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## Introduction

The increasing demand for regenerable energy resources with enhanced energy density encourages the race for finding new devices for energy-production and storage, including solar cells, fuel cells, rechargeable batteries and supercapacitors. Among such devices, supercapacitors are some of the most potential devices. They exhibit many advantages, including high energy density, a fast charge/discharge rate and excellent durability. These features enable supercapacitors to be efficiently used in hybrid electric vehicles and electronic devices. Electrochemical capacitors are classified into two major categories; they are electric double layer capacitors (EDLC) and pseudocapacitors (PC). The non-faradic process occurring in EDLC is caused by ion absorption on the active electrode materials at the electrode/ electrolyte interface. On the other hand, the faradic process occurring in PC is involved with the redox reactions originated



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A magnetic graphene composite derived from stage-1 FeCl<sub>3</sub>-graphite intercalation compounds was thermally treated for up to 75 min at 400 °C or for 2 min at high temperatures up to 900 °C. These heat-treatments of the magnetic graphene composite gave rise to the cubical expansion of graphene with the enlargement of inter-graphene distances. The specific capacitance of the magnetic graphene composite increased upon heating and reached 42 F g<sup>-1</sup> at a scan rate of 5 mV s<sup>-1</sup> in 1.0 M NaCl, after being treated for 2 min at 900 °C. This value corresponds to 840% increase in the capacitance activity superior to that (5 F g<sup>-1</sup>) of the pristine magnetic graphene composite before heat-treatment. This capacitance enhancement can play a significant role in the increase of the surface area that reached 17.2 m<sup>2</sup> g<sup>-1</sup> during the non-defective inter-graphene exfoliation. Moreover, the magnetic graphene composite heated at 900 °C was hybridized with polyaniline by *in situ* polymerization of aniline to reach a specific capacitance of 253 F g<sup>-1</sup> at 5 mV s<sup>-1</sup>. The current procedure of heat-treatment and hybridization with a conductive polymer can be an effective method for attaining a well-expanded magnetic graphene composite possessing an enhanced electrochemical activity with a relatively high energy density (141 W h kg<sup>-1</sup> in 1.0 M NaCl) and an excellent stability (99% after 9000 cycles of 20 A g<sup>-1</sup>).

by the charge transfer reactions of metal/metal oxide electrodes. EDLC and PC with various nano-architectures and morphologies have extensively been investigated to achieve the high-energy storage and the effective capacitance activity.<sup>1–5</sup>

CHEMISTRY

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Carbon-based materials including graphene are unique sources of EDLC due to their unique physical, chemical, electrical and mechanical properties, and conductive polymers or metal oxides are main components of PC owing to their strong electroconductivity. However, the energy density of carbon-based capacitors is not high enough in comparison with PC, and PC is not stable enough under stronger electrochemical conditions. Then the hybrids of EDLC with different materials including other carbon materials, metal oxides and polymers will provide the preferably appropriate platform for hybrid capacitors. Especially, the conjugation of conductive polymers<sup>6</sup> with carbon materials can play a crucial role in capacitance enhancement due to the increase in the conductivity and the addition of faradic capacitance to the EDLC. Among different conductive polymers used, polyaniline (PANI) has attracted exceptional attention due to its mild synthesis procedures.<sup>7,8</sup> In situ polymerization and electrodeposition are two main methods to bind the conductive polymers with graphene oxide (GO) and reduced graphene oxide (rGO), and the implantation of the conductive polymers on the graphenized functional groups is the main way for polymerization. However, GO or rGO

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provides the defective graphenized structure and thus the strong internal resistance drop in the charge/discharge process.<sup>9</sup>

In order to avoid the internal resistance drop, non-destructive exfoliation and polymerization processes are required. In our previous research, we have successfully exfoliated the defect-free graphene with remaining iron oxide nanoparticles via a mild amine treatment of graphite.<sup>10</sup> Herein, this defect-free graphene sheets were further expanded through the thermal procedure, and PANI was conjugated (hybridized) with the thermally expanded, non-defected graphene sheets. The as-prepared graphenes and their hybrids were devoted to the investigation of capacitance, one of the important electrochemical parameters of energy storage devices, since these materials were expected to be able to achieve the typical supercapacitor behaviour with favourable efficiency. Structural characterization was performed to scope the optimum condition that provides the effective capacitance. Hybrids of graphene (EDLC material) with electroconductive polymers (PC material) should become new generation capacitors.

