Imperceptible Supercapacitors with High Area-Specific Capacitance

Jin Ge,* Minshen Zhu, Eric Eisner, Yin Yin, Haiyun Dong, Dmitriy D. Karnaushenko, Daniil Karnaushenko, Feng Zhu, Libo Ma, and Oliver G Schmidt*

Imperceptible electronics will make next-generation healthcare and biomedical systems thinner, lighter, and more flexible. While other components are thoroughly investigated, imperceptible energy storage devices lag behind because the decrease of thickness impairs the area-specific energy density. Imperceptible supercapacitors with high area-specific capacitance based on reduced graphene oxide/polyaniline (RGO/PANI) composite electrodes and polyvinyl alcohol (PVA)/H2SO4 gel electrolyte are reported. Two strategies to realize a supercapacitor with a total device thickness of 5 µm—including substrate, electrode, and electrolyte—and an area-specific capacitance of 36 mF cm−2 simultaneously are implemented. First, the void volume of the RGO/PANI electrodes through mechanical compression is reduced, which decreases the thickness by 83% while retaining 89% of the capacitance. Second, the PVA-to-H2SO4 mass ratio is decreased to 1:4.5, which improves the ion conductivity by 5000% compared to the commonly used PVA/H2SO4 gel. Both advantages enable a 2 µm-thick gel electrolyte for planar interdigital supercapacitors. The impressive electromechanical stability of the imperceptible supercapacitors by wrinkling the substrate to produce folds with radii of 6 µm or less is demonstrated. The supercapacitors will be meaningful energy storage modules for future self-powered imperceptible electronics.

1. Introduction

Imperceptible electronics with total thicknesses below 10 µm can conform to moving 3D biological surfaces with minimal influence on the local mechanical properties of the surfaces.[1–6] Such ultrathin thicknesses minimize stress on the deformed positions, therefore, resulting in electromechanical stability upon extreme shape deformation, i.e., a bending radius of less than 10 µm.[1,2,5,7–10] Kaltenbrunner et al. report imperceptible electronics that could withstand bending radii of 5 µm or less with no loss of performance.[1] Researchers have since realized many impressive imperceptible electronics, including sensors,[1,4,7,11,12] amplifiers,[6] transistors,[2,8,13] solar cells,[5,10] displays,[9] integrated system,[14] and more.

Not included in this list, however, are imperceptible energy storage devices. Unlike other recently reported imperceptible electronics[4,5,7,13] where performance is minimally affected, reducing the thickness of energy storage devices to this level limits the mass loading of electrode materials, which is a big obstacle to achieve high area-specific energy density. To our knowledge, among the thin electrodes,[15–18] less than 1 µm, the recorded area-specific energy density is only 2 mF cm−2,[18] far below the requirement of practical application. Another key component of the energy storage devices—solid or quasi-solid electrolytes—also greatly influence the area-specific energy density. They have much lower ion conductivity compared with their liquid counterparts. Equipped with such type of thin electrolyte, the devices with planar interdigital structure will confront huge internal resistance.[19] Many efforts have been put to improve their ion conductivity, e.g., by increasing their water retention ability,[20] but their stability under ambient conditions was deficient. Sandwich-structured devices could realize high energy density with

Dr. J. Ge, Dr. M. Zhu, E. Eisner, Dr. Y. Yin, Dr. H. Dong,
Dr. D. D. Karnaushenko, Dr. D. Karnaushenko, Dr. L. Ma,
Prof. O. G. Schmidt
Institute for Integrative Nanosciences
Leibniz IFW Dresden
01069 Dresden, Germany
E-mail: j.ge@ifw-dresden.de; o.schmidt@ifw-dresden.de

Dr. F. Zhu, Prof. O. G. Schmidt
Material Systems for Nanoelectronics
TU Chemnitz
09107 Chemnitz, Germany
Dr. F. Zhu, Prof. O. G. Schmidt
Center for Materials
Architectures
and Integration of Nanomembranes (MAIN)
TU Chemnitz
09126 Chemnitz, Germany
Prof. O. G. Schmidt
School of Science
TU Dresden
01062 Dresden, Germany

DOI: 10.1002/smll.202101704
a thin and low-ion-conductive electrolyte between the cathode and anode,[21] however, this type of devices cannot be integrated with other imperceptible electronics on a single thin polymeric platform as easily as planar interdigital supercapacitors.

