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8 **Polyaniline/Reduced Graphene Oxide Hydrogel Film with Attached**
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11 **Graphite Current Collector for Flexible Supercapacitors**
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Abstract

Reduced graphene oxide (RGO) hydrogel films possess a low specific capacitance and have no flexible current collectors, which limit their use in flexible supercapacitors. To solve these problems, a novel polyaniline (PANI) modified RGO hydrogel film with an attached graphite current collector (PANI/RGO/G) was prepared. Based on this film, a flexible supercapacitor device was fabricated and characterized. PANI/RGO/G film demonstrates good flexibility and electron transport. The graphite current collector highly reduces the internal resistance of the device. It shows a high specific capacitance of 478 F g^{-1} at a current density of 2 mA cm^{-2} based on the mass of one electrode and a good cycling stability (86.5% retention after 5000 cycles). Moreover, during the fabrication of the device, a modified design was adopted to solve the problem of low extension of PANI/RGO/G hydrogel film. The obtained device also exhibits a good flexibility; its capacitance hardly changes after 500 cycles of bending at an angle of 90° .

Keywords: Flexible supercapacitor; Reduced graphene oxide; Graphite current collector; Polyaniline; Hydrogel film

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17 1. Introduction

18 The rapid development of flexible electronics highly demands novel energy storage devices,
19 which are light-weight, thin and flexible, apart from meeting required electrochemical
20 performance [1, 2]. Flexible supercapacitors have attracted significant attention due to their
21 safety and simple structure, as well as their intrinsic properties such as high power density, fast
22 charge–discharge rates, and long cycle life, which make them one of the most promising
23 candidates for flexible energy storage devices [3–5].

24 Flexible electrodes are one of the most important components in flexible supercapacitors.
25 RGO have been extensively studied as electrode material of flexible electrodes due to their two-
26 dimensional structure, high specific surface area, and excellent flexibility, as well as their easy
27 access, partial functionalization and low cost, compared to graphene [6–9]. Self-supported RGO
28 films with robust mechanical strength can be prepared by various methods [10–12]. However,
29 during the preparation, especially during the drying, the aggregation and restacking of individual
30 graphene nanosheets reduce their specific surface area and re-wettability to electrolytes, resulting
31 in blocking the diffusion of ions and decreasing the electrochemical performance [13–17]. Thus,
32 RGO hydrogel films have recently drawn attentions as their highly porous structure can store
33 abundant amount of electrolyte and provide continuous pathway for electrolyte ions [18–21].

34 However, due to the limited contribution of electrochemical double layer to capacitance, the
35 capacitance of RGO hydrogel film is still lower compared to those of pseudocapacitors that
36 involve Faradaic reactions for storing the charge [22]. Therefore, pseudocapacitive materials
37 such as transition metal oxides and conducting polymers are generally employed [23–25].

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4 38 Among them, polyaniline (PANI) has been extensively used due to its ease of synthesis, low
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6 39 cost, environmental friendliness and potentially large pseudocapitance [26]. Tremendous
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9 40 efforts have been made to introduce PANI into RGO with various forms such as particles
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11 41 [27–29], films [30–32] and foams [33–35]. However, the raw RGO or the archived RGO
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14 42 composites have dry states. Recently, several studies have been reported on the incorporation of
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16 43 PANI into wet-state and bulk RGO hydrogel films, showing inspiring results [23, 36–38].