## Experimental section

### Reagents

Indium tin oxide (ITO) glass and flake graphite (size 250–300  $\mu$ m) were purchased from Uni-Onward Co., Taiwan, and Ito graphite Co. Ltd, Japan, respectively. Dodecylamine, *N*-methylpyrrolidone (NMP), aniline and ammonium persulfate were bought from Acros Organics, UK. Polyvinylidene fluoride was a product from Sigma Aldrich, USA. Other reagents were of commercial grade. All materials were used as supplied, except that anhydrous iron chloride (FeCl<sub>3</sub>, Acros Organics, UK) was dried overnight under vacuum before being used.

### Instruments

Field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX) and elemental mapping measurements were achieved using a JEOL JSM-6500F microscope (Japan). Thermogravimetric analyses (TGA) were carried out on a Q 500 TA appliance (USA) in the range from room temperature to 850 °C and at a rate of 10.0 °C min<sup>-1</sup> under air flow. The Raman scattering spectrum was recorded using a Horiba Jobin Yvon iHR550 imaging spectrometer (Japan) with a laser excitation of 633 nm and a laser power of 10 mW. The spectrum was recorded at an exposure time of 80 s and with an accumulation of 10 scans. Magnetization measurement was performed using a TM-VSM151483N7-MRO (Tamakawa Co., Japan) at ambient temperature. Cyclic voltammogram (CV) and galvanostatic charge/discharge charts were obtained through a Zahner Zennium E electrochemical workstation (Germany). Brunauer-Emmett-Teller (BET) surface area was evaluated from the N<sub>2</sub> adsorption-desorption isotherm using a BELSORP-max (Japan).

### Heat-treatment of graphene

The preparation of a heat-treated magnetic graphene composite consists of two major steps. The first step is the exfoliation of the stage-1 FeCl<sub>3</sub>-graphite intercalation compound (GIC) following our previous report.<sup>10</sup> Briefly, graphite was heated with dried anhydrous iron chloride for 72 h at ~340 °C in a muffle furnace. The product, FeCl<sub>3</sub>-GIC, was reacted with dodecylamine for 6 h at 90 °C, washed with acidic ethanol and dried for 1 h at 60 °C. The second step is annealing *via* keeping the amine-exfoliated magnetic graphene composite for adequate time periods in a muffle furnace adjusted at high temperatures.

# Polymerization on a heat-treated exfoliated graphene composite

For polymerization of aniline, 0.3 mL of aniline was dissolved in 1.0 M  $H_2SO_4$  in ethanol and 100 mg of the heat-treated exfoliated graphene composite (for 2 min at 900 °C) was added. The mixture was stirred until completely dispersed, and 0.18 g of ammonium persulfate dissolved in a 1 M  $H_2SO_4$  ethanol solution was slowly added to the mixture. The mixture was continually stirred for one day, filtered, rinsed with ethanol and dried in a vacuum overnight at 50 °C.

#### **Electrochemical characterization**

To prepare working electrodes, 20 mg of the heat-treated magnetic graphene composite was added to 2.0 mg of polyvinylidene fluoride in a suitable amount of *N*-methylpyrrolidone, and the mixture was stirred overnight at 65 °C. The resulting homogeneous slurry was laid on the ITO substrate, which was cleaned ahead with UV-ozone treatment for 5 min,<sup>11</sup> and it was then dried overnight at 65 °C. The electrochemical properties were tested at room temperature by CV and galvanostatic charge/discharge measurements in an aqueous electrolyte solution (1.0 M NaCl) using a three-electrode system with Ag/AgCl as a reference electrode, platinum wire as a counter electrode. The cycling range was between -1.0 and 1.0 V, and the scan rates were varied from 1 to 200 mV s<sup>-1</sup>.

The capacitance (*C*), energy density (*E*) and power density (*P*) were calculated from the CV curves according to the following equations.<sup>12,13</sup>

$$C = i/s \tag{1}$$

$$E = \frac{1}{2}CV^2 \tag{2}$$

$$P = Es/V = \frac{1}{2}CVs \tag{3}$$

where *i* is the average current density, *s* is the scan rate, and *V* is the potential window. The current density  $(i = \int i(v) dv/mV)$  was calculated based on the integration of the area of the CV curve and normalization by mass *m* of the magnetic graphene, which was 2 mg on the  $1 \times 1$  cm<sup>2</sup> electrode.

The charge/discharge behaviors were also investigated at different current densities starting from 0.25 A  $g^{-1}$  up to 20 A  $g^{-1}$ .

## Results and discussion

# Characterization of the heat-treated expanded graphene composite

The amine-treated exfoliated graphene composite prepared from acceptor-type stage-1 FeCl<sub>3</sub>–GIC was further treated by heating in this study. The influence of heating on the graphene composite appeared as its volume increase: as seen in Fig. 1(left), heating for long periods of 20 and 75 min at 400 °C or heating for 2 min at temperatures higher than 400 °C yielded the enormous volume expansion. The expansion behavior has been reported on donor type GIC using thermal treatment,<sup>14</sup> high vacuum exfoliation,<sup>15</sup> arc discharge<sup>16</sup> and other procedures.<sup>17</sup> However, such a strong exothermic reaction leads to functionalization and defects of graphene, and consequently nondestructive methods have been strongly required.