Supercapacitors with reduced graphene oxide/polyaniline (RGO/PANI) composite electrodes are promising candidates for imperceptible energy storage devices because of their flexibility,[22,23] excellent energy density,[24,25] and high cycle stability.[26,27] However, two challenges need to be overcome. First, 3D interconnected RGO skeleton could improve the energy density of compacted RGO/PANI electrodes, however, current methods including spray coating and filtration of RGO/PANI nanosheets dispersion failed to achieve it. Electrodeposition could realize this structure and was able to pattern the RGO/PANI electrodes, but the resulting electrodes contained a large portion of void volume, which hamper the area-specific energy density.

Second, the commonly used polyvinyl alcohol (PVA)/H₂SO₄ gel electrolyte (1:1 of PVA-to-H₂SO₄ mass ratio, H₂SO₄ denotes concentrated sulfuric acid rather than pure one in this work) for RGO/PANI electrodes has a low ion conductivity under ambient condition. This property in a thin film (less than 2 µm) combined with a long ion diffusion distance as is typical with the planar interdigital structure will produce very high internal resistance.

In this work, we report planar, interdigital, imperceptible supercapacitors with high area-specific capacitance based on RGO/PANI composite electrode and PVA/H₂SO₄ gel electrolyte. We broke the trade-off between thickness and area-specific capacitance by reducing the excess void volume of the 3D interconnected RGO/PANI electrodes through mechanical compression, which does not contribute to the area-specific capacitance. This method decreases the thickness of the pristine RGO/PANI electrode by 83% while keeping 89% of the capacitance. To realize ultrathin gel electrolyte capable of providing sufficient ion diffusion efficiency, we developed an H₂SO₄-predominant gel (1:4.5 PVA/H₂SO₄) with increased ion conductivity 50 times higher compared to 1:1 PVA/H₂SO₄ gel while remaining stable under ambient condition. The compacted RGO/PANI electrodes coated with a 2 µm thick layer of H₂SO₄-predominant gel possess an area-specific capacitance that is 75% of a 100 µm-thick 1:1 PVA/H₂SO₄ gel, and 30 times higher than a 2 µm-thick 1:1 PVA/H₂SO₄ gel. The final device thickness could be reduced to 5 µm—including polymer film substrate, RGO/PANI electrodes, and gel electrolyte—and its area-specific capacitance was 36 mF cm⁻². We showcased the ultrahigh electromechanical stability of the 5 µm-thick imperceptible supercapacitors in a crumpling test which induced wrinkles with radii of 6 µm or less. We believe that our imperceptible supercapacitors, compatible with lithography-processed patterning, are promising candidates for energy storage modules in future integrated imperceptible electronics.

2. Result and Discussion

2.1. Structure and Typical Features of the Imperceptible Supercapacitor

Figure 1a illustrates the three components of our imperceptible supercapacitor: a thin parylene polymer film substrate with interdigital RGO/PANI electrodes coated in our 1:4.5 PVA/H₂SO₄ gel electrolyte. Detailed dimensions of the layout are shown in Figure S1 (Supporting Information). The 600 nm parylene substrate could withstand the stress and shape deformation during

Figure 1. Structure and typical features of the imperceptible supercapacitor. a) Schematic illustration of the composition and structure of the imperceptible supercapacitor. b) Optical image of a typical imperceptible supercapacitor. c) Scanning electron microscope (SEM) image of the cross section of the imperceptible supercapacitor. d) An imperceptible supercapacitor stuck to the surface of soap bubbles. e) An imperceptible supercapacitor mounted on a finger joint (left: bent state; right: straightened state). f) Patterned RGO/PANI electrodes on an ultrathin parylene substrate. g) SEM image of the RGO/PANI stripe indicated by the red circle in (f).
the processes of fabrication, manual handling, and wearing. Meanwhile, it isolates the corrosive PVA/H$_2$SO$_4$ gel electrolyte from the human skin. The RGO/PANI electrodes consist of a 3D RGO network as the skeleton and a thin PANI skin on its surface. The RGO/PANI networks are mechanically compacted, leaving a reduced void volume for the gel electrolyte to fill. The ultrathin H$_2$SO$_4$-predominant PVA/H$_2$SO$_4$ gel coats the RGO/PANI digits and gaps and fills the pores of the RGO/PANI networks. With a total device thickness of 5 µm (Figure 1c), the supercapacitor was both lightweight (=2 mg cm$^{-2}$) and ultraflexible. The device was straightened between the two plastic tips of a tweezer by the electrostatic force only (Figure 1b) and even conformed to the surfaces of soap bubbles (Figure 1d). The device adhered to the surface of a bent finger and deformed with the skin compliantly when the finger joint was straightened (Figure 1e). We repeated the bending-straightening behavior and did not notice the device affecting the skin: so-called imperceptible (Movie S1, Supporting Information).