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19 44 On the other hand, although residual hydrophilic groups on RGO increase the accessibility
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21 45 of aniline during the polymerization, they degrade the electrical conductivity of RGO [39–41].
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24 46 Consequently, the electron transport in RGO films cannot meet the demand of supercapacitor
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26 47 devices with large scales and high working currents. Therefore, current collectors are still
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29 48 necessary to RGO based supercapacitor devices. However, there are limited choices of flexible
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31 49 current collectors for aqueous electrolytes because of the corrosion of major metals [42–45].
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34 50 Therefore, gold foils or gold coated plastic substrates often appear in flexible devices [46–48].
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37 51 Besides the cost, the peeling of electrode films from current collectors during bending has been
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39 52 considered as a critical issue [49, 50]. One of the strategies is direct deposition of current
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41 53 collector on the surface of RGO films. Another problem with RGO hydrogel films is their weak
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44 54 mechanical properties such as low stretchability [23, 51]. Thus, there is a high risk of fracturing
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46 55 during bending when it is fixed on a flexible substrate [52].
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49 56 In this paper, we report a flexible supercapacitor device based on PANI/RGO/G hydrogel
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51 57 film. A graphite current collector was directly deposited on the surface of RGO hydrogel film
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54 58 modified by PANI through a diluted *in-situ* polymerization. During the fabrication of the
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56 59 supercapacitor device, a special structural design of device was adopted to solve the problem of
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59 60 weak mechanical properties of RGO hydrogel based films. As a result, high electrochemical
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4 61 performance of the device has been achieved due to (i) the high diffusion of electrolyte ions in
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6 62 hydrogel films, (ii) the contribution of high pseudocapacitance of PANI, and (iii) the enhanced
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9 63 electron transport endowed by a graphite current collector. Moreover, owing to the special
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12 64 design, this device exhibits a high flexibility. This study shows a promising possibility for the
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14 65 application of RGO hydrogel based films in flexible supercapacitors.

66 2. Experimental

67 2.1. Preparation of RGO/G and PANI/RGO/G hydrogel films

68 Graphite oxide was prepared by the oxidation of natural graphite flakes (325 mesh, Graphite
69 Tyn, Czech Republic) according to a modified Hummers' method [53]. The exfoliation of
70 graphite oxide to graphene oxide (GO) was achieved by ultra-sonication of the dispersion of
71 graphite oxide [54]. RGO colloid suspension was obtained by reducing GO dispersion with
72 electrostatic stabilization [11]. A typical procedure was as follows: 6 mL of 3 mg/mL GO
73 dispersion, 1 mL of ammonium hydroxide solution (30 – 32 wt. %) and 100 μL of hydrazine
74 hydrate (50 – 60 wt. %) were added in a flask filled with 200 mL of deionized water. This
75 mixture was then severely shaken. RGO colloid was obtained by placing this flask in a water
76 bath with temperature of 90 °C for 2 h. RGO hydrogel film was prepared by the vacuum
77 filtration of this obtained RGO colloid. To obtain a graphite current collector on RGO/G
78 hydrogel film, at the end of the filtration, the top of hydrogel film was rinsed by dilute
79 ammonia–water solution, and then 2 mL of 1 mg/mL graphite suspension was added into for the
80 successive filtration.

81 PANI/RGO/G hydrogel films were obtained by the *in-situ* polymerization of aniline onto an
82 RGO/G film. A typical procedure was as follows: RGO/G filter cakes were cut into rectangular

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4 83 pieces with a size of 1 cm × 2 cm. Two pieces of these films were immersed into 10 mL of 1 M
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6 84 HCl aqueous solution containing 90 μL of aniline monomer. The mixture was stored at 0 °C for 2
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9 85 h. 10 mL of 1 M HCl aqueous solution containing 0.155 g ammonium persulfate (pre-cooled to 0
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11 86 °C) was then poured into the above mixture. This mixture was left at 0 °C for another 24 h. The
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14 87 resulting films were immersed in HCl aqueous solution, ethanol, and deionized water
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16 88 subsequently. Finally, the films were compressed between two pieces of polyvinylidene fluoride
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19 89 (PVDF) filter membranes under 10 MPa. The schematic illustration of PANI/RGO/G hydrogel
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21 90 film formation is given in Figure 1.

23 91 2.2. Bending ability test of prepared hydrogel films on a PET substrate.

26 92 The test fixture is as follows: a hydrogel film (1 cm×3 cm) was compressed on a slide of
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28 93 polyethylene terephthalate (PET) substrate under 10 MPa. The thickness of PET was ~100 μm.
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31 94 Two titanium foils were placed on each end of the film; each covers an area of 0.5 cm × 1 cm.
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33 95 Then a piece of poly(dimethyl siloxane) (PDMS), with thickness of ~0.7 mm) was covered on the
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36 96 top. Two titanium foils were carefully fixed by clips for testing the resistances. Thus, the area of
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38 97 exposed hydrogel film was 1 cm × 2 cm. The applied bending angles were 90 °, 120 ° and 180 °.
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41 98 The number of bending was up to 600 with a range of bending angles of ± 90 °. The resistance
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43 99 was measured only when the film returned back to the initial state by a Keithley 6517A Digital
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45 100 Source Meter.