Because this volume expansion could cause the morphology change, FESEM observation was carried out. As seen in Fig. 1(right) (a-e), keeping long periods up to 75 min at 400 °C or heating for 2 min at high temperatures up to 900 °C gave rise to the enormous expansion of the interlayer distance of the graphene, different from graphene treated for 2 min at 400 °C (Fig. 1(a)). This regularly expanded morphology with accordion-like aspect was quite similar to that of the exfoliated products from graphene oxide via microwave heating,<sup>17</sup> laser heating<sup>18</sup> and explosive CO<sub>2</sub> pressure release,<sup>19</sup> from sulfuric acid-intercalated graphite<sup>20</sup> and from different donor-type GICs.<sup>21</sup> On the other hand, the expansion of the acceptor-type GIC was studied upon fluorinated graphite,<sup>22</sup> and the use of hydrogen peroxide yielded the exfoliation of magnetic graphene with a disordered morphology.<sup>23</sup> However, the procedures reported before indicated high defects of sheets because carbon dioxide release causes explosive reactions. Although the heating procedures of the acceptor-type GIC in the present study showed a similar expansion morphology via amine decomposition and release, this exfoliation procedure is more sophisticated, namely, easier, less defective, explosive or functionalized.

Since the expanded graphene layers may give rise to the change in the surface area, the N2 adsorption/desorption behavior of magnetic graphene was characterized by BET measurements. As seen in Fig. S1(a), ESI,† the magnetic graphene composite, which was treated for 2 min at 400 °C, revealed a nonhysteresis loop of type ( $\Pi$ ), indicating a non-porous structure with a very low surface area. However, the adsorption/desorption curves of the magnetic graphene composite exposed to 400 °C for 20, 45 and 75 min showed a hysteresis loop of type  $(\Pi)^{24}$  with a surface area of 2.3, 8.4 and 8.9  $m^2 g^{-1}$ , respectively, (see Table 1). In addition, a similar increase of the surface area was observed, when the magnetic graphene composite was treated for 2 min at high temperatures of 600, 800 and 900 °C (see Fig. S1(b), ESI<sup>+</sup>). The adsorption/desorption curves indicated a hysteresis loop of type ( $\Pi$ ) with surface areas of 4.3, 9.9 and 17.2 m<sup>2</sup> g<sup>-1</sup>, respectively, (see Table 1). Thus, the surface area increased with the thermal treatment. These results are consistent with the volume increase or the interlayer distance expansion of the magnetic graphene composite.<sup>25</sup> The increase of the surface area caused by



Fig. 1 (left) Photographic images of magnetic graphene composite after heat-treating at different time periods and temperatures. (right) FESEM images of magnetic graphene composite after heat-treating at (a) 2 min, 400 °C, (b) 20 min, 400 °C, (c) 75 min, 400 °C, (d) 2 min, 600 °C, and (e) 2 min, 900 °C. (f) Magnetic graphene composite (treated for 2 min at 900 °C)/PANI composite. Left: low magnification, right: high magnification.

| Treatment      | Surface area $(m^2 g^{-1})$ | Capacitance (F $g^{-1}$ ) at 1 mV $s^{-1}$ | Capacitance (F $g^{-1}$ )<br>at 5 mV $s^{-1}$ |
|----------------|-----------------------------|--|---|
| 2 min, 400 °C  | 0.5                         | 32   | 8   |
| 20 min, 400 °C | 2.3                         | 68   | 21  |
| 45 min, 400 °C | 8.4                         | 76   | 34  |
| 75 min, 400 °C | 8.9                         | 85   | 34  |
| 2 min, 600 °C  | 4.3                         | 75   | 39  |
| 2 min, 800 °C  | 9.9                         | 86   | 39  |
| 2 min, 900 °C  | 17.2                        | 95   | 42  |

the heating process was also observed for carbon nanotubes and it played an important role in the capacitance enlargement of carbon nanotubes.<sup>26</sup> The thermally exfoliated graphene composite also increased the surface area with the oxidation procedure.<sup>27</sup> However, as seen in Table 1, the obtained surface area of the expanded graphene composite was incredibly smaller than graphene oxide of donor-type GIC (2400 m<sup>2</sup> g<sup>-1</sup>,<sup>28,29</sup> 891 m<sup>2</sup> g<sup>-1</sup> and 745 m<sup>2</sup> g<sup>-130,31</sup>) and fullerene tubes (1600 m<sup>2</sup> g<sup>-1</sup>)<sup>32</sup> at similar heating procedures, since the present heat-treated graphene composite does not have enough pores to adsorb gas.