The pattern of the RGO/PANI electrodes was defined by the underlying gold current collectors. Therefore, by altering the pattern of the gold layer during the lithographic processes, RGO/PANI electrode patterns could be designed (Figure 1f). The minimum resolution of the RGO/PANI electrodes could achieve 70 µm (Figure 1g) by using a gold current collector with 10 µm of width. These lithographic processes are common among imperceptible electronics and allow for the RGO/PANI electrodes to be integrated parallel to other components while maintaining a single continuous thin-film device with high electromechanical stability.

2.2. Fabrication of the Imperceptible Supercapacitor

Figure 2a illustrates the fabrication processes for the imperceptible supercapacitor. The polydimethylphenylsilsloxane (PDMDPS) acted as the releasing layer. It bound the parylene film to the glass substrate during the lithographic patterning of the interdigital gold current collectors and the electrodeposition of the 3D RGO/PANI electrodes. Afterward, the final device, even with a 600 nm parylene film as the substrate,
could be easily peeled off from the carrier without damaging the device.

The 3D RGO electrode, obtained through a facile electrodeposition method,[39] consisted of interconnected wrinkled RGO nanosheets (Figure 2b,c). Its porosity and high conductivity allowed the uniform electrodeposition of PANI on its surfaces (Figure 2d,e). The 3D RGO/PANI electrodes could yield high area-specific capacitance, however, the thickness was ≈24 μm (Figure 2f) which is too high for imperceptible electronics. The micrometer-scale pores, which account for the major volume of the electrode, were much larger than the dimension of the minimum ion diffusion channels (nanometer scale).[29–31] Therefore, we decreased the thickness by removing the unnecessary void volume of the pristine 3D RGO/PANI electrodes. To achieve this, we put a fluoroalkylsilane-modified glass plate on the top and compressed the electrodes mechanically (Figure S2, Supporting Information). The porous electrodes collapsed into compact ones with a smooth surface (Figure S3, Supporting Information) and the thickness decreased to 4 μm (Figure 2g); six times less than the pristine thickness (Figure 2f). Meanwhile, the frame of the compact 3D RGO/PANI electrode was still accessible to the electrolyte via nanoporous ion-diffusion channels (Figure S4, Supporting Information). For the remainder of this paper, all the compressed RGO/PANI electrodes had a thickness of ≈4 μm. After the compressing treatment, the lateral electric conductivity of the RGO/PANI electrodes increased from 0.9 to 93.3 S m−1 (Figure S5, Supporting Information). Through a one-after-one deposition strategy (Figure S6, Supporting Information), able to avoid the interruption between adjacent electrodes, the above fabrication method can be easily extended to complicated RGO/PANI patterns.

The 1:4.5 PVA/H2SO4 gel electrolyte was applied to the whole interdigital area, followed by a vacuum process to fill the gel into the small gaps between the RGO/PANI walls. Then gel electrolyte was leveled by spinning. The thickness of the gel could be controlled by the spinning rate and the concentration of the PVA/H2SO4 solution. With only ≈2 μm of 1:4.5 PVA/H2SO4 gel (gel thickness in the finger gap area) applied on the interdigital compressed RGO/PANI electrodes area (Figure 2h and Figure S7, Supporting Information), the total device with ≈5 μm thickness achieved the high area-specific capacitance of 31.6 mF cm−2 at a scan rate of 5 mV s−1 (Figure 2i). For a normal device to realize a similar value (i.e., 34.0 mF cm−2), the total device thickness needed to increase to ≈120 μm, including ≈20 μm of the pristine 3D RGO/PANI electrode and ≈100 μm of 1:1 PVA/H2SO4 gel electrolyte. The advantage of our thin device could be further highlighted by comparing it with the state-of-the-art ultrathin supercapacitor which had 2 mF cm−2 at a scan rate of 5 mV s−1 and 3.5 μm of thickness including the substrate and electrolyte (the thickness of electrolyte was not mentioned by the authors).[38]