48 101 2.3. Fabrication of flexible supercapacitor devices

50 102 The packing substrate (PDMS) of the device was prepared from SYLGARD® 184 (Dow
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53 103 Corning Corporation). It represents a slide (thickness = 0.2 cm) with a cavity (2.5 cm long, 1.3
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55 104 cm wide, 0.15 cm deep). Two prepared PANI/RGO/G films were put into the cavity, separated
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58 105 and surrounded by poly(vinyl alcohol)-H₂SO₄ (PVA-H₂SO₄) gel electrolyte (10 g PVA (M_w, ~
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145,000) dissolved in 90 g 1 M H₂SO₄ solution). Two titanium foils were placed on each edge of the films with an area of 1 cm × 0.5 cm. This part of the films was pre-dried on a hot plate for seconds at a temperature of about 80 °C and separated by Parafilm. The effective electrode area was 1 cm × 1.5 cm. Then a PET substrate was put on the top for sealing. Finally, the titanium foils were fixed by a clip.

2.4. Characterization

The morphology of the prepared hydrogel films were investigated by scanning electron microscopy (SEM, FEI Nova NanoSEM450). The electrochemical characterization was carried out by cyclic voltammetry (CV), galvanostatic charge–discharge test and electrochemical impedance spectroscopy (EIS) using Autolab PGSTAT128N (Metrohm, Netherlands). The electrochemical performance of the prepared hydrogel films was first investigated in a three-electrode system with an Ag/AgCl reference electrode and a Platinum counter electrode in 1M H₂SO₄. The measurement for assembled devices was carried out in a two-electrode system. The capacitance of each device was calculated from the galvanostatic curves at different current densities using Eq. (1), where i is the discharge current and dV/dt stands for the slope of the discharge curve.

$$C_{device} = i/(-dV/dt) \tag{1}$$

The gravimetric capacitance of each device (C_t) was calculated by Eq. (2), and the specific capacitance of a single electrode (C_s) was calculated by Eq. (3), where m is the total mass of two electrodes.

$$C_t = C_{device}/m \tag{2}$$

$$C_s = 4C_t \tag{3}$$

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4 128 The areal capacitance of each device (C_A) was calculated by Eq. (4), where A is the
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7 129 footprint area of two electrodes.

$$10 \quad C_A = C_{device}/A \quad (4)$$

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12 131 The areal energy density (E_A) and power density (P_A) of devices was derived from Eqs. (5)
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14 132 and (6), where ΔV represents the potential window excluding the IR_{drop} , which is the potential
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17 133 drop at the beginning of the discharge in the charge–discharge profile.

$$19 \quad E_A = 1000C_A \Delta V^2/7200 \quad (5)$$

$$22 \quad P_A = E_A/t \quad (6)$$

27 137 3. Results and Discussion

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31 138 In order to increase the electron transport in RGO hydrogel film, graphite flakes were
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33 139 deposited on one side of RGO hydrogel, serving as a current collector, after the successive
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36 140 filtration of RGO dispersion and graphite flakes suspension, as illustrated in Figure 1.
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39 141 Approximately 28 wt. % of graphite flakes are bonded to the surface of RGO/G and remain there
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41 142 during the preparation of PANI/RGO/G. This is because some graphite flakes are inserted into
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44 143 the gap of RGO nanosheets, which is visible in SEM images (see Figure 2). After compressing
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46 144 the RGO/G and PANI/RGO/G hydrogel films, graphite flakes are strongly attached to the RGO
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49 145 matrix, thus rendering the flexibility and improving the mechanical properties of the films. The
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51 146 final thickness of RGO/G film was about 80 μm with a mass loading of $\sim 0.9 \text{ mg cm}^{-2}$, where the
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54 147 mass loading of RGO is about 0.65 mg cm^{-2} . Figure 1 displays a digital image of a compressed
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56 148 RGO/G filter cake from both sides of graphite current collector and RGO hydrogel. This RGO/G
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59 149 exhibits a high flexibility, as shown in the inset image. A prepared flexible PANI/RGO/G

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4 150 hydrogel film is also presented in Figure 1; it has a size of 1 cm × 2 cm, a thickness of ~115 μm
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7 151 and a mass loading of 1.7 mg cm⁻². The mass loading of PANI/RGO without graphite current
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9 152 collector is about 1.47 mg cm⁻².

