Integration of ultrathin graphene/polyaniline composite nanosheets with a robust 3D graphene framework for highly flexible all-solid-state supercapacitors with superior energy density and exceptional cycling stability†

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Here we report a unique hierarchical free-standing graphene/polyaniline (G/PANI) composite electrode with ultrathin G/PANI composite nanosheets embedded in the skeleton of a three-dimensional (3D) graphene framework. Due to the intrinsic structural advantage of ultrathin G/PANI composite nanosheets and their synergetic interaction with the 3D graphene network, the 3D-G/PANI composite electrode can deliver a high specific capacitance of 777 F g\(^{-1}\) and 990 F cm\(^{-3}\) at 1 A g\(^{-1}\) and an exceptional cycling stability with 85% capacitance retention after 60 000 deep cycles in a three-electrode cell configuration. The further assembled all-solid-state supercapacitor based on the 3D-G/PANI composite electrode can not only show extraordinary mechanical flexibility allowing bending, twisting and folding, but also demonstrate remarkable electrochemical performance under its folded state, including an ultrahigh specific capacitance of 665 F g\(^{-1}\) and 847 F cm\(^{-3}\) for the 3D-G/PANI composite electrode, excellent rate capability with a capacitance retention of 86% at 20 A g\(^{-1}\) and superior cycling stability with no capacitance decay after 10 000 cycles, as well as ultralow self-discharge characteristics. Furthermore, the entire ultrathin device (\(\sim\)45 \(\mu\)m, much thinner than a commercial standard A4 paper) can deliver volumetric, gravimetric and areal energy densities up to 14.2 mW h cm\(^{-2}\), 10.9 W h kg\(^{-1}\) and 64 \(\mu\)W h cm\(^{-2}\), respectively, which are much higher than those of current high-level commercial supercapacitors (\(\sim\)5 W h kg\(^{-1}\)) and even lithium thin-film batteries (\(\sim\)8 mW h cm\(^{-2}\), 4 V/500 \(\mu\)A h).

Introduction

Nowadays, a rapid development has been achieved in portable and wearable electronics because of their extraordinary application potential in smart devices, micro-robotics, electronic skin, sensor networks, and epidermal and implantable medical devices.\(^1\)-\(^4\) Therefore, there is a huge demand to design and fabricate compatible energy storage devices that are ultrathin, lightweight, flexible and wearable, as well as exhibiting high electrochemical performance. Among various power sources, flexible all-solid-state supercapacitors (ASSs) are promising candidates because of their high power density, fast charge/discharge capacity, broad working temperature and preferable safety as against batteries.\(^5\)-\(^7\) As the central component of ASSs, the electrode material must possess high capacitance, superior electrical and mechanical properties, excellent cycling stability, and the capacity to accommodate large levels of strain without sacrificing performance.\(^8\)-\(^12\)

Due to the fast and reversible redox reactions as well as desirable electrochemical performance, pseudocapacitive materials, including transition metal oxides and conducting polymers, have shown great promise in ASS electrodes. Particularly, conducting polymers, such as polyaniline (PANI), have received intense interest because of their ultrahigh theoretical capacitance, low cost, low environmental impact, and adjustable structure and morphology. However, the relatively low experimental capacitance and poor cycling stability of conducting polymers derived from the volumetric changes and mechanical degradation during the charging/discharging process greatly compromise their potential and severely impede their practical application.\(^13\)-\(^16\) Introducing carbon nanomaterials into conducting polymers has demonstrated great potential to address these problems since lightweight and highly conductive carbon nanomaterials also feature superior mechanical strength and flexibility. The integration can mitigate the mechanical stress originating from conducting...
polymers and improve the mechanical stability of the composite. Besides, the synergistic effect between carbon nanomaterials and conducting polymers can contribute to better electrochemical properties of the hybrid material.\textsuperscript{13,17-19} Despite considerable interest and progress to date, it remains a considerable challenge to create a novel high-performance carbon/conducting polymer composite electrode to achieve simultaneously superior mechanical flexibility, high rate capability, and most importantly high energy density and long cycle life for the ultimate entire ASS to promote its application in wearable and flexible electronics. This challenge could be mainly ascribed to the fact that the carbon/conducting polymer composite electrodes reported in most previous work show a common structural feature in which conducting polymers usually reside on the outer surface of the carbon substrate without further protection and an ultrathin conducting polymer layer has not been integrated efficiently.