2.3. Impacts of the Compressing Treatment and H2SO4 Content of PVA/H2SO4 Gel on the Performance of the RGO/PANI Electrodes

To study the influence of compression on the active surfaces, we evaluated the capacitances of the pristine and compressed RGO/PANI electrodes using the same electrolyte given that the capacitance is proportional to the area of active surfaces. First, we tested both devices in 1 mol L−1 (1 M) H2SO4 solution. The CV curves indicated a reduction of area-specific capacitance by only 11% after the compressing treatment (Figure 3a), much smaller compared with the decrease of the thickness by 83% (Figure 2f,g). Thus, the compression treatment was able to greatly decrease the thickness of the electrode without completely sacrificing the area-specific capacitance. However, when using a 1:1 PVA/H2SO4 gel electrolyte with a sufficient thickness (100 μm), the area-specific capacitance reduced by 27% (Figure 2b), twice as much loss compared to using 1 M H2SO4 solution. The reason is that the PVA/H2SO4 gel (1:1) electrolyte has much lower ion conductivity compared with the 1 M H2SO4 solution. Under the high scan rate of 50 mV s−1, the small ion diffusion channels could not allow sufficient ion diffusion to the active surfaces of RGO/PANI network quick enough. The greater reduction of area-specific capacitance also indicated that the utilization of the active surfaces could be improved by raising the ion conductivity of the gel electrolyte.

Using a thin 1:1 PVA/H2SO4 gel electrolyte could also result in extremely high charge transfer resistance for planar interdigital supercapacitors and therefore underutilize the active surfaces. Coated with ≈2 μm of 1:1 PVA/H2SO4 gel, the compressed RGO/PANI electrodes yielded low capacitance (0.4 mF cm−2); only 2.5% of that using ≈100 μm of 1:1 PVA/H2SO4 gel (Figure 3c and Figure S8, Supporting Information). Even with a thickness to ≈14 μm, the capacitance (3.8 mF cm−2) was still four times lower compared to the same ≈100 μm thick gel. Therefore, it is impossible to realize imperceptible planar interdigital supercapacitors with high area-specific capacitance using this gel electrolyte.

Previous studies found that improving the water content of the gel electrolyte could boost the ion conductivity.[20,32] However, most of the hydrogels, including the 1:1 PVA/H2SO4 gel, lose water gradually and finally possess low ion conductivity under ambient condition. The water retention of PVA/H2SO4 gel could be potentially improved by increasing the concentration of H2SO4. Because the partial pressure of atmospheric water vapor above an H2SO4 solution decrease dramatically as the H2SO4 concentration increases, for example, from ≈1200 Pa for 50 wt% H2SO4 solution to 17 Pa for 80 wt% H2SO4 solution at 25 °C.[33] In other word, high H2SO4 content leads to strong absorption of water from the ambient air. Therefore, we hypothesized that increasing the H2SO4 content of PVA/H2SO4 gel would improve its water content under ambient condition and consequently improve its ionic conductivity.