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12 153 The morphology of various prepared hydrogel films is shown in Figure 2. RGO film
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14 154 exhibits a porous structure, which provides continuous ionic pathways across the piled RGO
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17 155 layers (Figure 2a). Importantly, RGO flakes stand on the surface, as can be seen from the side
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19 156 perspective of the sample (Figure 2b). That is why graphite flakes can be embedded into the
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21 157 RGO film during the filtration and then held tightly after the compression. The high
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24 158 magnification image of RGO/G surface inserted in Figure 2c obviously shows that small hard
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26 159 graphite flakes are embraced by soft RGO sheets. This makes this graphite current collector
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29 160 deformable along with the RGO film without splitting during bending. This deposition method
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31 161 seems to be a low-cost and efficient strategy to create a flexible current collector on RGO
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34 162 hydrogel film.

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36 163 The surface and cross-sectional morphology of PANI/RGO film before the compression is
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39 164 demonstrated in Figures 2d, e, f (surface) and Figures 2g, h, i (cross-section), respectively. As
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41 165 can be seen, the surface of PANI/RGO film (Figure 2d) becomes more uniformly porous than
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44 166 that of RGO (Figure 2a) due to the PANI deposition, which decreases the restacking of RGO
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46 167 nanosheets during freeze-drying. Figures 2e and 2f are the highly magnified images of
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49 168 PANI/RGO film, which show that PANI nanoarrays grow on the surface of RGO nanosheets.
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51 169 Figures 2g, h and i demonstrate the cross-section of the PANI/RGO film from low to high
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53 170 magnification. This film has a thickness of about 450 μm (Figure 2g). The highly magnified
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56 171 image (Figure 2h) demonstrates a layer-by-layer structure with a highly developed porous
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58 172 structure. Figure 2i confirms that PANI nanoarrays are present not only on the surface but also

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4 173 inside the hydrogel. This fine growth of PANI nanoarrays and their uniform distribution benefit
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6 174 from the interconnected channels within hydrogel, which enables the diffusion of aniline, as well
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9 175 as from the low concentration of aniline in the reaction media, which guarantees a well-
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11 176 controlled nucleation-growth of PANI. A thin PANI nanoarray layer (59 wt. % in PANI/RGO)
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14 177 deposited on RGO tends to endow the electrode with excellent electrochemical performance [31].

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16 178 RGO/G and PANI/RGO/G films were first analyzed by CV measurements in a three-
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19 179 electrode system in 1 M H₂SO₄ with a potential window from -0.2 to 0.8 V *versus* Ag/AgCl. The
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21 180 CV curves in Figure 3 show a remarkable difference between the electrochemical activities of
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24 181 RGO/G and PANI/RGO/G. RGO/G shows only one pair of redox peaks due to the transition
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26 182 between quinone/hydroquinone groups in RGO (see Figure 3a), which is typical for carbon
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29 183 materials [55, 56]. However, two pairs of redox peaks (C₁/A₁, C₂/A₂) from PANI/RGO/G
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31 184 indicate the presence of pseudocapacitive PANI (Figure 3b). Redox transitions between a
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33 185 semiconducting state (leucoemeraldine form) and a conducting state (emeraldine form) are
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35 186 responsible for the peaks C₁/A₁, and the Faradaic transformation of emeraldine to pernigraniline,
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38 187 for the redox peaks C₂/A₂ [57]. The presence of PANI substantially enhances the specific
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41 188 capacitance of RGO/G hydrogel film. As a result, PANI/RGO/G exhibits a higher specific
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43 189 capacitance of 806 mF cm⁻² (548 F g⁻¹ excluding the mass of graphite current collector),
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46 190 compared to that of RGO/G (142 mF cm⁻², and 218 F g⁻¹ excluding the mass of graphite current
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49 191 collector) at a scan rate of 5 mV s⁻¹ based on the three-electrode system.

