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# Tailored Polyimide-Graphene Nanocomposite as Negative Electrode and Reduced Graphene Oxide as Positive Electrode for Flexible Hybrid Sodium-ion Capacitors

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**ABSTRACT:** Redox-active polyimide materials hold a great promise for electrochemical energy storage applications, especially for flexible energy storage devices. However, the low utilisation efficiency due to poor electrical conductivity of the materials remains one of the greatest challenges. In this work, we designed and prepared polyimide-graphene composite materials and tested their electrochemical properties in sodium-ion capacitors. By manipulating the interfacial chemistry and interactions between the polyimide and graphene, composite electrode materials with different polyimide particle sizes and morphologies were obtained. Sodium-ion storage capacity was significantly improved, from  $\sim 50 \text{ mAh g}^{-1}$  for pure polyimide to  $225 \text{ mAh g}^{-1}$  for a polyimide-graphene composite. A hybrid sodium-ion capacitor fabricated with freestanding polyimide-graphene composite as the negative electrode and reduced graphene oxide as the positive electrode delivered energy densities of  $55.5 \text{ Wh kg}^{-1}$  and  $21.5 \text{ Wh kg}^{-1}$  at power densities of  $395 \text{ W kg}^{-1}$  and  $3400 \text{ W kg}^{-1}$ , respectively. A flexible sodium-ion capacitor with outstanding mechanical properties was also demonstrated.

**KEYWORDS:** flexible device, sodium-ion capacitor, polyimide, graphene, composite electrode

## INTRODUCTION

Flexible energy storage devices are important components in flexible electronics.<sup>1,2</sup> It is important to develop cost-effective flexible energy storage devices with both high specific energy and power. Among the various energy storage systems,<sup>3-5</sup> sodium ion capacitors (NICs) are of particular importance because they can possess both high specific energy and power, and sodium is a widely available resource. Presently, advanced electrode materials suitable for the NIC technology are being investigated.<sup>6-14</sup>

Redox polymers are promising sodium-ion storage materials for flexible NICs, due to their flexibility,<sup>15</sup> non-toxicity,<sup>16</sup> low cost,<sup>17</sup> structural adaptability<sup>18</sup> and lower sensitivity to the large sodium ions.<sup>19</sup> Polyimides (PIs) are cost-effective polymers with functional groups, which have been demonstrated to be electrochemically active for ion storage.<sup>20,21</sup> However, polyimides have a poor electrical conductivity.<sup>22</sup> Thus, a large quantity of conductive carbons (30-60 wt%) is needed in fabrication of polyimide electrodes.<sup>23,24</sup> This leads to a poor utilization of the electrochemically active sites (functional groups).<sup>25</sup> It is thus important to develop polyimide electrodes with significantly improved electrical conductivity.<sup>20,26</sup> While using nanomaterials such as nanoparticles can enhance the accessibility of the electrochemically active sites for redox reactions,<sup>27,28</sup> these small particles tend to aggregate to form larger ones.

The use of three-dimensional (3D) porous graphene to support nanoparticles is a promising approach to preparing composite electrode materials. Graphene can not only act as a conductive substrate,<sup>29,30</sup> but also provide active sites for nucleation or polymerisation.<sup>31,32</sup> Wei and co-workers<sup>23</sup> have demonstrated a facile strategy for fabricating graphene-polyimide composite electrode materials with application potentials as a cathode for flexible lithium batteries. Xu et. al.<sup>25</sup> have shown an *in-situ* polymerization and self-assembly strategy to prepare graphene foam-polyimide composite films as binder-free cathode for flexible lithium-ion batteries and sodium-ion batteries.

In this paper, we describe a strategy for controlling the morphology and size of polyimide particles by manipulating the interfacial chemistry and interactions between polyimide and graphene. Sodium-ion storage mechanism in the composite was investigated. A sodium-ion capacitor full cell fabricated with the composite as the anode and reduced graphene oxide as the cathode delivered energy densities of 55.5 and 21.5 Whkg<sup>-1</sup> at power densities of 395 and 3400 Wkg<sup>-1</sup>, respectively. A flexible sodium-ion capacitor was also fabricated to demonstrate application potentials for flexible energy storage devices.

## RESULTS AND DISCUSSION

**Preparation and Characterisation of Polyimide-Graphene Nanocomposites.** Three freestanding and flexible polyimide-graphene composite samples (Figure S1), designated as PI-GF (GF = graphene foam), PI-rGO and PI/rGO-rGO, were prepared in this study. Scheme 1 shows the schematic illustration of preparation method. The details of the method of preparation can be found in the Supporting Information. The three samples contained a similar content of PI as can be seen from the TGA data shown in Figure S2. The presence of polyimide in the composites was confirmed by the Fourier transform infrared (FTIR) and <sup>13</sup>C magic angle spinning nuclear magnetic resonance (MAS NMR) spectra depicted in Figure S3. The peak at 1380 cm<sup>-1</sup> is due to the stretching vibration of the imide C–N group. The peaks at 1782, 1715 and 723 cm<sup>-1</sup> correspond to the asymmetric stretching vibration ( $\nu_{as}$ ), symmetric stretching vibration ( $\nu_s$ ) and bending vibration ( $\delta$ ) of the imide group C=O, respectively.<sup>33</sup> The peaks in the <sup>13</sup>C MAS NMR spectra at 165.0, 137.6, 129.5 and 115.9 ppm are assigned to the imide carbonyl carbon, the non-protonated aromatic carbon of the benzimide group, the protonated aromatic benzimide carbon, and the N-substituted aromatic carbon, respectively.<sup>34</sup>