To further analyze the influence of the heating procedure, TGA was carried out for the heat-treated graphene composite. As shown in Fig. 2(a), the remaining organic moiety (dodecylamine) (below 600 °C) was observed due to weight loss in the magnetic graphene composite treated for 2 and 20 min at 400 °C and for 2 min at 600 °C. Meanwhile, the weight loss below 200 °C observed in the composites treated for 20 min at 400 °C and for 2 min at 600 °C might be due to volatile byproducts resulted from heat-treatment at medium temperatures and periods, since such weight drop is not found for composites treated for 2 and 75 min at 400 °C and 2 min at 900 °C. That is, the contaminant byproducts and the organic moiety disappeared or diminished, respectively, in the magnetic graphene composite after heating for 75 min at 400 °C and, eventually, both completely disappeared in the magnetic graphene composite treated for 2 min at 900 °C. The disappearance of the organic moiety (dodecylamine) may be associated with the variation in the morphology (Fig. 1) of the magnetic graphene composite, since the expansion between graphene layers allows the release of the inserted organic moiety. Therefore, it is supposed that the release of the organic moiety was due to the increase of the interlayer distance. At temperatures (above 700 °C) higher than the decomposition of the graphene moiety, the weight loss did not occur and the solid residues were colored reddish brown, indicating the remaining of iron oxide. Then, the fraction of the residues gradually increased with increasing heat-treating time period and temperature. Supposing that the magnetic graphene composite initially contained an additive (organic moiety: dodecylamine) and it was removed with heat-treatment, its removal changed the iron oxide content from 20 wt% in the additive-included magnetic graphene composite treated for 2 min at 400 °C to 42 wt% in the additive-free magnetic graphene composite treated for 2 min at 900 °C.



**Fig. 2** (a) TGA of magnetic graphene composite heat-treated for 2, 20 and 75 min at 400 °C and for 2 min at 600 and 900 °C. (b) TGA of magnetic graphene composite (treated for 2 min at 900 °C)/PANI composite by comparison to magnetic graphene composite treated for 2 min at 900 °C.

The G (sp<sup>2</sup> orbital) band in Raman spectra results from the first order Raman scattering due to the electron-hole interaction in the T point of the Brillouin zone.<sup>33</sup> Whereas, the D (sp<sup>3</sup> orbital) band should be observed at around 1350 cm<sup>-1</sup> as a result of the breathing mode of sp<sup>2</sup> electron orbitals in a second order Raman scattering with an interval process in the electronphonon interaction. Raman scattering spectra (Fig. 3) show the non-defective effective expansion of all thermal-treated magnetic graphene composites without any observable D band as well as of the magnetic graphene composite without thermal treatment. Here, two G bands observed at 1580 and 1619 cm<sup>-1</sup> can be attributed to G bands of exfoliated graphene and stage I FeCl<sub>3</sub>-GIC with strain shift, respectively.<sup>34,35</sup> This difference in band positions arises from the low Fermi energy level of FeCl<sub>3</sub>-GIC due to the charge transfer from graphene (donor) to FeCl<sub>3</sub> (acceptor).<sup>36</sup> Dodecylamine-incorporated FeCl<sub>3</sub>-GIC is thermally exfoliated with heating, and the remaining dodecylamine is completely removed after heating for 2 min at 900 °C, as confirmed by TGA measurements (Fig. 2). Then the G band of exfoliated graphene becomes majority. However, the heating of the magnetic graphene composite for a long time period at 400 °C was not sufficient to completely exfoliate the graphene sheets. This was obviously observed as the third G band at 1600 cm<sup>-1</sup>, which can be assigned to the second intercalation stage (maybe, stage II), indicating a change in the intercalation stage with partial exfoliation. After all, the heating at 900 °C achieved almost complete exfoliation of the graphene sheets compared to the case of longer time heating at 400 °C.



Fig. 3 Raman spectra of magnetic graphene composite heat-treated for 2, 20 and 75 min at 400  $^\circ\text{C}$  and for 2 min at 600 and 900  $^\circ\text{C}.$ 



Fig. 4 Magnetization curves of magnetic graphene composite treated for 2 min at 500, 600, 700 and 900  $^\circ\text{C}.$ 

The magnetic property after heat-treatment was evaluated by magnetization measurements. As seen in Fig. 4, a superparamagnetic profile was observed for every magnetic graphene composite treated at different temperatures. The result indicates that the heat-treatment did not affect the superparamagnetic properties, although the saturation magnetization increased with increasing heat temperature. The existence of the Fe element in the magnetic graphene composite after thermal treatment was confirmed by elemental maps (Fig. S2, ESI†), which display the distribution of Fe and O atoms on a piece of magnetic graphene composite treated for 2 min at 900 °C. Both atoms were distributed on the whole graphene composite, indicating the uniform distribution of iron oxide in the magnetic graphene composite.