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51 192 However, during the fabrication of the flexible supercapacitor devices, it was found that the
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53 193 prepared hydrogel films exhibit weak mechanical properties when fixed on a flexible PET
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56 194 substrate. The bending fixture and bending test results are demonstrated in Figure 4. As can be
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59 195 seen, the employed graphite current collector rarely decreases the bending ability of the films,

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4 196 but the deposition of PANI does (Figure 4b). More importantly, the damage of each film
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7 197 deteriorates as the angle and the number of bending increase (Figure 4c). The structural design
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9 198 plays an important role in the flexibility of devices. Several strategies have been reported, such
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12 199 as using the planar configuration, reducing the thickness and optimizing the mechanical neutral
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14 200 plane [58–60]. Here we demonstrate an alternative approach to solve the problem of weak
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16 201 mechanical properties of RGO/G and PANI/RGO/G hydrogel films. The schematic diagram of
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19 202 supercapacitor fabrication is shown in Figure 5. As can be seen, when PANI/RGO/G film is
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22 203 fixed on a PET substrate, the top and the bottom of the film have the same length. After getting
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24 204 bent, the lengths are getting different upon the radius from the center of concentric circles shown
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26 205 in Figure 5a. Thus, the top of PANI/RGO/G is stretched, and stresses are generated both within
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29 206 and between the PANI/RGO/G and PET substrate [61]. Since PANI/RGO/G hydrogel has low
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31 207 tensibility, it tends to be torn up. Taking into account that there is no strong interaction between
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34 208 PANI/RGO/G and PET, PANI/RGO/G can be exfoliated from the PET substrate during the
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36 209 bending. Thus, a free-movement configuration was adopted for the obtained hydrogel films as
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39 210 shown in Figure 5b. PANI/RGO/G and PET substrate are separated by gel electrolyte, and only
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41 211 one side of PANI/RGO/G is provided with current collector (titanium foils). As a result,
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44 212 PANI/RGO/G is suspended in gel electrolyte. When it bends, due to the large deformation and
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46 213 creep of PVA-H₂SO₄ gel electrolyte, PANI/RGO/G can freely move, thus the stress applied to
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49 214 PANI/RGO/G from the gel electrolyte is much lower than that from the PET substrate. This free-
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51 215 movement configuration has been adopted to assemble the flexible supercapacitor device (Figure
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53 216 5c).