Herein, we report a unique hierarchical three-dimensional (3D) graphene/PANI (3D-G/PANI) composite with ultrathin G/PANI composite nanosheets embedded in the skeleton of a robust 3D graphene framework, which can be mechanically pressed into a highly conductive and flexible film and used directly as a free-standing electrode. Due to the intrinsic structural advantage of ultrathin G/PANI composite nanosheets and their synergetic interaction with the 3D graphene framework, the 3D-G/PANI composite electrode can deliver a high specific capacitance of 777 F g\textsuperscript{-1} and 990 F cm\textsuperscript{-3} at 1 A g\textsuperscript{-1} and an exceptional cycling stability with 85% capacitance retention after 60 000 deep cycles in a three-electrode cell configuration. The further assembled ASS based on the 3D-G/PANI composite electrode can not only show extraordinary mechanical flexibility allowing bending, twisting and folding, but also demonstrate remarkable electrochemical performance under its folded state, including an ultrahigh specific capacitance of 665 F g\textsuperscript{-1} and 847 F cm\textsuperscript{-3} for the 3D-G/PANI composite electrode, excellent rate capability with a capacitance retention of 86% at 20 A g\textsuperscript{-1} and superior cycling stability with no capacitance decay after 10 000 cycles, as well as ultralow self-discharge characteristics. Furthermore, due to the current collector-free feature, the entire ultrathin device (\textsim\textasciitilde 45 \textmu m, much thinner than a commercial standard A4 paper) can deliver volumetric, gravimetric and areal energy densities up to 14.2 mWh cm\textsuperscript{-3}, 10.9 W h kg\textsuperscript{-1} and 64 \textmu W h cm\textsuperscript{-2}, respectively, which have exceeded that of commercial lithium thin-film batteries (\textsim 8 mWh cm\textsuperscript{-3}, 4 V/500 \textmu A h) or supercapacitors (\textsim 5 W h kg\textsuperscript{-1}) and represent the best comprehensive performance among all carbon/conducting polymer-based ASSs reported thus far.

**Experimental**

**Graphene oxide (GO) synthesis and purification**

GO was prepared by oxidation of natural graphite powder according to the modified Hummers’ method.\textsuperscript{20} Briefly, graphite (3.0 g) was added to concentrated sulfuric acid (70 mL) under stirring at room temperature, then sodium nitrate (1.5 g) was added, and the mixture was cooled to 0 \textdegree C. Under vigorous agitation, potassium permanganate (9.0 g) was added slowly to keep the temperature of the suspension lower than 20 \textdegree C. Successively, the reaction system was transferred to a 35–40 \textdegree C water bath for about 0.5 h, forming a thick paste. Then, 140 mL of water was added, and the solution was stirred for another 15 min. An additional 500 mL of water was added followed by a slow addition of 20 mL of H\textsubscript{2}O\textsubscript{2} (30%), turning the color of the solution from brown to yellow. The mixture was filtered and washed with 1 : 10 hydrochloric acid aqueous solution (250 mL) to remove metal ions followed by repeated washing with water and centrifugation to remove the acid. The resulting solid was dispersed in water by ultrasonication for 1 h to make a GO aqueous dispersion (0.5 wt%). The obtained brown dispersion was then subjected to 30 min of centrifugation at 4000 rpm to remove any aggregates. Finally, it was purified by dialysis for one week to remove the remaining salt impurities for the following experiments.