To verify our hypothesis, we prepared PVA/H2SO4 gels with different H2SO4 concentrations and measured the resistance of the gels via electrochemical impedance spectroscopy using our planar two-electrode layout (Figure 3d).[14,15] The diameters of the semicircles in each curve indicate the resistance for that specific gel (Figure 3e) which decreases significantly when H2SO4 concentration increase (Figure 3f). From 1:1 to 1:4.5, the resistance of the various PVA/H2SO4 gels decreased by 99.5% (corresponding ion conductivity increased from ≈1 to ≈50 S m−1). But the further increase to 1:5 led to a negligible decrease of resistance. The resistance of 1:4.5 and 1:5 PVA/H2SO4 gel changed minimally after staying under the ambient condition for 31 d while the resistance of PVA/H2SO4
Figure 3. Influence of the properties of electrode and electrolyte on the performance. CV curves of a) pristine and compressed 3D RGO/PANI electrodes tested in 1 M H₂SO₄ solution, and b) pristine and compressed 3D RGO/PANI electrodes tested with 100 µm-thick 1:1 PVA/H₂SO₄ gel electrolyte. c) The capacitances of the compressed 3D RGO/PANI electrodes versus the thicknesses of 1:1 PVA/H₂SO₄ gel electrolyte. t denotes the thickness of the gel electrolyte in the gap between the interdigital RGO/PANI electrodes. The capacitances were derived from the CV curves (50 mV s⁻¹ of scan rate, Figure S8, Supporting Information). d) Schematic of the planar two-electrode measurement of the ion conductivity. w = 6 mm, l = 5 mm, t = 2 µm. e) Nyquist plots of the PVA/H₂SO₄ gels. Frequency ranged from 0.1 to 100 kHz. f) The resistance of the PVA/H₂SO₄ gels obtained from the Nyquist plots. g) Raman spectra of 1:1 and 1:4.5 PVA/H₂SO₄ gels. h) CV curves of the compressed 3D RGO/PANI electrodes applied with 1:1 and 1:4.5 PVA/H₂SO₄ gels, respectively. i) Corresponding Nyquist plots of the devices in (h). j) Scan-rate-dependent capacitance of the compressed 3D RGO/PANI electrodes applied with 1:4.5 PVA/H₂SO₄ gel electrolyte. The capacitances were derived from the CV curves (Figure S9, Supporting Information). k) Charge–discharge cycle test of the compressed RGO/PANI electrodes applied with 100 µm-thick 1:1 PVA/H₂SO₄ gel and 2 µm-thick 1:4.5 PVA/H₂SO₄ gel, respectively. Current density: 0.5 mA cm⁻². l) Time evolution of the open-circuit voltage of our imperceptible supercapacitor.
gels with ratios from 1:1 to 1:4 increased. Particularly, the commonly used 1:1 PVA/H$_2$SO$_4$ experienced three times increase of resistance. With the pursuit for lower resistance, higher stability, and lower content of H$_2$SO$_4$, we selected 1:4.5 PVA/H$_2$SO$_4$ gel for our device. The Raman spectra of 1:1 and 1:4.5 PVA/H$_2$SO$_4$ gels confirmed that 1: 4.5 PVA/H$_2$SO$_4$ gel had much higher water content (Figure 3g). The peak in the frequency region from 2800 to 3000 cm$^{-1}$ is assigned to the C-H asymmetric stretching modes of CH$_3$ from the PVA. And the peak in 3100 to 3700 cm$^{-1}$ arises from O-H stretching vibration of water molecules.[38] These findings demonstrate that higher H$_2$SO$_4$ concentration in PVA/H$_2$SO$_4$ gels improves both the conductivity of the gel and its water retention ability.

Coated with ≈2 μm of the 1:4.5 PVA/H$_2$SO$_4$ gel electrolyte, the compressed RGO/PANI electrodes yielded 12 mF cm$^{-2}$ at the scan rate of 50 mV s$^{-1}$, which is 30 times higher than using 1:1 PVA/H$_2$SO$_4$ gel electrolyte (Figure 3h). The charge transfer resistance decreased by three orders of magnitude from 130 kΩ to 70 Ω (Figure 3i). At a low scan rate of 1 mV s$^{-1}$, the capacitance was measured to be 36 mF cm$^{-2}$ (Figure 3j and Figure S9, Supporting Information). The compressing treatment also reduced the amount of gel electrolyte (Figure S10, Supporting Information). The compressed RGO/PANI electrodes absorbed less gel electrolyte and left more amount of gel electrolyte in the gap area, which results in a lower internal resistance compared with the pristine RGO/PANI electrodes.

The charge–discharge cycle tests show that the compressed RGO/PANI electrodes with 1:4.5 PVA/H$_2$SO$_4$ gel exhibited similar degradation of the capacitance compared to that using 1:1 PVA/H$_2$SO$_4$ gel (Figure 3k). Therefore, improving the content of H$_2$SO$_4$ of the gel electrolyte brought no negative effect to the stability of the RGO/PANI electrodes.