# Electrochemistry of the heat-treated expanded magnetic graphene composite

The heat-treated expanded magnetic graphene composite was evaluated by electrochemistry. As analyses of the capacitance behavior, charge/discharge and CV measurements were performed



**Fig. 5** Charge/discharge curves of magnetic graphene composite treated for 20 min at 400 °C. (a) Cycles at current densities of 0.25, 0.4 and 1.0 A  $g^{-1}$ . (b) Multiple cycles at current density of 1.0 A  $g^{-1}$ .

in an aqueous solution of 1.0 M NaCl as an eco-friendly electrolyte, unlike other researches using organic electrolytes.<sup>37</sup> Moreover, the condition of 1.0 M NaCl can provide a wide potential window in the range between -1.0 to +1.0 V (for Ag/AgCl reference electrode). The charge/discharge periods showed an excellent dependence on the current densities from 0.25 to 1.0 A g<sup>-1</sup> for magnetic graphene composite treated for 20 min at 400 °C (see Fig. 5(a)). Namely, increasing current density caused the decrease of the charge/discharge periods with a negligible potential drop at all investigated current densities.

In addition, identical symmetrical charge/discharge curves for magnetic graphene composite treated for 20 min at 400 °C were observed even on multiple cycles at current density of 1 A  $g^{-1}$  (see Fig. 5(b)). Similar charge/discharge behavior at different current densities and on multiple cycles was also detected for magnetic graphene composite treated for 75 min at 400 °C (see Fig. S3, ESI†). In addition, the charge/discharge periods at 1.0 A g<sup>-1</sup> were dependent on the heating periods (2, 20 and 75 min) at 400 °C (see Fig. S4, ESI†). This increase in the charge/discharge periods caused by prolonging the heating time period from 2 to 75 min may be relative to the enlargement of the surface area (Table 1). Moreover, typical charge/ discharge curves with symmetrical isosceles triangle shape were observed in whole 700 cycles for magnetic graphene composite treated for 2 min at 800 °C (see the first and the last nine cycles in Fig. S5, ESI<sup>+</sup>). Additionally, the non-observable potential drop during charge/discharge processes reveals the superior performance of iron oxide on graphene as well as iron oxide on other carbon materials.38,39



**Fig. 6** CV curves of magnetic graphene composite. (a) Treated for 2 and 20 min at 400 °C. Scan rate: 25 mV s<sup>-1</sup>. (b) Treated for 20 min at 400 °C. Scan rate: 5, 25 and 50 mV s<sup>-1</sup>. (c) Treated for 2 min at 400 °C and 900 °C. Scan rate: 25 mV s<sup>-1</sup>. (d) Treated for 2 min at 900 °C. Scan rate: 5, 25 and 50 mV s<sup>-1</sup>.

The current-potential curves in Fig. 6 showed a rectangular shape, indicating the achievement of an efficient EDLC. In Fig. 6(a), the CV profile of the magnetic graphene composite exposed 20 min at 400 °C displayed wider current density than that heated 2 min. In other words, more efficient electric double layer was formed after longer heating time. This widening of CV indicates the significant improvement of the conductivity and the ion penetration into the electrode materials.40 The current-potential curves in Fig. 6(b) also revealed the gradual increase in the current density associated with increasing scan rate (5 to 50 mV  $s^{-1}$ ), representing a typical behavior of EDLC. The CV profiles were quite similar to that from a composite of Fe<sub>3</sub>O<sub>4</sub> and carbon nanotube with polyaniline.<sup>41</sup> Moreover, no redox peaks of metal oxide particles were observed in the CV profiles. This result indicates the homogenous distribution of iron oxide particles in the exfoliated graphene layers. This result is similar to previous reports using polypyrrole/graphene oxide/ ZnO nanocomposites.<sup>42,43</sup> In addition, similar tendencies of current density enhancement and of scan rate effect were observed at the same scan rate of 25 mV  $\rm s^{-1}$  for magnetic graphene composite heated at 900 °C against 400 °C (Fig. 6(c)) and with increasing scan rate for magnetic graphene composite heated at 900 °C (Fig. 6(d)).