**Fabrication of GO/PANI composite nanosheets and PANI nanofibers (PNFs)**

The GO/PANI composite nanosheets were synthesized by in situ polymerization. In a typical procedure, 1.1 mL aniline monomer was added into the methylbenzene solution (20 mL) and stirred for 30 min to form a uniform mixture solution, named solution A. Ammonium persulphate ([NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (APS)], concentrated hydrochloric acid (6 mL) and aqueous GO solution (containing 110 mg of GO) were dissolved and uniformly dispersed in 40 mL of deionized water (the molar ratio of aniline monomer/APS was 4 : 1), named solution B. The polymerization was performed by the addition of solution A to B, and the mixture was stirred for 12 h at room temperature. Finally, a uniformly dispersed solution with emerald color was obtained, which was then filtered and washed with methanol and 1 M hydrochloric acid aqueous dispersion. PNFs were prepared by the same method as GO/PANI composite nanosheets but without adding GO. The GO/PANI aqueous dispersion (4 mg mL\textsuperscript{-1}) and the PNF aqueous dispersion (2.15 mg mL\textsuperscript{-1}) were both prepared by ultrasonic dispersion of filtered products in deionized water. The weight percent of PANI in GO/PANI composite nanosheets is \textsim 70 wt%.

**Fabrication of 3D-G/PANI, 3D-G/PNF, 3D-G and carbon black/ PANI (CB/PANI) composite films**

The 3D-G/PANI and 3D-G/PNF were prepared according to the following procedure: 15 mL of GO/PANI or PNF aqueous dispersion was taken and mixed with 15 mL of GO aqueous solution (4 mg mL\textsuperscript{-1}), then some sodium ascorbate aqueous solution was added into the above aqueous dispersion, and the homogeneous mixture was heated at 95 \textdegree C for 1.5 h without stirring. The as-prepared 3D-G/PANI and 3D-G/PNF hydrogels were taken out of the vial and immersed in pure water to remove any impurities for the following experiments. By varying the amount of GO in the above reduction reaction, the percent of PANI in 3D-G/PANI can be facilely adjusted. The size and shape of 3D-G/PANI and 3D-G/PNF hydrogels can also be easily controlled by changing the type of reactor. 3D-G hydrogels were prepared under the same conditions with GO as the starting material for comparison as well. Finally, these hydrogels were freeze-dried into aerogels and compressed under \textsim 10 MPa pressure for 10 min to form free-standing films. Before preparing the...
CB/PANI film, GO/PANI composite nanosheets were firstly reduced in sodium ascorbate aqueous solution at 95 °C for 1.5 h. Then the reduced GO/PANI composite nanosheets, CB, poly(vinylidene fluoride) (PVDF) and N-methyl-2-pyrrolidone (NMP) (the weight ratio of reduced GO/PANI : CB : PVDF was 5.5 : 3.5 : 1) were mixed and coated on Ti foil. After drying, the free-standing CB/PANI composite film was taken off.

**Fabrication of 3D-G/PANI-based ASSs**

First, the PVA-H2SO4 gel electrolyte was prepared as follows: 1 g H2SO4 was added into 10 mL de-ionized water, and then 1 g PVA powder was added. The whole mixture was heated to 85 °C under stirring until the solution became clear. Second, two 3D-G/PANI electrode strips with a size of about 0.8 cm x 4 cm were immersed in the hot solution for 15 min with a small part kept out for electrical connection and picked out for air-drying in a fume hood at room temperature for several hours to evaporate excess water. Then the two electrodes were pressed together under a pressure of ~1 MPa for 10 min, which allowed the polymer gel electrolyte on each electrode to combine into one thin separating layer to form an integrated device. The typical average thickness of the whole device based on 3D-G/PANI was around 45 μm determined by SEM.

**Results and discussion**

The 3D-G/PANI composite can be prepared by controlled in situ polymerization of the PANI nanolayer on the GO surface to form a layered structure and sandwiched between two PTFE sheets.