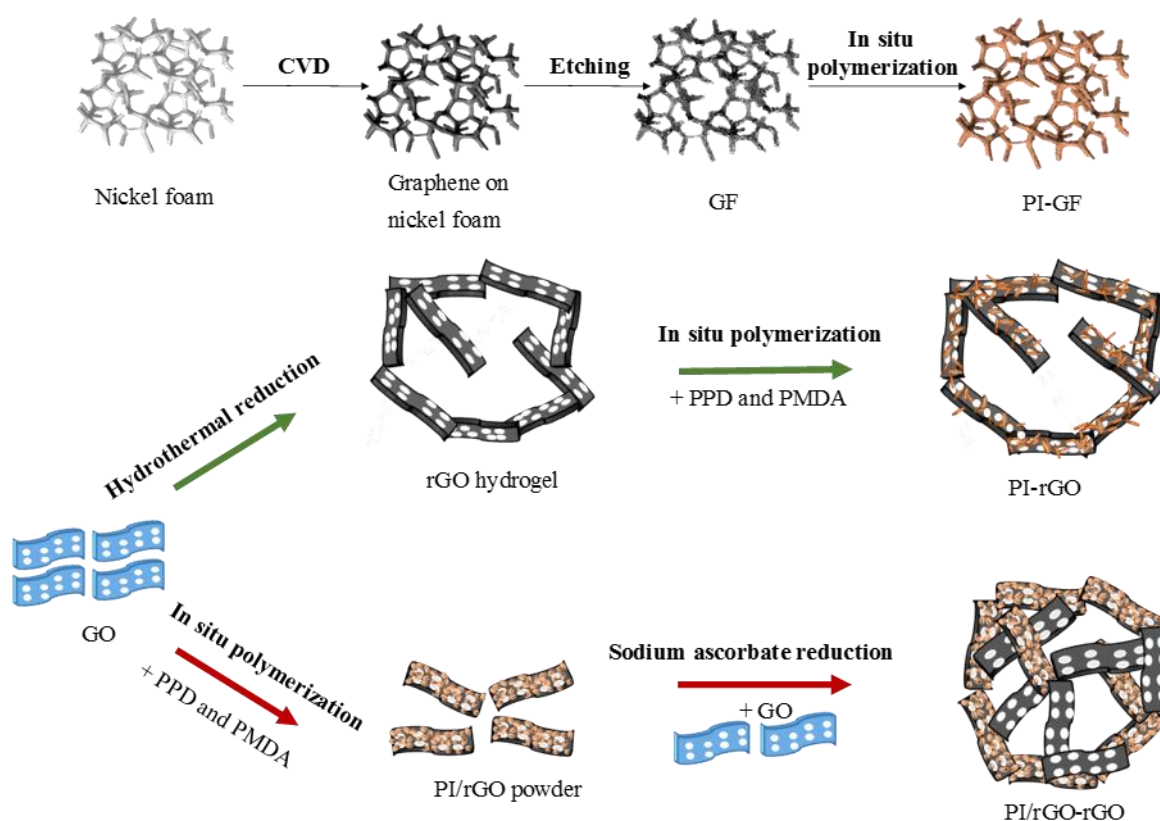
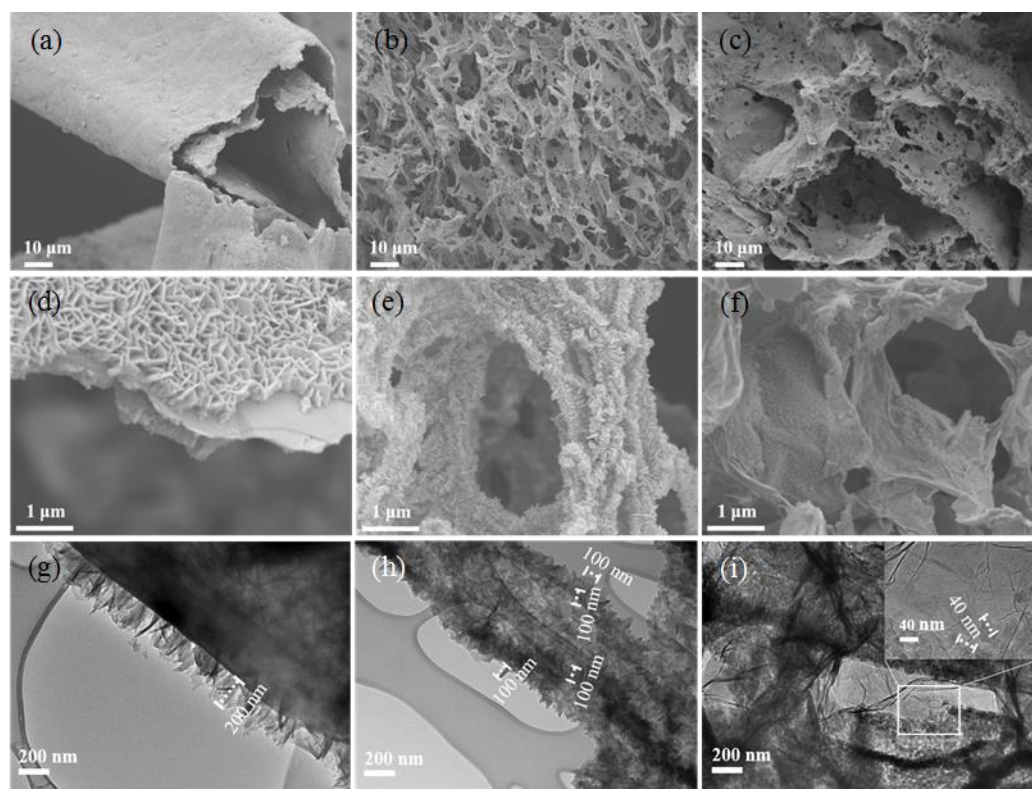
**Scheme 1.** Schematic illustration of preparation of samples PI-GF, PI-rGO and PI/rGO-rGO.

Figure 1 shows the field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of the samples. Flat polyimide nanosheets with an average height of 200 nm grown on both sides of the graphene foam can be clearly seen in Figure 1a, d and g. The FESEM images of PI-GF shown in Figure S4 confirmed the full and conformal inheritance of continuous topographic features of the nickel foam template. For the sample PI-rGO, the rGO is coated with vertically aligned but smaller protuberant polyimide nanoflakes with an average height of 100 nm (Figure 1b, e and h). In contrast to the former two nanocomposites, PI/rGO-rGO was made by a two-step method. The 3D framework was constructed with a polyimide/rGO/polyimide sandwich-like structure (Figure S5) embedded in a conductive rGO framework (Figure 1c, f and i). Polyimide grains with an average diameter of 40 nm were distributed uniformly on the graphene sheets of PI/rGO-rGO. Compared with the pure polyimide particles of  $\sim 15\ \mu\text{m}$  in diameter (Figure S6), all the nanocomposites show nanosized polyimide structures in a 3D interconnected porous network.