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56 217 The electrochemical performance of assembled flexible supercapacitor devices with various
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58 218 hydrogel films is shown in Figure 6. The effect of graphite current collector on electrochemical
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4 219 performance of these devices was studied. Figures 6a and 6b show the galvanostatic discharge
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7 220 profiles of PANI/RGO and PANI/RGO/G at various current densities of 1, 2, 5 and 10 mA cm⁻²,
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9 221 respectively. Each IR_{drop} of PANI/RGO/G is extremely lower than that of PANI/RGO at the
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11 222 corresponding current density. The IR_{drop} vs current densities are summarized in the inset graph
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14 223 in Figure 6d. The slope of IR_{drop} vs current density is related to the *Internal Resistance* ($R=$
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16 224 IR_{drop}/i) of the device, which determines its maximum voltage during discharge and,
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19 225 consequently, the maximum power [62]. Because of the contribution from pseudocapacitive
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21 226 PANI, PANI/RGO/G exhibits a much higher specific gravimetric capacitance (C_s) of 409 F g⁻¹
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24 227 (478 F g⁻¹, excluding the mass of graphite current collector), compared to that of RGO/G (110 F
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27 228 g⁻¹ including, and 152 F g⁻¹ excluding the weight of graphite current collector, respectively), and
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29 229 similar to that of PANI/RGO (457 F g⁻¹) at a current density of 2 mA cm⁻². The PANI/RGO/G
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32 230 device yields a gravimetric capacitance (C_t) of 120 F g⁻¹ based on the total mass of two
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35 231 electrodes, and an areal specific capacitance of 352 mF cm⁻², which is much higher than that of
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37 232 RGO/G (49 mF cm⁻²) at a current density of 2 mA cm⁻². The PANI/RGO/G device displays good
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40 233 rate performance with only 11.9 % capacitance loss when current density increases from 1 mA
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42 234 cm⁻² to 10 mA cm⁻². As shown in Figures 6c and 6d, the CV profile of dry PANI/RGO/G is
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45 235 distorted and turns to be spindle-like as the scan rate increases (from 5 to 100 mV s⁻¹), while that
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47 236 of PANI/RGO/G hydrogel film exhibits much better retention. This is attributed to the high ion
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50 237 transport in PANI/RGO/G hydrogel film. This is confirmed by the impedance curves of the
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52 238 assembled devices with various films in Figure 6e. The charge transfer resistance (R_{ct}) of
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55 239 PANI/RGO/G, extracted from the intercept of the low-frequency impedance spectrum with the
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57 240 real axis, is 3.5 Ω, which is almost the same as that of RGO/G but much lower than those of
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59 241 PANI/RGO and dry PANI/RGO/G. This indicates that the graphite current collector reduces the
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4 242 resistance of the films and that the interconnected porous structure of hydrogel films ensures fast
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7 243 ion diffusion. It is known that the enhanced ion and electron transport within PANI/RGO/G can
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9 244 endow its assembled device with high electrochemical performance [63]. Indeed, the fabricated
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12 245 device demonstrates a higher energy density of $27.8 \mu\text{Wh cm}^{-2}$ (8.1 Wh kg^{-1} , at a current density
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14 246 of 2 mA cm^{-2}) and a larger power density of 3.5 mW cm^{-2} (1.0 kW kg^{-1} , at a current density of
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17 247 10 mA cm^{-2}) compared to those of PANI/RGO ($20.8 \mu\text{Wh cm}^{-2}$ (6.5 Wh kg^{-1}) and 2.0 mW cm^{-2}
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19 248 (0.6 kW kg^{-1}) at the corresponding current density, respectively (inset image in Figure 6f).
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22 249 Furthermore, this device exhibits a good cycling stability (Figure 6f), unlike general PANI-based
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24 250 supercapacitors, which suffer from limited cycling life due to the swelling and shrinking of
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27 251 PANI during the charge–discharge process. Indeed, the cycling performance shows capacitance
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29 252 retention as high as $\sim 86.5\%$ over 5000 cycles at a high current density of 5 mA cm^{-2} , which is
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32 253 attributed to the “soft” and self-adaptive nature of RGO hydrogels, as well as to the strong
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34 254 adhesion of PANI on RGO nanosheets through π - π interaction [23, 36].
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38 255 The flexibility of the fabricated device and its influence on the electrochemical performance
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40 256 were further investigated. Figure 7a shows the CV curves of PANI/RGO/G device at different
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43 257 bending angles at a scan rate of 10 mV s^{-1} . When the bending angle is from 90° to 180° , only a
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45 258 slight change can be observed. The capacitance retentions of the device after different numbers
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48 259 of bending are presented in Figure 7b. When the bending angle keeps at 90° , the device has
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50 260 almost the same capacitance as the initial one even after 500 times of bending. When the bending
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53 261 angle is increased up to 120° , the capacitance retention can be as high as above $\sim 95\%$. The
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55 262 obtained results confirm that the improved flexibility has been achieved by using the free-
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58 263 movement configuration. The inset digital image in Figure 7b shows that when the bending angle
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60 264 turns from 0° to 120° , the gel electrolyte is sheared by two parallel films on each side. The films
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4 265 keep their initial length, the elongation occurring in the gel electrolyte. Due to the high
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6 266 deformation and creep of the gel electrolyte, a slight shear force is applied to the hydrogel films.
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9 267 Because of the narrow potential window of aqueous electrolyte and PANI, this device can
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11 268 be charged only to 0.8 V, which is not sufficient for the most practical applications. To obtain
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14 269 higher desired voltages, several devices can be connected in series. Figure 8 shows the
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16 270 charge–discharge performance of a packed cell with three devices connected in series. As can be
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19 271 seen, this cell can be charged up to 2.4 V and demonstrates almost the same charge–discharge
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22 272 time as a single device at a current density of 1 mA cm⁻². This cell can light a light-emitting
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24 273 diode (LED) lamp with a forward voltage of 1.8 V, as seen in the inset photograph.
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27 274 4. Conclusions