**Material characterization**

SEM measurements were performed on a Zeiss Ultra 55 field emission scanning electron microscope. TEM studies were conducted on a FEI Tecnai G2 20TWIN electron microscope at an operating voltage of 200 kV. XRD analysis was performed on a Rigaku D/Max 2500 X-ray diffractometer with CuKα radiation (λ = 1.54 Å) at a generator voltage of 40 kV and a generator current of 20 mA with a scanning speed of 5° min⁻¹ from 5 to 50°. FT-IR spectral measurements were performed using a Nicolet 6700 instrument. Raman spectra were recorded with an XploRA Laser Raman spectrometer at 532 nm. XPS data were obtained by using a Perkin-Elmer PHI 5300 using the Mg K\text{α} source (1253.6 eV).

Electrochemical measurements

All the electrochemical experiments were carried out by using an electrochemical workstation (CHI 660E, CH Instruments Inc.). The three-electrode measurements were performed at room temperature in 1 M H2SO4 aqueous electrolyte with Pt sheets as the counter electrode and Ag/AgCl as the reference electrode. The symmetrical supercapacitor devices were measured in a two-electrode cell configuration with PVA-H2SO4 or 1 M H2SO4 as the electrolyte.

**Fig. 1** Schematic illustration of preparation of the 3D-G/PANI composite. (a) Aniline monomer dissolved in toluene and GO uniformly dispersed in a mixed aqueous solution of ammonium persulfate and hydrochloric acid. (b and c) Formation of a microemulsion with GO located at the interface. (d) Nucleation and growth of PANI. (e–g) Wrapping and embedding of G/PANI composite nanosheets in the 3D porous graphene framework. (h) Porous 3D-G/PANI film.
GO/PANI composite nanosheets followed by a self-assembly process with GO under reduction conditions as illustrated in Fig. 1. The solution processable GO/PANI composite nanosheets (Fig. 2a inset) were firstly prepared by microemulsion in situ polymerization of the aniline monomer on the surface of GO (Fig. 1a–d). Scanning electron microscopy (SEM) and atomic force microscopy images (Fig. 2a, b and S1†) revealed that an ultrathin layer of ordered PANI nanothorn arrays with a thickness of ~20 nm was uniformly grown on both sides of GO with no free PANI observed, indicating that the nucleation and growth of PANI only occurred on the surface of GO. Due to coexistence of hydrophilic oxygen-containing functional groups and hydrophobic conjugated domains within the basal plane, the amphiphilic GO sheets tended to disperse at the interface of toluene and water.21 Under stirring, GO sheets were continually moved from one position to another, while the aniline monomer and ammonium persulfate were strictly restricted in their own solution phase. As a result, the further growth of PANI on GO was frequently interrupted, which effectively avoided the excessive growth of PANI and successfully resulted in an ultrathin PANI nanolayer and ultrasmall PANI nanothorns. In contrast, in the control experiment without adding GO sheets, only PANI nanofibers (PNFs) with a mean diameter of ~50 nm and a length of more than hundreds of nanometers were produced (Fig. S2†). The interaction between GO and in situ grown PANI was studied by UV-vis absorption spectra (Fig. 2c). GO featured a maximum absorption peak at 231 nm (π-π* transition of the benzenoid ring at 342 nm). Distinctly, the band of PANI at 780 nm bathochromically shifted to 837 nm upon the formation of GO/PANI composite nanosheets, which was attributed to the increase of the π conjugation of PANI due to the strong π–π interaction between PANI and GO sheets.24,25 Transmission electron microscopy (TEM) images also revealed that the whole surface of GO was uniformly coated by a thin layer of PANI nanothorns (Fig. 2d and e) compared to the pure GO (Fig. 2f), in agreement with the results of SEM. The elemental mapping (Fig. 2g–j) further demonstrated the uniform distribution of carbon, oxygen and nitrogen throughout the entire GO/PANI composite nanosheet.