The structure is a result of the surface of graphene providing sufficient nucleation sites for the growth of the polyimide particles,<sup>31</sup> resulting in a decreased size.<sup>35</sup> The uniform distribution of the polyimide was confirmed by the energy-dispersive X-ray (EDX) mapping images (Figure S7).



**Figure 1.** (a-f) FESEM images and (g-i) TEM images of (a, d, g) PI-GF, (b, e, h) PI-rGO and (c, f, i) PI/rGO-rGO at different magnifications (the inset of i is an enlarged image of PI/rGO-rGO).

The structures adopted by the polyimides in PI-GF are profoundly different in size and form from those in PI/rGO-rGO, while the polyimide in PI-rGO has an intermediate shape and size. It is evident that the nature of the interface between the polyimide and the graphene plays an important role in determining the final structure.<sup>29,36,37</sup> The surface of the graphene foam (GF) has few functional groups (Figure S8a, b and Table S1), and therefore interactions at the interface are driven by the  $\pi$ - $\pi$  interactions between aromatic rings of the polyimides and GF.<sup>29</sup> In the case of GO, the surface contains abundant oxygen- and nitrogen-containing

groups (Figure S8a, b, c and Table S1) which are able to interact with the functional groups of the polyimide chains. We conclude that the interactions of functional groups of GO and the polyimide are more specific and stronger than the  $\pi$ - $\pi$  interactions. For the rGO with fewer residue surface functional groups (Figure S8a, b and Table S1),  $\pi$ - $\pi$  interactions and relatively weaker interactions between functional groups will both play a role.

On the basis of above observations, a mechanism of formation of the polyimide-graphene nanocomposite materials is proposed and illustrated in Scheme 2. In the formation of PI-GF, the aromatic rings of the polyimide are involved in  $\pi$ - $\pi$  interactions with  $sp^2$ -hybridised carbons of graphene. The polyimide chains are supposed to continue to grow parallel to the graphene plane at the interface. Then under the intermolecular force among the polyimides, multiple chains self-assemble to form flat polyimide nanosheets. Finally, with the chains at the interface parallel to the graphene plane, the self-assembled polyimide nanosheets stand perpendicularly on the surface of the GF.

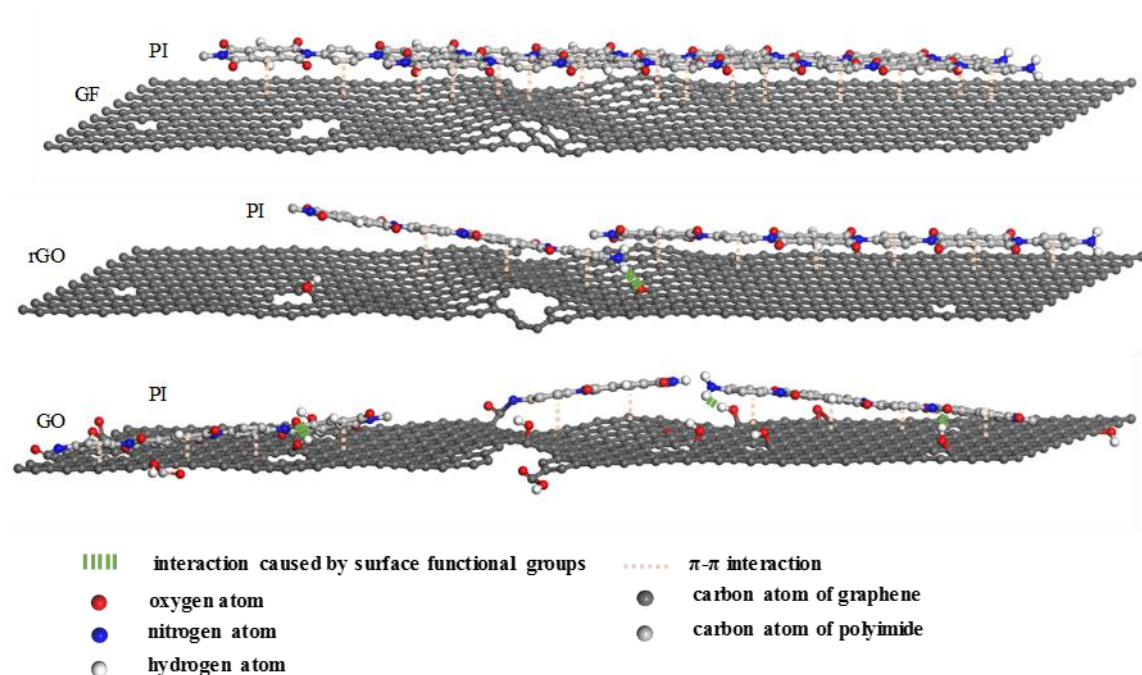
In the case of PI/rGO-rGO, since GO was used in the first step in the synthesis, surface functional groups are believed to be involved. The diamines and dianhydrides undergo in situ polymerization and self-assembly at the interface, under the interaction between the functional groups. At the same time, GO undergoes thermal reduction leading to the removal of surface functional groups, which causes a gradual lessening of interactions between the functional groups and increasing participation of  $\pi$ - $\pi$  interactions between the polyimides and GO. The randomly distributed functional groups on the surface of GO lead to random growth and assembly of the polyimides, finally forming irregular-shaped nanograins of PI on the rGO.

The rGO has a content of surface functional groups intermediate between GO and GF (Figure S8a, b and Table S1). In the formation of PI-rGO, the polyimide chains grow parallel to the graphene plane due to extensive  $\pi$ - $\pi$  interactions, and the self-assembly of the polyimide chains is affected by interactions between the functional groups of the polyimides



and the residue functional groups on the surface of rGO,<sup>32</sup> leading to protuberant polyimide nanoflakes standing perpendicularly on the rGO.