The capacitance as a function of scan rate for the heattreated magnetic graphene composite is plotted in Fig. 7(a). It is a well-known behavior that the capacitance value decreased with increasing scan rate, as electrolyte ions do not have sufficient time to diffuse into the working electrode.<sup>44</sup> On the other hand, it is important to notice that the magnetic graphene composite heated at 400 °C showed elevated capacitance with increasing heating time. That is, while the capacitance of the magnetic graphene composite without heat-treatment was  $21 \text{ F g}^{-1}$  at a scan rate of  $1 \text{ mV s}^{-1}$ , the capacitance values at the same scan rate increased up to 85 F g<sup>-1</sup> (402% increase) after the treatment up to 75 min at 400 °C, as seen in Table 1, where the capacitance values at a scan rate of 5 mV s<sup>-1</sup> are listed by way of comparison. These capacitance values were also higher than that of iron oxide films.<sup>45</sup> Because iron oxide along with other metal oxide nanoparticles<sup>46,47</sup> can act as a spacer to prevent the aggregation of the graphene sheets, it can intensify the capacitance value of the graphene.

A similar capacitance improvement was also confirmed upon heating the magnetic graphene for 2 min at 600 °C and higher temperatures (see Fig. 7(b) and Table 1). The improvement by heating at 900 °C reached 450% (at 1 mV s<sup>-1</sup>) of the magnetic graphene without heat-treatment. Thus, it can be noted that the enhancement of the capacitance activity can be enlarged by the heating time up to 75 min at 400 °C and the temperature up to 900 °C at 2 min heating. It is noteworthy that such strong enhancement has never been observed in any other previous researches, although there was a report that the capacitance achieved 155% improvement under magnetic field compared to the pristine magnetic graphene (5 F g<sup>-1</sup>).<sup>48</sup> The capacitance value (95 F g<sup>-1</sup> at 1 mV s<sup>-1</sup>) after 2 min heating at 900 °C was superior to iron carbide<sup>38</sup> and oxides<sup>49</sup> incorporated into different carbon materials<sup>39</sup> including carbon fiber<sup>50</sup>



Fig. 7 Plots of capacitance of magnetic graphene composite as a function of scan rate. (a) Treated for 2, 20, 45 and 75 min at 400  $^{\circ}$ C. (b) Treated for 2 min at 400, 600, 800 and 900  $^{\circ}$ C.

graphene,<sup>51</sup> graphene oxide, carbon layer and N-doped graphene.<sup>52</sup>

Fig. 8(a) shows the capacitance retention of magnetic graphene composite treated for 2 min at 900 °C. The magnetic graphene composite exhibited an excellent stability of 96% after 1000 cycles of charges and discharges at 2.0 A  $g^{-1}$ . The stability and longer cyclability were also larger than those of complexes of other carbon materials with iron oxides.<sup>53</sup> Incidentally, the most important factor to determine the efficiency of the supercapacitor may be its energy density and power density. Fig. 8(b) showed a maximum energy density of 53 W h kg<sup>-1</sup> at 1 mV s<sup>-1</sup> for magnetic graphene composite treated for 2 min at 900 °C, and it decreased with increasing the scan rate. On the other hand, the power density increased with decreasing energy density to reach 745 W h kg<sup>-1</sup> at a scan rate of 50 mV s<sup>-1</sup>, where the energy density came down to 8.5 W h kg<sup>-1</sup>. The value (53 W h kg<sup>-1</sup>) of energy density indicates the superior capacitance enhancement in comparison with different iron oxides incorporated with different carbon materials.<sup>38,48,53</sup> Moreover, the maximum energy densities were close to that (93.9 W h kg<sup>-1</sup>) of iron oxide mixed with other metal oxides,<sup>54</sup> which were pseudocapacitors. In addition, the current energy density was also close to those  $(5-67 \text{ W h kg}^{-1})$ of different carbon materials including carbon nanotubes,<sup>52</sup> carbon nanohorns,<sup>26</sup> graphene oxide incorporated Fe<sub>3</sub>O<sub>4</sub>,<sup>55</sup> FeOOH<sup>56</sup> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>57</sup>

As the increase of the capacitance could be attributed to the surface area, the relationship between the capacitance at a scan rate of 1 mV s<sup>-1</sup> and the surface area was plotted in Fig. 9. When the magnetic graphene composite was heated for 2–75 min



**Fig. 8** (a) Stability test of capacitance of magnetic graphene composite treated for 2 min at 900 °C. Current density: 2.0 A g<sup>-1</sup>. (b) Energy density and power density of magnetic graphene composite treated for 2 min at 900 °C as a function of scan rate.