The monolithic 3D-G/PANI composites were then prepared by heating a homogeneous aqueous mixture of GO and GO/PANI composite nanosheets with sodium ascorbate as the reducing agent followed by freeze-drying. Due to the flexible processability of the aqueous mixture, the sizes and shapes of 3D-G/PANI composites can be easily tailored by changing the type of reactor (Fig. 3a). SEM images revealed that the 3D-G/PANI composite had an interconnected 3D macro-porous network with pore sizes ranging from submicrometers to several micrometers (Fig. 3b). Meanwhile, G/PANI composite nanosheets were embedded in the skeleton of the 3D graphene framework and wrapped by graphene sheets (Fig. 3c), which is a multifunctional structure since it not only reduced the re-

Fig. 2 (a) Low- and (b) high-magnification SEM images of GO/PANI composite nanosheets. (c) UV-vis absorption spectra of GO, PANI and GO/PANI. (d) Low- and (e) high-magnification TEM images of GO/PANI composite nanosheets. (f) High-magnification TEM image of GO sheets. Corresponding elemental mapping images of GO/PANI (g) for C (h), O (i), and N (j).

Fig. 3 (a) Digital photographs of the monolithic 3D-G/PANI composite. (b) Low- and (c) high-magnification SEM images of the 3D-G/PANI composite. (d) Digital photograph of the flexible 3D-G/PANI composite film prepared by mechanical pressing of the 3D-G/PANI composite. (e) Low- and (f) high-magnification SEM side view of the flexible 3D-G/PANI composite film. (g) Digital photographs of the flexible 3D-G/PANI composite film at its initial, folded and recovered states. (h) I–V curves of the 3D-G/PANI composite film at its initial, folded and recovered states.
Fig. 4 (a) CV curves of 3D-G/PANI, 3D-G/PNF, CB/PANI and 3D-G in a three-electrode system at a scan rate of 10 mV s\(^{-1}\). (b) Galvanostatic charge/discharge curves of the four electrodes at a current density of 1 A g\(^{-1}\). (c) Comparison of specific capacitance versus different current densities. (d) Cycling stability of the 3D-G/PANI, 3D-G/PNF and CB/PANI electrodes at a current density of 5 A g\(^{-1}\). (e) Schematic illustration of multiple electron transport channels in 3D-G/PANI during the charging process. (f) Schematic illustration of the efficient protection of PANI from swelling and shrinking during the charge/discharge process.

Stacking of graphene sheets but also afforded additional electron transport channels and mechanical protection for a fast, complete and sustainable redox reaction of PANI (Fig. 1c–g). The 3D-G/PANI composite was further characterized by a series of spectra which confirmed the efficient de-oxygenation of GO and the integration of graphene and PANI (Fig. S3–S6†).

With excellent mechanical stability, a piece of 3D-G/PANI composite with a thickness of ~2 mm could be greatly compressed into a ~17 μm-thick highly flexible film with a packing density of 1.27 g cm\(^{-3}\) (Fig. 3d). Due to the robust interlock of graphene sheets in the 3D graphene framework, the 3D-G/PANI composite film showed a well maintained 3D interconnected porous network and excellent mechanical flexibility (Fig. 3e and f). There was no obvious crease in the appearance or change in the electrical conductivity before and after folding the 3D-G/PANI composite film (Fig. 3g, h and S7†). Even after repeated folding for 100 times, the composite film exhibited nearly the same electrical properties.

To interpret the structure–property relationship, we also prepared 3D-G, 3D-G/PNF and carbon black/PANI (CB/PANI) for comparison. The 3D-G/PNF was prepared by assembly of graphene and PNFs similar to 3D-G/PANI in which G/PANI composite nanosheets were replaced by PNFs while keeping the 3D graphene framework. Due to their aggregation and branched structure (Fig. S2†), only part of PNFs were in direct contact with graphene in 3D-G/PNF (Fig. S8†). The CB/PANI was prepared by a traditional physical mixing method in which the same G/PANI composite nanosheets were mixed with CB but without a 3D graphene framework. The CB/PANI showed a compact structure with CB nanoparticles simply attached on the surface of G/PANI composite nanosheets and most PANI exposed (Fig. S9†).