**Scheme 2.** Schematic illustration of the mechanism of formation of the PI-graphene composites. Visual Molecular Dynamics was used to create the graphic.<sup>38</sup>



**Polyimide-Graphene Nanocomposites as Negative Electrode.** The CV profiles between 0.005-3.0 V vs. Na/Na<sup>+</sup> of the PI electrode, PI-GF, PI-rGO and PI/rGO-rGO at a scan rate of 0.2 mV<sup>-1</sup> are shown in Figure S9. All first-cycle profiles show a peak at ~1.25 V, which disappeared in the subsequent cycle. This peak is assigned to the formation of a solid electrolyte interface, which may cause the irreversible capacity loss in initial cycles. Except for PI-GF, there is an obvious peak at ~ 0.25 V, particularly for PI-rGO and PI/rGO-rGO. This peak corresponds to the irreversible trapping of sodium ions in the carbon black in the PI electrode or surface defects of rGO in PI-rGO and PI/rGO-rGO.<sup>39,40</sup> Figure 2a displays the CV curves on the second cycle of different electrodes plotted for comparison. The GF and rGO electrodes show a quasi-rectangular shape without any peaks. It can be observed that the PI



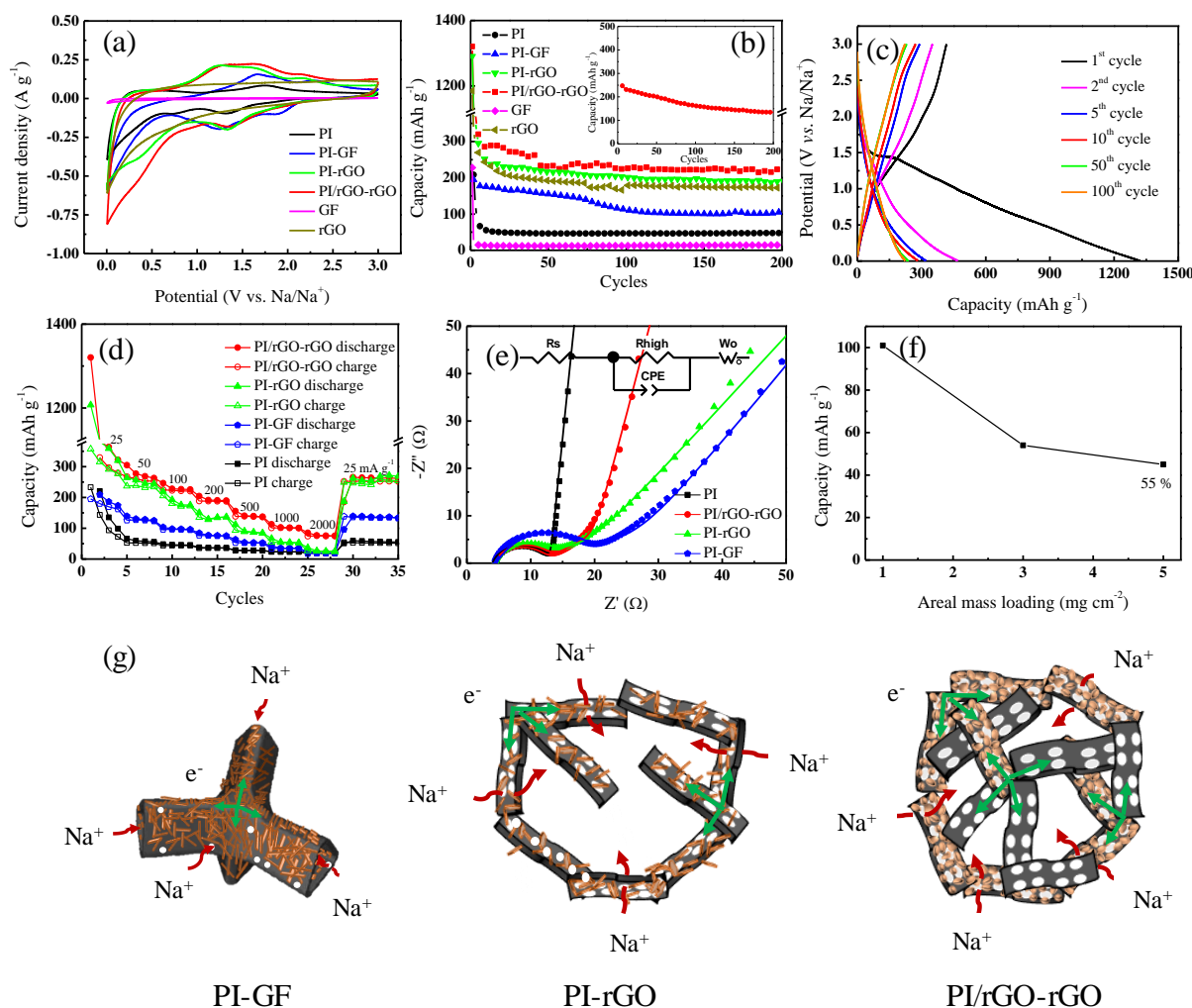
electrode showed the lowest current response while composite PI/rGO-rGO showed the highest current response. The two broad cathodic peaks appearing at potentials of 0.75 and 1.25 V are due to sodiation of the carbonyls to form radical anions and dianions.<sup>41</sup> The broad peak between 1-2 V during the reverse anodic scan is due to the desodiation of the sodiated polyimide.

In line with CV results, all the nanocomposites exhibited much higher capacity than the pure polyimide ( $\sim 50 \text{ mAh g}^{-1}$ , Figure 2b). The higher capacity of the composite materials during cycling is due to the decreased size of polyimide particles in the composites, which exposes more active sites for the redox reactions of carbonyl groups with sodium ions.<sup>42</sup> On the other hand, the higher capacity of PI/rGO-rGO and PI-rGO than PI-GF can be attributed to the contribution from rGO ( $43 \text{ mAh g}^{-1}$  at the 200<sup>th</sup> cycle). Sodium ions are stored in the rGO by adsorption on the graphene sheets, interaction with heteroatoms, and intercalation in the interlayers.<sup>43,44</sup> It should be noted that the current density and specific capacity were only calculated according to the mass of polyimide for PI-GF since GF does not contribute significantly to the charge storage. The narrow interlayer spacing ( $3.5 \text{ \AA}$ ) and absence of abundant surface functional groups on GF are the main causes of the lower sodium ion intercalation and adsorption (Figure S10).<sup>45</sup> However, the calculations for PI-rGO and PI/rGO-rGO were based on the entire composite electrode since rGO contributes significantly to the overall capacity. Among the nanocomposites, the PI/rGO-rGO retained the highest capacity of  $225 \text{ mAh g}^{-1}$  at the 200<sup>th</sup> cycle at  $25 \text{ mA g}^{-1}$  and  $134 \text{ mAh g}^{-1}$  at the 200<sup>th</sup> cycle at  $100 \text{ mA g}^{-1}$ . Additionally, the discharge and charge profiles of PI/rGO-rGO show sloping curves (Figure 2c), indicating fast redox reactions of the PI/rGO-rGO electrode.<sup>22</sup> The fast kinetics for the redox- reaction during the discharge and charge processes identifies it a promising electrode for hybrid sodium-ion capacitors.<sup>46</sup>