Self-discharging is a well-known problem for supercapacitors. To serve as the power supply module of imperceptible electronics, the imperceptible supercapacitor should retain the electrochemical energy for a long time. Given that the time evolution of the open-circuit voltage (OCV) of a fully charged device can reveal the self-discharge rate, we charged our thin device with a current of 0.1 mA cm$^{-2}$ until reaching 0.8 V, then recorded the OCV for more than 10 h. Figure 3l shows that the OCV of our thin device dropped to 0.4 V in 45 min, then decreased very slowly to 0.23 V in 10 h. Such self-discharging rate is lower than PANI-based supercapacitors reported previously.[37]

It should be noted that the humidity had a great influence on the performance of the devices. Gel electrolyte absorbed/desorbed water from the air with high/low humidity, which increased/decreased the capacitance of the device. The capacitance of our supercapacitor device decreased by more than four times when the humidity decreased from 86% to 13% (Figure S11, Supporting Information). Our experiments were performed under ambient conditions, the humidity was around 35% which was close to the real application scenario.

2.4. Electromechanical Stability of the Imperceptible Supercapacitor

A crumpling test is a touchstone to demonstrate the electromechanical stability of imperceptible electronics. We crumpled our imperceptible supercapacitors by first laminating the device on pre-stretched commercial VHB tape and then releasing the strain (Figure 4a). The relaxation of the tape induced extreme shape deformation on the device (Figure 4b,c). We observed many wrinkles on the surface of the imperceptible supercapacitor under 100% compression (Figure 4d). The bending radii of the wrinkles reached 6 μm or less. To our knowledge, this value is 83 times lower than the state-of-the-art flexible supercapacitor (down to 1 mm).[38–41] and illustrates the flexibility of our device which allows our device to conform with moving skin while remaining unnoticed by the user (Figure 1e). Moreover, we found no cracks at the peak of the wrinkled position (Figure 4f), reflecting the high compliance of the RGO/PANI-PVA/H$_2$SO$_4$ composite coating upon extreme shape deformation.

To evaluate the influence of shape deformation on the capacitance of the imperceptible supercapacitor in the crumpling test, we laminated a 500 nm polyethylene naphthalate (PEN) film onto the surface of the device to avoid shorts between adjacent RGO/PANI fingers after being compressed. Figure 4g shows that although the device experienced a decrease in capacitance by 22% when compressed, the capacitance completely recovered once the strain was removed. We repeated this experiment hundreds of times on the same device and found that the capacitance of our imperceptible supercapacitor decreased by 30% after 100 cycles, and then remained stable for the next 400 cycles (Figure 4h,i). The fast decrease of capacitance after the first 100 cycles may be caused by delamination between the gold current collector and the RGO/PANI electrodes (Figures S12 and S13, Supporting Information). Because the interaction force between the RGO/PANI layer and the gold surface was weak. Their interface was very susceptible to mechanical stress. After releasing the bending with ultrasmall radii, the size mismatch between the inelastically stretched RGO/PANI layer and the local parylene substrate would cause large stress, resulting in the separation of the interface and the formation RGO/PANI wrinkles. These wrinkles could reduce the stress caused by the following compression and would become more and more stable with the increase of cycle times. The compression test demonstrated the durability of our imperceptible supercapacitor, for which we have found no significant comparison among other recently developed flexible supercapacitors. Mounted on the moving human skin by hand cream, the supercapacitor could comply with the movement and retain the capacitance (Figure S14, Supporting Information). The parylene foil substrate could protect the skin from the harmful gel electrolyte for, at least, 2 h. But the H$^+$ will eventually diffuse through the parylene foil and harm the skin. Further works are still required to solve this problem.