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31 275 In this work, we have demonstrated a flexible supercapacitor device with high
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33 276 electrochemical performance and improved flexibility by using PANI/RGO/G hydrogel films
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36 277 and a free-movement configuration. The modification of RGO/G hydrogel film by PANI results
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39 278 in an enhanced areal capacitance of 352 mF cm⁻² (478 F g⁻¹) and energy density of 27.8 μWh
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41 279 cm⁻² (8.1 Wh kg⁻¹) compared to those of RGO/G (49 mF cm⁻², 152 F g⁻¹) at a current density of
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44 280 2 mA cm⁻². Moreover, a low-cost but efficient method was adopted to create a flexible current
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47 281 collector on RGO hydrogel film using graphite flakes. This graphite current collector reduces the
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49 282 internal resistance of the device ($R_{ct} = 3.5 \Omega$), which manifests itself in an enhanced power
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52 283 density up to 3.5 mW cm⁻² (1.0 kW kg⁻¹) at a current density of 10 mA cm⁻². Moreover, this
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54 284 device also exhibits a good cycling stability (86.5% retention after 5000 cycles) at a high current
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57 285 density of 5 mA cm⁻², as well as an improved flexibility, where its capacitance hardly changes
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59 286 after 500 cycles of bending at a bending angle of 90°. Due to the free-movement configuration,
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287 PANI/RGO/G is suspended in gel electrolyte. The large deformation and creep of PVA-H₂SO₄
288 gel electrolyte decreases the applied stress from the PET substrate to PANI/RGO/G. This study
289 shows a new approach to the application of mechanically weak film electrodes, especially RGO
290 hydrogel based films, in flexible supercapacitors.

291

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7 **Captions for figures:**
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10 **Fig. 1.** Schematic illustration of the preparation process. (a) Successive filtration of RGO colloid
11 and graphite suspension to deposit graphite flakes on the surface of RGO hydrogel. (b) Insertion
12 of graphite flakes and *in-situ* polymerization of aniline onto RGO. (c) Digital images of flexible
13 RGO/G and PANI/RGO/G hydrogel films after compression.
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20 **Fig. 2.** SEM images of the surface of RGO hydrogel from (a) top view and (b) side perspective,
21 (c) the surface of graphite side of RGO/G film (inset image shows its high magnification image),
22 (d) the surface of PANI/RGO hydrogel and (e, f) at high magnification, (g) the cross-section of
23 PANI/RGO hydrogel and (h, i) at high magnification.
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30 **Fig. 3.** Cyclic voltammogram curves of (a) RGO/G and (b) PANI/RGO/G at various scan rates
31 from 5 to 50 mV s⁻¹ collected in a three-electrode system with an Ag/AgCl reference in 1 M
32 H₂SO₄. Note that the y-scale in (a) is much smaller than (b).
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37 **Fig. 4.** (a) Image of one fixed set for bending ability test and the illustration of the bending angle.
38 Normalized resistances of prepared hydrogel films after bending as a function of (b) the bending
39 angle and (c) the number of bending (the red cross indicates when the fracture occurs).
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45 **Fig. 5.** (a) Schematic diagram of PANI/RGO/G hydrogel film on a PET substrate and the
46 different extensions upon the radius caused by bending. (b) Free-movement configuration and its
47 mechanism to reduce the stress force during bending. (c) Illustration for constructing flexible
48 supercapacitor devices using a free-movement configuration (cross section).
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54 **Fig. 6.** Electrochemical performance of symmetric flexible devices using various prepared films.
55 Galvanostatic discharge curves of (a) PANI/RGO and (b) PANI/RGO/G devices at various
56 current densities from 1 mA cm⁻² to 10 mA cm⁻²; inset graph shows the summary of their IR_{drop}
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4 vs current densities. Cyclic voltammograms of (c) dry PANI/RGO/G and (d) PANI/RGO/G
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6 hydrogel film device at different scan rates from 5 mV s⁻¹ to 100 mV s⁻¹. (e) Nyquist plots
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8 demonstrate the effect of graphite current collector and wet-state of the films on R_{ct}. (f) Cycling
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10 stability of RGO/G and PANI/RGO/G devices at a high current density of 5 mA cm⁻² (inset
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12 image shows their areal energy densities vs average power densities).

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15 **Fig. 7.** Flexibility of PANI/RGO/G device using a free-movement configuration. (a) Cyclic
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17 voltammograms at various bending angles at 10 mV s⁻¹. (b) Capacitance retention after various
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19 bending cycles at angles of 90° and 120° (inset image shows the deformation of gel electrolyte).
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23 **Fig. 8.** Charge–discharge curves of a single and three PANI/RGO/G devices in series at 1 mA
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25 cm⁻². Inset photograph displays a red LED lighted by these three devices in series.
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