As expected, all nanocomposites achieved a higher capacity than the pure polyimide at the same current density (Figure 2d). This is not only because of the decreased size of polyimide

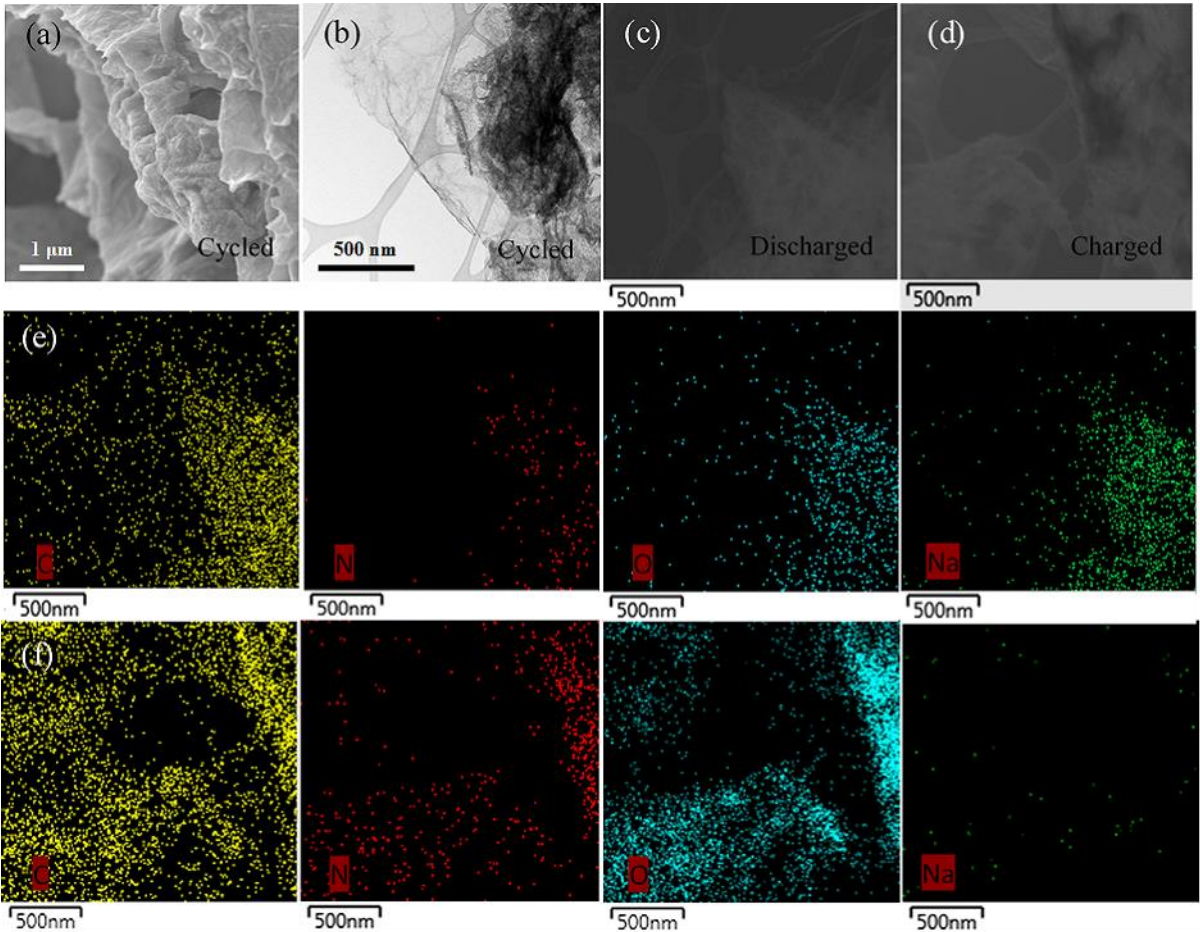
particles exposing more active sites, but also because the 3D interconnected porous framework results in decreased distance diffusion of the electrolyte ions. PI/rGO-rGO shows the best rate performance with a high capacity of 75 mAh g<sup>-1</sup> at a high current density of 2000 mA g<sup>-1</sup>, demonstrating excellent rate capability of the PI/rGO-rGO electrode.

Electrochemical impedance spectroscopy (EIS) measurements of a symmetric cell with two identical electrodes were conducted to provide more accurate impedance data of the electrode-electrolyte interface than that of typical EIS measurements of asymmetric cells with a metal as counter electrode.<sup>47</sup> The Nyquist plots in Figure 2e exhibit a depressed semicircle in the high frequency region, a 45° slope in the middle frequency region and a quasi-vertical line at low frequency, which can be simulated by an equivalent circuit (Figure 2e inset). The intercept on the real axis in the high frequency region is the internal electrolyte resistance ( $R_s$ ). The 45° slope relates to the Warburg element open circuit terminus ( $W_o$ ), reflecting the ionic resistance for the electrolyte-filled pores in the electrode.<sup>48</sup> The depressed semicircle corresponds to the charge-transfer resistance ( $R_{ct}$ ). A smaller  $R_{ct}$  indicates more electron-transfer pathways and faster electrolyte-ion diffusion, which can lead to enhanced cycling stability and rate performance.<sup>49</sup> The PI/rGO-rGO has nearly the same  $R_{ct}$  as the PI electrode using carbon black as the conductive additive, suggesting an excellent inner electrical network built by the rGO in the second preparation step. The more highly developed electron conductive pathways in PI/rGO-rGO account for its superior rate performance compared with the other two composites (Figure 2g). Due to the highly-developed 3D interconnected porous and conductive network of PI/rGO-rGO, the capacity retention can remain at 55 % when the areal mass loading increased five times from 1 mg cm<sup>-2</sup> to 5 mg cm<sup>-2</sup> (Figure 2f), demonstrating great potential for high mass loading in practical applications.



