP ink-5 also exhibit typical profile of pseudocapacitive CPs, which demonstrates highly reversible charge-discharge behavior (Figure S19, Supporting Information). To further demonstrate the practical application of CP ink, wearable MSCs array was printed through a facile mask-assisted spray coating method, the procedure of which is explicitly described in the Experimental Section and Figure S20 (Supporting Information). PVA/H2SO4 gel electrolyte and polydimethylsiloxane (PDMS) were drop-casted onto the device in sequence serving as electrolyte and encapsulating layer. Notably, the thickness of an encapsulated wearable MSC is estimated to be approximate 350 μm by a screw micrometer (Figure S21, Supporting Information). Undoubtedly, the neglecting thickness of wearable MSC will endow it with great potential for wearable and on-chip electronics.

To point it out, a typical co-planar interdigital configuration for the fabrication of MSCs is employed here because this kind of architecture gives rise to increased ability of the electrolyte to percolate into the layers of PANI/CA nanosheets and consequently leading to full utilization of the electrochemical surface area (Figure 3a).[45,46] Electrochemical performance of MSC was tested in two electrode system. CV curves with different scan rates ranging from 5 to 100 mV s⁻¹ of individual MSC are depicted in Figure 3b, in which distinct redox peaks corresponding to pseudocapacitive PANI can be traced with various scan rates. GCD profiles (Figure 3c) show a typical charge-discharge pattern of CP ink-based supercapacitors with negligible IR drop, due to the good conductivity of CP ink and gold current collector. Specific capacitance of single device (based on the overall loading mass of electrode materials) calculated from GCD curves is depicted in Figure S22 in the Supporting Information. This device demonstrates a considerable specific capacitance of 86.2 F g⁻¹ at 0.5 A g⁻¹. Even at large current density of 10 A g⁻¹, its specific capacitance can be maintained at 571 F g⁻¹ (66.2%), evidently, indicating a good rate capability. To probe the relationship between electrode thickness and areal capacitance of wearable MSCs, we prepared MSCs with a series of electrode thicknesses ranging from 2.25 μm to 25.62 μm through varying the ink volume we used for spray-coating printing (Figure S23, Supporting Information). We found the minimum areal capacitance of 3.4 mF cm⁻² was obtained with an average electrode thickness of 2.25 μm, and the maximum areal capacitance of 96.6 mF cm⁻² was achieved with an average electrode thickness of 25.62 μm (Figure S24, Supporting Information). Additionally, this MSC also demonstrate a high volumetric capacitance of 26.0 F cm⁻³ (based on the volume of electrode). EIS test was used to explore the charge transport process of the device (Figure S25, Supporting Information). In the low-frequency region, the slope is nearly vertical, suggesting ideal capacitive behavior. While the high-frequency intercept on the real impedance axis indicates the MSC resistance, which is approximately 6.5 Ω for an individual device. Cyclic stability of MSC was tested using GCD technology at a galvanostatic current density of
10 mA cm$^{-2}$ against 10 000 charge/discharge cycles (Figure 3d). The MSC can maintain 77.1% of its initial capacitance over 10 000 charge/discharge cycles, suggesting relatively good cycling stability. Inset picture of Figure 3d shows the charge/discharge curves of initial and last cycles during the cycling procedure. Despite some capacitance degradation, the profile of charge/discharge curves remains nearly unchanged, indicating again the considerable cyclic stability of the MSC device. Ragone plots of as-prepared MSCs (Figure 3e) reveal a considerable energy density of 2.4 mWh cm$^{-3}$ at the power density of 238.3 mW cm$^{-3}$. Even with a high power density of 756.7 mW cm$^{-3}$, the energy density can still be maintained at 1.6 mWh cm$^{-3}$, indicating excellent rate performance. As a result, this work outperforms many previously reported works regarding conducting polymer-based supercapacitors in terms of both energy density and power density.[34–37] Additionally, the performance of this work is also comparable with recently reported MSCs using other inks considering areal capacitance and volumetric capacitance (Table S2, Supporting Information).[20,21,23,47–52] For practical application of MSCs, the environmental and external stress applied on device are usually complicated and unpredictable. Therefore, it is indispensable to characterize the stability of individual device against different mechanical loadings. In this regard, we have probed electrochemical performance of single device with various mechanical loadings (bending and twisting). It can be concluded that the device can maintain its electrochemical performance at different mechanical loadings because the CV curves remain nearly unchanged at bending and twisting state (Figure S26, Supporting Information). CV tests of individual MSC with different bending angles ranging from 0° to 180° suggest the MSC can maintain its electrochemical performance, irrespective of bending angles (Figure S27, Supporting Information). Moreover, the wearable MSC can undergo 2000 consecutive bending cycles without sacrificing its electrochemical performance (Figure S28, Supporting Information). Based on these results, we think the MSCs can be well applied in wearable electronics considering complicated and unpredictable deformations.