The intrinsic electrochemical performances of the 3D-G/PANI composite film, 3D-G/PNF, CB/PANI and 3D-G electrodes were evaluated by means of CV, galvanostatic charge/discharge and cycling life tests in a three-electrode system (Fig. 4). 3D-G exhibited a quasi-rectangular shape incorporated with a very weak couple of redox peaks at about 0.5 V, which are associated with the remaining oxygen-containing groups (Fig. 4a), implying the predominant electrical double-layer capacitive behavior of 3D-G. In contrast, two pairs of evident redox peaks corresponding to the faradic reaction from PANI (Fig. S10†) emerged for 3D-G/PANI, 3D-G/PNF and CB/PANI.26,27 Generally, the area of each enclosed curve suggests its specific capacitance. Thus, 3D-G/PANI exhibited a much larger capacitance than 3D-G/PNF, CB/PANI and 3D-G electrodes. The CV curve of 3D-G/PANI basically retained faradaic peaks even when the scan rate reached up to 100 mV s\(^{-1}\) (Fig. S11†), which is indicative of a quick charge-propagation capability of the pseudocapacitance in the 3D-G/PANI electrode.

The galvanostatic charge/discharge curves (Fig. 4b) of 3D-G/PANI, 3D-G/PNF, CB/PANI and PNFs all showed prominent deviation from the quasi-triangle shape exhibited by 3D-G, especially in the potential range of 0.3–0.6 V, which also confirmed the significant contribution of pseudocapacitance of PANI. The specific capacitance values derived from the galvanostatic charge/discharge curves for 3D-G/PANI, 3D-G/PNF, CB/PANI, 3D-G and PNFs (Fig. S12 and S13a†) are shown in Fig. 4c and S13b†. 3D-G/PANI exhibited the largest specific capacitance of 777 F g\(^{-1}\) (990 F cm\(^{-3}\)) at a current density of 1 A g\(^{-1}\), which was much higher than those of 3D-G (208 F g\(^{-1}\)), 3D-G/PNF (448 F g\(^{-1}\)), CB/PANI (410 F g\(^{-1}\)) and PNFs (351 F g\(^{-1}\)). Upon increasing the current density up to 20 A g\(^{-1}\), 3D-G/PANI still retained 78% specific capacitance of that at 1 A g\(^{-1}\), higher than 3D-G/PNF (73%), CB/PANI (71%) and PNFs (42%). The greatly improved electrochemical performance of 3D-G/PANI was also evidenced by Nyquist plots (Fig. S14†) that showed a much smaller semicircle and a much shorter 45° Warburg region for 3D-G/PANI, confirming a lower charge transfer resistance and more rapid ion diffusion within the 3D-G/PANI due to its hierarchical porosity.

Cycling stability is a long-term unresolved issue for practical application of pseudocapacitive conducting polymers. Notably, the 3D-G/PANI composite electrode showed an excellent electrochemical and environmental stability with 85% capacitance retention after 60 000 charge/discharge cycles (Fig. 4d), which is much better than that of 3D-G/PNF (29% capacitance retention after 30 000 cycles) and CB/PANI (20% capacitance retention after 30 000 cycles) and further confirmed by a slight change of morphology after cycling (Fig. S15†).

The outstanding electrochemical performance of our 3D-G/PANI electrode can be attributed to its unique hierarchical
structure. First, the in situ growth of an ultrathin PANI nanolayer on graphene sheets not only facilitates electron transfer and ion diffusion for a fast faradaic reaction and high utilization of PANI, but also decreases volumetric change and mechanical stress of PANI during the doping/dedoping process. Second, compared with previous reports that PANI just resides on the surface of the carbon substrate, the PANI in our work is wrapped by graphene sheets which can not only act as additional electron transport channels for higher capacitance and better rate performance (Fig. 4e) but also efficiently buffer the swelling and shrinking of PANI and mitigate the mechanical stress during the charge/discharge process due to their excellent flexibility and mechanical strength and do favor to a better stability (Fig. 4f). Third, the embedding of G/PANI composite nanosheets in the skeleton of the 3D graphene framework will further reduce the re-stacking of graphene sheets, which is beneficial for further improving the surface area and electrochemical performance. Fourth, the interconnected porous structure of 3D-G/PANI can facilitate electrolyte diffusion into pores as well as electron transport throughout the entire composite framework.