**Figure 2.** (a) CV curves on the second cycle and (b) cycling performance of PI electrode, PI-GF, PI-rGO, PI/rGO-rGO, GF and rGO (inset: cycling performance of PI/rGO-rGO at 100 mA g<sup>-1</sup> from 5<sup>th</sup> cycle); (c) the discharge and charge curves of PI/rGO-rGO at different cycles; (d) the rate performance of the PI electrode, PI-GF, PI-rGO and PI/rGO-rGO; (e) Nyquist plots for a symmetric cell using two identical electrodes at a state of charge (SOC) of 0 % (inset: simulated equivalent circuit); (f) the retention of specific capacity as a function of mass loading for PI/rGO-rGO at 500 mA g<sup>-1</sup>; (g) the schematic illustration of pathways for electron conduction (green arrows) and sodium ion diffusion (red arrows) in the 3D polyimide and graphene composites.

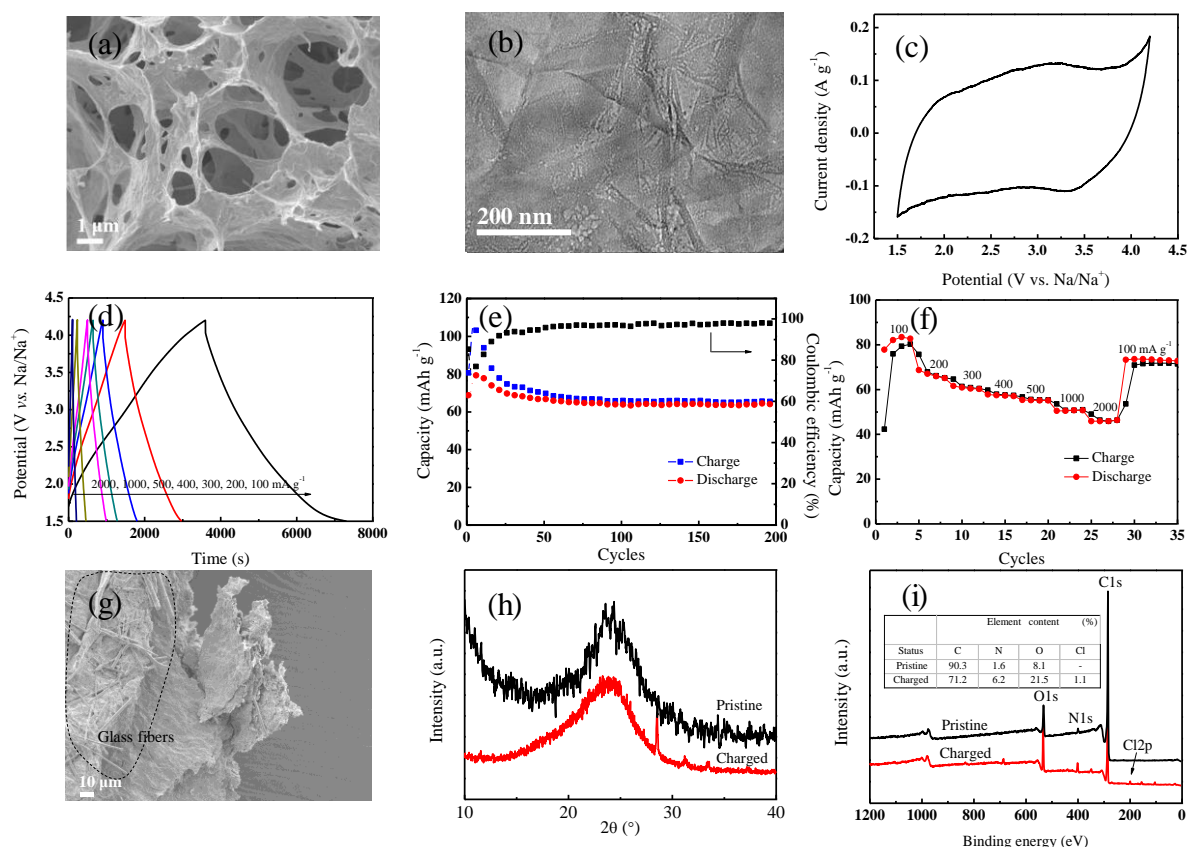
After long-term cycling, the morphology and structure of the PI/rGO-rGO electrode were preserved (Figure 3a-d) compared with the pristine electrode (Figure 1h and i). The EDX mapping images (Figure 3e and f) of the discharged and charged PI/rGO-rGO electrodes confirmed the reversible storage of sodium ions in the composite electrodes.



**Figure 3.** (a) FESEM and (b) TEM images of the PI/rGO-rGO electrode after 200 cycles; the scanning transmission electron microscopy (STEM) images of (c) discharged and (d) charged PI/rGO-rGO electrode; the EDX mapping images of (e) discharged and (f) charged PI/rGO-rGO electrode.

**Reduced Graphene Oxide as Positive Electrode.** Reduced graphene oxide (rGO) displays an interconnected 3D macroporous morphology (Figure 4a) with nanopores on the sheets (Figure 4b), consistent with the results of nitrogen adsorption-desorption measurements

(Figure S11). The CV measurements for the rGO positive electrode (Figure 4c) were conducted at a high potential range from 1.5 to 4.2 V (vs. Na/Na<sup>+</sup>), which is not favourable for intercalation/deintercalation of the anions.<sup>50</sup> The current peak at the high potential of 4 V vs. Na/Na<sup>+</sup> may be due to the decomposition of the electrolyte. The CV curve with a very slightly biased rectangular shape and the slightly bent galvanostatic charge and discharge (GCD) profiles (Figure 4d) demonstrated a capacitor-like response. This suggests an electrical double-layer capacitance (EDLC) charge storage mechanism combined with a surface redox reaction.<sup>51</sup> The rGO electrode shows a high capacity of ~70 mAh g<sup>-1</sup> and nearly 100 % coulombic efficiency at the 200<sup>th</sup> cycle (Figure 4e). This is significantly higher than the capacity (44 mAh g<sup>-1</sup>) of a commercial AC (Figure S12). The excellent rate capability and capacity recovery were also confirmed by results presented in Figure 4f. A high capacity of 46 mAh g<sup>-1</sup> was achieved at 2000 mA g<sup>-1</sup>, and a reversible capacity of 72 mAh g<sup>-1</sup> was recovered when the current density was reduced to 100 mA g<sup>-1</sup>. It can be seen from Figure 4g that the morphology of rGO was preserved after long-term cycling. The glass fibres marked in the FESEM image are from the separator. The negligible differences in the X-ray diffraction (XRD) patterns (Figure 4h) between the pristine and charged state confirms lack of intercalation by the perchlorate anions. The sharp peak of the XRD pattern of the charged electrode may come from the impurity. The changes in percentages of chlorine to oxygen are not at the ratio of 1:4 (Figure 4i), which further confirms that the charge storage mechanism is not solely based on EDLC. Therefore, we deduce that the capacity of the rGO electrode operated at high potential range of 1.5-4.2 V arises from the EDLC of perchlorate anions and the pseudocapacitance from reversible surface redox reactions<sup>52</sup> between the residue surface functional groups and sodium ions.