To further demonstrate the high electromechanical performance of our imperceptible supercapacitor, we fabricated a device with four imperceptible supercapacitors connected in series (detailed parameters and CV curves shown in Figures S15 and S16, Supporting Information) that outputted a high enough voltage to power either a light-emitting diode (LED) or a digital watch. Our device when fully charged could lit up a commercial LED for more than 2 min (Figure 4j and Movie S2, Supporting Information) and continue to operate after being crumpled manually (Figure 4k). The supercapacitor has potential applications in stretchable electronics when being laminated on
a prestretched elastomer. By connecting its cathode and anode with shape-compliant eutectic gallium-indium liquid metal, the device powered a digital watch both while compressed and relaxed (Figure 4l,m and Movie S3, Supporting Information).

3. Conclusion

We demonstrated imperceptible planar interdigital supercapacitors with high area-specific capacitance and unprecedented electromechanical stability, enabled by thin substrate, compacted 3D RGO/PANI composite electrodes, and thin 1:4.5 PVA/H$_2$SO$_4$ gel electrolyte. The mechanical compression treatment of the 3D RGO/PANI electrodes dramatically reduced the thickness of the electrodes with a little cost on the active surfaces and may be applicable to other 3D electrodes. The 1:4.5 PVA/H$_2$SO$_4$ gel had 50 times higher ion conductivity than the commonly used 1:1 PVA/H$_2$SO$_4$ gel and was quite stable under ambient condition. Coated with only 2 $\mu$m of our modified electrolyte, the compacted 3D RGO/PANI electrodes possessed a high area-specific capacitance. For future designs of imperceptible energy storage devices, our efforts in this work indicate that attention should be paid to the thickness of the total device, including substrate, electrode, and electrolyte, rather than electrode only, and to the area-specific energy density rather than volume-specific or mass-specific energy density. Crumpling test...
is also recommended to evaluate the electromechanical stability upon extreme shape deformation. Our imperceptible supercapacitors may enrich the family of imperceptible electronics with imperceptible energy storage devices and ultimately promote the development of self-powered integrated imperceptible electronics for healthcare, biomedical applications, and other fields.

Human Ethics Approval Declaration

For the experiment shown in Figure 1e and Figure S14 (Supporting Information), the supercapacitor mounted on the skin did not interact with any skin tissue. The volunteer in this demonstration is the first author of this paper. No ethical approval is required in this case.

Supporting Information

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

Acknowledgements

The authors thank Ronny Engelhard, Stefan Baunack, Carol Schmidt, Sandra Nestler, Cornelia Krien, and Franziska Hebenstreit for technical support. This work was supported by the Leibniz Program of the German Research Foundation (SCHM 1298/26-1). Leibniz-Junior Research Group (J21/2017), and the German Research Foundation (KA5051/1-1).

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

graphene, imperceptible electronics, polyaniline, ultraflexible supercapacitors, ultrathin gel electrolytes

Received: April 7, 2021
Published online: May 12, 2021
[32] Z. Song, J. Ding, B. Liu, X. Liu, X. Han, Y. Deng, W. Hu, C. Zhong, Adv. Mater. 2020, 32, 1908127.
[33] J. I. Gmitro, T. Vermeulen, AIChE J. 1964, 10, 740.
[34] T. Soboleva, Z. Xie, Z. Shi, E. Tsang, T. Navessin, S. Holdcroft, J. Electroanal. Chem. 2008, 622, 145.
[35] X. Qian, N. Gu, Z. Cheng, X. Yang, E. Wang, S. Dong, J. Solid State Electrochem. 2001, 6, 8.
[36] K. Kudo, J. Ishida, G. Syuu, Y. Sekine, T. Ikeda-Fukazawa, J. Chem. Phys. 2014, 140, 044909.
[37] M. M. Pérez-Madrigal, F. Estrany, E. Armelin, D. D. Díaz, C. Alemán, J. Mater. Chem. A 2016, 4, 1792.
[38] L. Liu, Y. Yu, C. Yan, K. Li, Z. Zheng, Nat. Commun. 2015, 6, 7260.
[39] Y. Yun, K. R. Nandnapalli, J.-H. Choi, W. Son, C. Choi, S. Lee, Nano Energy 2020, 78, 105356.
[40] C.-S. Kwak, T. H. Ko, J. H. Lee, H.-Y. Kim, B.-S. Kim, ACS Appl. Energy Mater. 2020, 3, 2394.
[41] R. T. Ginting, M. M. Ovhal, J.-W. Kang, Nano Energy 2018, 53, 650.