With a high electrical conductivity of 1957 S m⁻¹, superior mechanical flexibility and favorable porous structure, the 3D-G/PANI composite films were further used as electrodes to assemble flexible ASSs without any current collectors or supporting substrates (Fig. 5a). With two slightly separated 3D-G/PANI electrodes solidified in the PVA-H₂SO₄ gel electrolyte, the integrated device showed an average total thickness of 45 μm (Fig. S16†), which is much thinner than a commercial standard A4 paper (typically ~90 μm), indicating its great potential for powering ultrathin electronic devices. More importantly, due to the mechanical robustness of 3D-G/PANI film electrodes and their efficient integration with the polymer gel electrolyte, the ASS exhibited remarkable mechanical flexibility and durability, which allowed bending, twisting and even folding without influencing its electrochemical performance (Fig. 5b and c). Even after repeated folding for 100 times, only slight change in the cyclic voltammetry (CV) curves was...
observed and a high capacitance retention of 95% was achieved for the device (Fig. 5d). Hence, the electrochemical performance of the 3D-G/PANI composite-based ASS was all obtained under its highly flexible (folded) condition.

The 3D-G/PANI electrode in the solid-state device showed a high specific capacitance of 665 F g\(^{-1}\) at 1 A g\(^{-1}\), which is very close to the value measured in the device with 1 M H\(_2\)SO\(_4\) aqueous electrolyte (680 g\(^{-1}\), Fig. 5e), indicating an efficient infiltration of the polymer gel electrolyte into the 3D network. Upon increasing the current density to 20 A g\(^{-1}\), 3D-G/PANI in the polymer gel electrolyte still maintained 86% specific capacitance, highlighting its excellent rate capability (Fig. 5f and S17†). The volumetric capacitance of 3D-G/PANI was thus calculated to be 847 F cm\(^{-3}\) in the gel electrolyte and 866 F cm\(^{-3}\) in 1 M H\(_2\)SO\(_4\) based on its packing density of 1.27 g cm\(^{-3}\). Notably, the specific capacitance especially the volumetric capacitance of 3D-G/PANI in the device is higher than the recently reported record value (Tables S1 and S2†), demonstrating the prominent advantage of the multiple structural features of 3D-G/PANI. Moreover, the 3D-G/PANI-based ASS revealed a unprecedented cycling stability with 100% capacitance retention even after 10 000 deep charge/discharge cycles (Fig. 5g), which is significantly better than all previously reported carbon/conducting polymer composites to the best of our knowledge, and also superior to graphene/transition metal oxides and even carbon materials.

On the level of practical applications, the stack energy density and power density normalized by the total volume or mass of the device usually comprising electrodes, current collectors, electrolyte, and separator (and/or packaging) are key parameters for evaluating the energy-storage performance of the device. A comparison of Ragone plots based on the entire device is thus shown in Fig. 5h and i. Due to the current collector-free feature, our ultrathin device showed a remarkable volumetric energy density of 14.2 mW h cm\(^{-3}\), a value considerably higher than that of almost all carbon/conducting polymer-based flexible ASSs, such as carbon cloth/graphitic petals/PANI (CC/GPs/PANI) (3.4 mW h cm\(^{-3}\)),\(^{35}\) polypyrrole-coated (PPy-coated) paper (1 mW h cm\(^{-3}\))\(^{36}\) and multilayered carbon nanotube/poly(dimethylsiloxane)/PANI (MWCNT/PDMS/PANI) (0.15 mW h cm\(^{-3}\))\(^{37}\). Moreover, the volumetric energy density of our device is also 16-fold higher than that of commercially available 2.75 V/44 mF AC-EC (~0.7 mW h cm\(^{-3}\)),\(^{37}\) 59-fold higher than that of 3.5 V/25 mF EC (~0.2 mW h cm\(^{-3}\)),\(^{38}\) and even nearly 1.5 times higher than that of the 4 V/500 µA h thin-film lithium battery (~8 mW h cm\(^{-3}\))\(^{38}\). With a large volumetric power density (3.4 W cm\(^{-3}\), 600-fold higher than that of the 500 µA h thin-film lithium battery (~5.5 mW cm\(^{-3}\)), our device definitely bridges the gap between the flexible ASSs and lithium thin-film battery. The gravimetric energy density and power density of our device were also compared with those of previously reported ASSs and commercial supercapacitor devices (Fig. 5i). The lightweight 3D-G/PANI composite-based flexible ASS is able to deliver a maximum gravimetric energy density of 10.9 Wh kg\(^{-1}\), which is obviously higher than that of commercial supercapacitors (~5 Wh kg\(^{-1}\))\(^{39}\) and most symmetrical supercapacitors (0.35–6.8 Wh kg\(^{-1}\))\(^{39,40,41}\). The maximum areal energy density of our device (64 µW h cm\(^{-2}\)) is also among the best ASSs based on carbon/conducting polymer nanocomposites (0.26–51 µW h cm\(^{-2}\)) (Fig. S18†).\(^{42–46}\)