**Figure 4.** (a) FESEM image, (b) TEM image, (c) CV curve at a scan rate of  $1 \text{ mV s}^{-1}$ , (d) GCD profiles at different current densities, (e) cycling performance at the current density of  $100 \text{ mA g}^{-1}$  and (f) rate capability of rGO; (g) the FESEM image of rGO electrode after 200 cycles; the (h) XRD patterns and (i) X-ray photoelectron spectroscopy (XPS) survey of the pristine rGO electrode and the rGO electrode charged to 4.2 V.

**Electrochemical Performance of a Hybrid Sodium-ion Capacitor.** Following assessment of the performance of the polyimide-graphene nanocomposites in half cells, PI/rGO-rGO was selected as the negative electrode and rGO as the positive electrode to assemble a hybrid capacitor. The mass ratio of positive electrode to negative electrode was set at approximately 3:1, based on the capacities of both electrodes with some overcapacity of the rGO positive electrode to allow better potential stability for the PI/rGO-rGO negative electrode.<sup>53</sup> Based on the above study of the negative electrode and positive electrode, a working mechanism of the PI/rGO-rGO//rGO NIC is proposed (Figure 5a). Upon charging, the PI/rGO-rGO negative

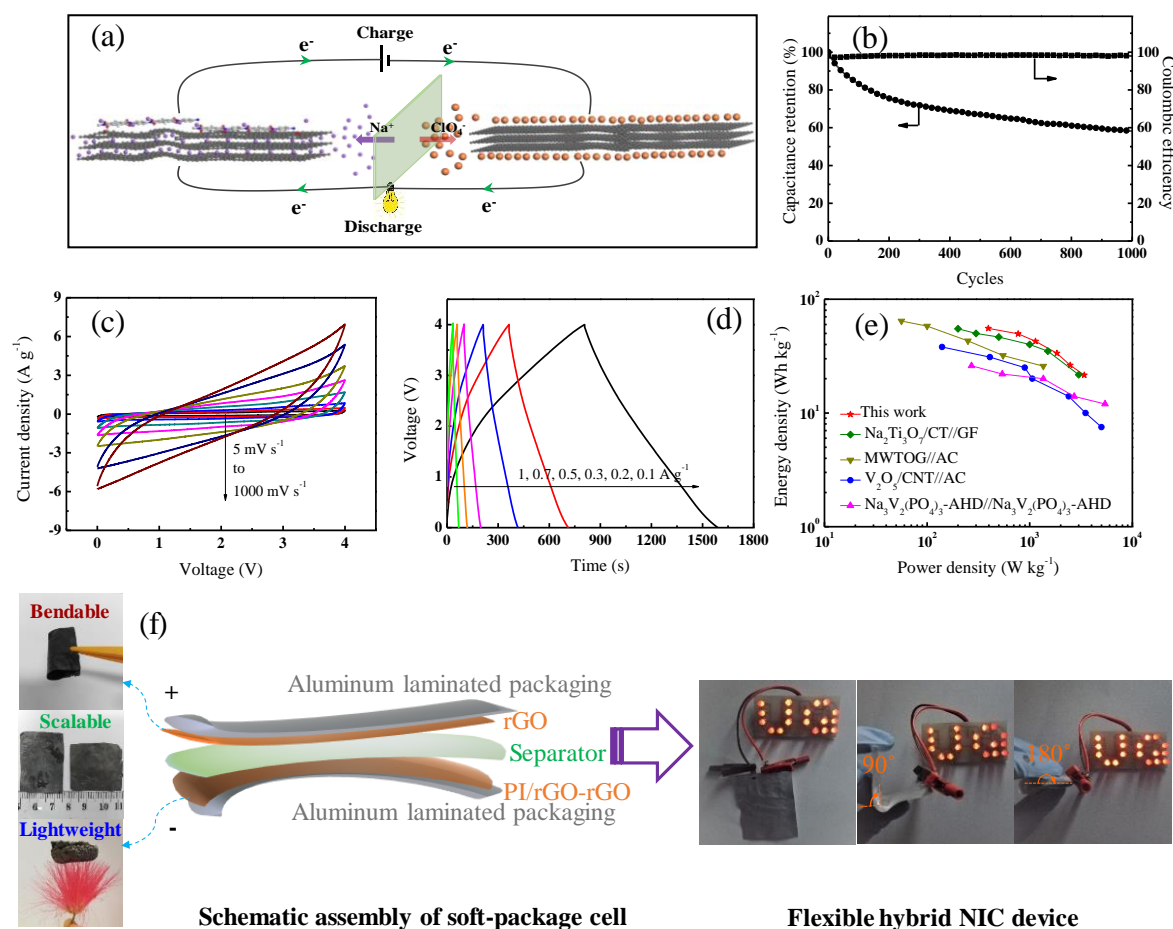
electrode experience a reversible redox reaction of sodium ions via enolization with the carbonyl groups of the polyimide and reversible storage of sodium ions in rGO, while the rGO positive electrode adsorbs perchlorate anions reversibly and releases sodium ions from the functional groups on the surface. During the subsequent discharge, the reverse process occurs.