To investigate the integrability of as-prepared MSCs array, the parallel and tandem connected circuits of MSCs were examined and interpreted in detail. As shown in Figure 4a, the potential window can be remarkably enlarged to 2.4 V (with a scan rate of 20 mV s$^{-1}$) through serial connection of three devices. Thus, the energy output ($E = 1/2CV^2$) can be boosted correspondingly compared with single device (only 0.8 V potential window). Figure 4b shows CV curves of single device and three devices parallel-connected circuit (with a scan rate of 20 mV s$^{-1}$), it can be clearly observed that the output current can be greatly enhanced through parallel connection, therefore the as-delivered capacitance can be remarkably enhanced. GCD curves of tandem circuit (Figure 4c) and parallel circuit (Figure 4d) demonstrates enlarged potential window and prolonged discharge time, respectively, which is in good agreement with the behaviors of CV curves. EIS plots indicate that the equivalent series resistance can be increased proportionally in tandem circuit while parallel circuit can efficiently decrease the equivalent series resistance (Figure S29, Supporting Information). As a visualized demo, three serial connected wearable MSCs can easily power some daily electronics such as a LED bulb (Figure 4e) and a LCD timer (Figure 4f) with a working potential of 2–4 V (Movie S3, Supporting Information).

The excellent performance and considerable uniformity of MSCs attribute to the ultrathin 2D structures and promising
hydrophilicity of PANI/CA nanosheets. On one hand, the ultrathin flexible nanosheets of CP ink with a large mean lateral dimension stack together to form a dense and continuous electrode film, which gives a rise to high volumetric capacitance. Notably, the stacking behavior of PANI/CA layers is not as same as graphene restacking phenomenon based on strong π–π interaction which often leads to sacrifice of specific surface area. The surface of PANI/CA nanosheets is intrinsically scratchy and such hierarchical structure naturally construct interlayer transport channels for solvated ions. On the other hand, the PANI/CA bulk electrode featuring outstanding hydrophilicity can be easily penetrated by aqueous PVA/H2SO4 electrolyte, leading to the full utilization of electrochemical active materials and rapid charge/discharge dynamics. Meanwhile, polymeric PANI/CA electrodes could contact electrolyte at the molecular level attributed to the swollen behavior of polymeric materials with water and ions, which is favorable for building an efficient electrochemical process.

3. Conclusion

In summary, we proposed an assemble-disperse strategy for the scalable fabrication of air-stable low-cost conducting polymer ink to print wearable MSCs. The CP ink provides a high specific capacitance of 386.9 F g\(^{-1}\) (at 0.5 A g\(^{-1}\)) along with good conductivity. Derived from this CP ink, the as-printed wearable MSCs demonstrate high areal capacitance (96.6 mF cm\(^{-2}\)), large volumetric capacitance (26.0 F cm\(^{-3}\)), excellent rate capability, as well as considerable energy density of 2.4 mWh cm\(^{-3}\) at the power density of 238.3 mW cm\(^{-3}\), which surpass most state-of-the-art conducting polymer-based supercapacitors. The developed air-stable, cost-effective and environmentally friendly conductive polymer ink not only offers a promising prospect for printable electrochemical energy storage devices, but also can be extended to other printed electronics applications that underpin next-generation wearable bioelectronics.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.