at 400 °C, the surface area as well as the capacitance increased (see Fig. 9(a)). A similar tendency was obtained, when the magnetic graphene composite was heated for 2 min at 400–900 °C (see Fig. 9(b)). The plot of capacitance as a function of surface area (Fig. 9(c)) indicates that the capacitance increases with increasing surface area, being independent of the heating periods or temperatures. This universal relation certificates the direct relation of capacitance to surface area. The increase of the surface area allows electrolyte ions to easily access the electrode, resulting in increasing of the electric double layer effect and the capacitance value.<sup>58</sup>

# Effects of polyaniline hybridized on the expanded magnetic graphene composite

The expanded magnetic graphene composite with an accordionlike morphology (treated for 2 min at 900  $^{\circ}$ C) was hybridized with PANI by *in situ* polymerization. It was found from SEM images in Fig. 1(f) that the morphology of the expanded graphene composite was preserved without any defects after PANI deposition, although the entire black color of graphene changed to brown after the deposition of green polyaniline. The texture of expanded graphene may allow the polymer to be embedded in the open sheets. This complexation prevents the destruction and/or the stacking of the magnetic graphene sheets. In other words, polymerization after the expansion of graphene is an important



**Fig. 9** (a) A 3D plot of capacitance of magnetic graphene composite heat-treated at 400 °C as functions of surface area and heating time. (b) A 3D plot of capacitance of magnetic graphene composite heat-treated for 2 min as functions of surface area and heating temperature. (c) A plot of capacitance as a function of surface area. Scan rate:  $1 \text{ mV s}^{-1}$ . Red circles and blue squares denote same data as those in (a) and (b), respectively.

sequence to maintain the efficiency of both expansion and polymerization. In addition, iron atoms were distributed on the whole graphene/PANI composite, indicating the conservation of Fe after PANI deposition (Fig. S6, ESI†). Elemental analyses in Fig. S7 (ESI†) show the amount of iron atoms that remained after polymerization. Moreover, the generation of nitrogen atoms after polymerization indicates the successful polymerization, since the magnetic graphene composite heat-treated for 2 min at 900 °C already lost the amine moiety (dodecylamine). The TGA curve after the polymerization displayed the effective weight loss by the decomposition of PANI (Fig. 2(b)). These results indicate that the PANI was successfully hybridized with the expanded graphene composite without changing its morphology and the existence of iron.

To ensure the performance of the graphene/polymer composite, CV measurements were performed. The CV curves could be collected at a wide potential window (-1.0 to +1.0 V)even after hybridization, indicating no effect of PANI on the potential window. The PC character was observed along with the EDLC character in the CV curves (see Fig. 10(a)): At the scan rate of 25 mV s<sup>-1</sup>, redox peaks at 0.46 and -0.62 V, which are characteristic of PC, were observed with the rectanglebased EDLC aspect. The characteristics of PC diminished with the increasing scan rate, and the CV displayed the feature of EDLC at a high scan rate, similar to the CV feature of the



Fig. 10 CV results of magnetic graphene/PANI composite by comparison to magnetic graphene treated for 2 min at 900 °C (before polymerization). (a) CV curves of composite at different scan rates, (b) Capacitance as a function of scan rate, and (c) energy density as a function of scan rate.

 Table 2
 Capacitance and energy density of magnetic graphene/PANI composite in comparison with magnetic graphene before hybridization

|                                | Magnetic graphene<br>composite (treated<br>2 min, 900 °C) |   | Magnetic graphene (treated<br>2 min, 900 °C)/PANI composite |   |
|--------------------------------|---|---|---|---|
| $      Scan rate (mV s^{-1}) $ | Capacitance (F $g^{-1}$ )                                 | Energy density<br>(W h kg <sup>-1</sup> ) | Capacitance (F $g^{-1}$ )                                   | Energy density<br>(W h kg <sup>-1</sup> ) |
| 5                              | 42  | 84  | 253   | 141                                       |
| 15                             | 23  | 46  | 130   | 72  |
| 20                             | 18  | 36  | 73  | 41  |
| 25                             | 18  | 36  | 67  | 37  |
| 30                             | 17  | 34  | 57  | 32  |
| 40                             | 16  | 32  | 50  | 28  |
| 50                             | 15  | 30  | 37  | 21  |

magnetic graphene composite treated for 2 min at 900  $^{\circ}$ C (Fig. 6(c)).