It should be noted that analyses of the electrochemical tests of the hybrid capacitor were based on the overall mass or the total volume of the freestanding PI/rGO-rGO negative electrode and rGO positive electrode. The hybrid NIC shows a capacitance retention of ~ 60 % at the 1000<sup>th</sup> cycle at a wide voltage of 4 V, with a high coulombic efficiency near to 100 % (Figure 5b). Such a wide voltage can cause a capacity decade, which may be resulted from the degradation of the residue oxygen functionalities on the surface of rGO.<sup>54,55</sup> The decomposition of electrolyte might be also responsible for the capacity decay, since the current peak of rGO electrode was observed at the high potential which may be due to the electrolyte decomposition. The CV curves (Figure 5c) generally displays a rectangular shape, indicating that the hybrid NIC mainly shows capacitive behaviour. The shape of the CV curves is retained at a high scan rate of 1000 mV s<sup>-1</sup>, demonstrating high power capability of the hybrid NIC.<sup>56</sup> Figure 5d shows negligible initial voltage loss (IR drop) of the discharge profiles, suggesting a low internal resistance and fast current-voltage response of the hybrid NIC. A high gravimetric energy density of 55.5 Wh kg<sup>-1</sup> was achieved at a gravimetric power density of 395 W kg<sup>-1</sup>, and the hybrid NIC can retain a gravimetric energy density of 21.5 Wh kg<sup>-1</sup> at the gravimetric power density of 3400 W kg<sup>-1</sup> (Figure 5e). Such a combination of high gravimetric energy and power densities is superior to many other NICs (Figure 5e). The volumetric performance of the NIC was also evaluated, as is shown in Figure S13. High volumetric energy densities of 58.8 Wh L<sup>-1</sup> and 20.7 Wh L<sup>-1</sup> were achieved at the gravimetric power densities of 426 W L<sup>-1</sup> and 3546 W L<sup>-1</sup>, respectively. The electrochemical performance demonstrated that this hybrid system integrating a battery-like component and capacitor-like



component is promising to overcome the challenges of the capacitance mismatch and sluggish kinetics, bridging the gap between batteries and capacitors.

To test the potential of the hybrid NIC in practical applications, larger-sized electrodes were made by increasing ten-times the amounts of reagents in assembling soft-package hybrid NIC cells (Figure 5f). The scalable freestanding electrode was very flexible and very light, for example freestanding on a Persian silk flower. The flexible hybrid NIC can light up an electronic device containing 18 light-emitting diode (LED) lamps under different bending status after 1 min charge. The NIC shows no obvious change for the charge and discharge curves at the bending angles ranging from 0° to 180° (Figure S14a). As is shown in Figure S14b, the NIC kept a capacitance retention of 57 % when the mass loading was increased from 6.2 mg cm<sup>-2</sup> to 13.1 mg cm<sup>-2</sup>. The capacitance of the NIC shows negligible changes within the temperature range from 25 °C to 55 °C. The NIC demonstrates good production scalability of the electrode materials and great potential for application in flexible electronic devices.



**Figure 5.** (a) The schematic illustration of the configuration of the PI/rGO-rGO//rGO NIC cell (the movement of electrolyte ions showing the discharge process); the electrochemical performance of the PI/rGO-rGO//rGO NIC: (b) cycling performance at a current density of  $100 \text{ mA g}^{-1}$ , (c) CV curves at different scan rates of 5, 10, 20, 50, 100, 200, 500 and  $1000 \text{ mV s}^{-1}$ , (d) GCD curves at different current densities, (e) gravimetric energy-power density performance in comparison with other reported NICs (MWTOG//AC<sup>8</sup>,  $\text{Na}_2\text{Ti}_3\text{O}_7/\text{CT}/\text{GF}$ <sup>57</sup>,  $\text{V}_2\text{O}_5/\text{CNT}/\text{AC}$ <sup>58</sup>,  $\text{Na}_3\text{V}_2(\text{PO}_4)_3\text{-AHD}/\text{Na}_3\text{V}_2(\text{PO}_4)_3\text{-AHD}$ <sup>59</sup>, MWTOG:  $\text{TiO}_2$  meso-cage graphene nanocomposite, CT: carbon textile, GF: reduced graphene oxide film, CNT: carbon nanotube, AHD: ambient hydrolysis deposition); (f) the schematic assembly of a soft-package hybrid NIC using flexible freestanding electrodes and its practical application to LED panel. Visual Molecular Dynamics was used to create the graphic in (a).<sup>38</sup>

## CONCLUSIONS

In summary, polyimide-graphene nanocomposites with different polyimide particle sizes (ranging from ca. 40 to 200 nm) were prepared using different graphene substrates. A flexible, freestanding and light polyimide-graphene nanocomposite prepared using the two-step self-assembly method exhibited a capacity of 225 mAh g<sup>-1</sup> at the 200<sup>th</sup> cycle in sodium-ion batteries, much higher than that of the pure polyimide (~ 50 mAh g<sup>-1</sup>). This remarkable improvement in sodium ion storage capacity is due to the small particle size of the polyimide grown in the graphene framework and the high conductivity of the graphene. This preparation method can be scalable for mass-production of high-performance freestanding polyimide-graphene nanocomposite electrodes, making commercialisation feasible. It should also be noted that the entire synthesis process is very simple and green without introduction of any chemicals harmful to environment. In addition, the reduced graphene oxide can be a suitable positive electrode, presenting a much higher capacity (~ 70 mAh g<sup>-1</sup>) than commercial activated carbons (44 mAh g<sup>-1</sup>) via electrical double layer capacitive and pseudocapacitive mechanisms. A flexible hybrid sodium-ion capacitor was assembled using the freestanding polyimide-graphene nanocomposite as the negative electrode and reduced graphene oxide as the positive electrode. A high energy density of 55.5 Wh kg<sup>-1</sup> at a power density of 395 W kg<sup>-1</sup> and energy density of 21.5 Wh kg<sup>-1</sup> at a power density of 3400 W kg<sup>-1</sup> were achieved, outperforming many other sodium-ion capacitors. This paper demonstrates an innovative and scalable strategy for synthesizing polyimide-graphene composite electrode materials for next-generation, green and flexible energy storage devices.

## ASSOCIATED CONTENT

Supporting Information Available: Experimental section, additional figures and table as mentioned in the manuscript, involving sample characterizations and electrochemical measurements.

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### Notes

There are no conflicts to declare.

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