For practical application, the leakage current and self-discharge characteristics of the device are also very important factors to consider, which, unfortunately, received insufficient attention in many studies. The leakage current of our device
decreased significantly in the first 5 min (from 1.8 mA to 28 μA) and quickly stabilized at 11.7 μA after 0.5 h (Fig. 6a) (0.012 μA mF⁻¹, normalized by capacitance), which is greatly lower than that of the carbon nanotube/PANI-based ASS (0.034 μA mF⁻¹)¹⁹ and PANI-based ASS (0.038 μA mF⁻¹).⁷ The leakage current was ascribed to the shuttle reaction induced self-discharge course which was further investigated (Fig. 6b). The device underwent a rapid self-discharge process in the first half hour; however, the self-discharge course became very slow after several hours. Finally, the device delivered a stable output voltage of ~0.53 V after 4 h and 63% of the initial charged potential was well retained even after one day, which is significantly higher than that of the polypyrrole-based ASS (~0.2 V),²⁶ PANI/Au/paper-based ASS (0.3 V)⁷ and carbon nanotube/PANI-based ASS (0.46 V).¹⁹ The advantage of low self-discharge course is highly desirable for the applications of the devices in flexible and wearable electronics.

To further demonstrate the practical usage of the flexible ASS based on 3D-G/PANI, three supercapacitor units were connected in series to create a tandem device. As shown in Fig. 5c, the potential window is extended from 0.8 V for a single device to 2.4 V for the tandem device. Moreover, the tandem device shows almost unchanged charge/discharge time compared with an individual cell at the same current density, illustrating that the performance of each supercapacitor unit is well maintained in the tandem device. Upon charging to 2.4 V, the tandem device can efficiently power a 5 mm diameter red (2.0 V, 20 mA) round light-emitting diode (LED) indicator (Fig. 6d) for more than 10 min. Furthermore, even each supercapacitor unit in the tandem device was twisted (Fig. 6e) or folded (Fig. 6f), the brightness of the LED remained unchanged, demonstrating the great potential of our device as a flexible power source.

**Conclusions**

In summary, we have developed a high-performance monolithic 3D-G/PANI composite electrode with *in situ* polymerized G/PANI composite ultrathin nanosheets wrapped and embedded into a robust 3D graphene framework for assembling ASSs directly without current collectors. The highly flexible device demonstrates an ultralong cycling life with 100% capacitance retention after 10 000 cycles, as well as superior volumetric, gravimetric and areal energy densities much higher than those of almost all carbon/conducting polymer-based ASSs, commercial supercapacitors and even lithium thin-film batteries. This study provides an exciting pathway to greatly promote the electrochemical performance of carbon/conducting polymer composite electrodes by elaborate integration of both components. The excellent comprehensive performance of our device indicates its great potential to bridge the gap between flexible ASSs and lithium thin-film batteries and be used as the next-generation flexible power source for wearable electronics.

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