Fig. 10(b) and Table 2 indicate that the capacitance of the composite decreased with the increase of the scan rate along with the behavior of the heat-treated graphene composite (treated for 2 min at 900 °C before the hybridization) without PANI hybridization, but the capacitance was much higher than the magnetic graphene composite before hybridization. In particular, the capacitance value of 253 F  $g^{-1}$  at 5 mV  $s^{-1}$  of the composite was 482% higher than the capacitance (42 F  $g^{-1}$  at the same scan rate) of the magnetic graphene composite before hybridization. However, compared to the capacitance value of PANI alone (approximately 200 F  $g^{-1}$ ),<sup>9,59</sup> the capacitance of the composite can be considered to be enhanced by the additive effect by the hybridization of the heat-treated magnetic graphene composite with PANI. The calculated energy density (Fig. 10(c) and Table 2) was also heightened in comparison with the heat-treated graphene, indicating the sufficient increase in the energy density after hybridization. Meanwhile, if the polymerization process was performed directly on the aminetreated magnetic graphene composite without heat-treatment, the obtained capacitance did not show significant enhancement (data are not included). Therefore, the polymerization of aniline after the expansion process by heating allowed the achievement of enhanced capacitance and energy density due to the direct adsorption of the polymer onto the surface of sufficiently expanded graphene after the heat-treatment.

Similar behavior of charge/discharge cycles to that of the heat-treated magnetic graphene composite (2 min at 900  $^{\circ}$ C) before hybridization was obtained for the graphene after hybridization, and there was no observed internal resistance drop in the curves (Fig. 11(a)). These results clearly support the non-functionality of magnetic graphene after hybridization, allowing the smooth ion transfer to the electrode without strong resistance.

The stability of the electrode loaded hybrid material is one of the most important characteristics of the material to be used in supercapacitors. Therefore, the stability of the capacitance was investigated *via* charge/discharge curves for 9000 cycles at a current density of 20 A  $g^{-1}$  (Fig. 11(b)). The results clearly showed an excellent stability (99%) of the hybridized graphene compared to the non-hybridized graphene (96%, see Fig. 8(a))



**Fig. 11** (a) Charge and discharge behavior at 1.0 A  $g^{-1}$  of magnetic graphene/PANI composite. (b) Stability test of capacitance of magnetic graphene/PANI composite. Current density: 20 A  $g^{-1}$ .

and the pristine graphene (94%, data not included). These results indicate the significant role played by the polymer in causing the stability of the working electrode and the enhanced capacitance performance.

## Conclusions

In the current investigation, the magnetic graphene composite exfoliated *via* dodecylamine treatment was heat-treated at a high temperature of 900  $^{\circ}$ C and the defect-free expanded graphene containing iron oxide nanoparticles was prepared. The heat-treated magnetic graphene composite displayed remarkable volume expansion, which was involved deeply in the interlayer opening of graphene sheets and the enlargement of the graphene surface area. This simple one step heating procedure for a very short time (2 min) at higher temperature can open the door to release the amine moiety and cause efficient exfoliation for the layers of graphite.

In addition, the present report shows the importance of effective graphene exfoliation to enhance its electrochemical performance. The expanded magnetic graphene composite provided an enhanced capacitance performance with a wide potential window, excellent charge/discharge properties and non-observed internal resistance drop at all current densities. As a result, this material achieved the favourable efficiency as a supercapacitor. The capacitance universally increased with increasing surface area, namely, interlayer expansion of graphene. This indicates that the obtained open structure of graphene sheets allows easy diffusion of electrolyte ions on the graphene surface on the electrode and, hence, intensifies capacitance of the electrode.

Moreover, the heat-treated expanded magnetic graphene composite could be successfully hybridized by conductive PANI retaining its morphology and magnetic properties. The obtained hybrid composite maintained the same electrochemical characteristics of an enhanced capacitance performance with a wide potential window, excellent charge/discharge properties and non-observed internal resistance drop at all current densities as the heat-treated magnetic graphene composite before hybridization. However, the magnetic graphene/PANI hybrid composite displayed an excellent stability (99% at 20 A  $g^{-1}$ ) and a higher energy density (141 W h kg<sup>-1</sup>). Especially, It should be worthy of remark that the obtained capacitance reached 253 F  $g^{-1}$  at a scan rate of 5 mV  $s^{-1}$ . These values are remarkably higher than those of the heat-treated magnetic graphene composite before hybridization, because the hybridization of conductive PANI allows easier ion diffusion in the electrode material with higher conductivity.

The current thermal treatment and the conductive polymer hybridization can provide a scalable, easy and cheap method toward the graphene/iron oxide/conductive polymer-based supercapacitor devices. The procedures supply a facile and non-defective way for the graphite expansion and the polymer hybridization to enhance the electrochemical characteristics. The investigation clearly indicates that the composite with iron oxide and a conductive polymer is considered a promising candidate toward supercapacitor applications with the enhanced activity and stability. Moreover, we focus on the extended research of graphene composites with iron oxide which have many possibilities in lithium-ion batteries, medical, catalytic, and environmental applications.<sup>60</sup>

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