**Fabrication and enhanced supercapacitive performance of
graphene/nano-carbide derived carbon composites**

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Abstract

Introducing carbon nanotube (CNT) or carbon black (CB) among graphene sheets has been demonstrated an effective strategy to impede the restacking of graphene sheets and eventually enhances the supercapacitive performance. However, due to their relatively low specific surface area (SSA) and undeveloped pores, the introduced CNT or CB itself has limited contribution to the electrochemical performance. To address the problem, we have synthesized a graphene/nanometer-sized

carbide-derived carbon (graphene/nano-CDC) composite. Benefiting from the introduction of the porous nano-CDC, the graphene/nano-CDC composite behaves higher SSA and developed pore structure, and thus superior supercapacitive performance. The specific capacitance of the graphene/nano-CDC composite can reach 195 F g^{-1} at a scan rate of 5 mV s^{-1} , a 179% increase compared with RGO (only 70 F g^{-1}). Most interestingly, even at the scan rate of 5000 mV s^{-1} , its cyclic voltammogram curves can still keep a relatively typical rectangle shape and the capacitance retention can maintain 67% (130 F g^{-1}), approximately 5 times higher than those of the RGO (13%, 9 F g^{-1}). In addition, the specific capacitance of the graphene/nano-CDC composite is quite stable over the entire cycle numbers, and has no significant degradation even after 10000 cycles.

Keywords: Nanomaterial; Graphene; Carbide-derived carbon; Composite; Supercapacitive performance

1. Introduction

Supercapacitors or electrochemical double-layer capacitors (EDLCs) are highly promising in many applications where high power with quick repetitive recharging and long cycle life are needed, such as consumer electronics, medical electronics and electric transportation technology [1-5]. Up to now, lots of the materials as the electrode for supercapacitor, e.g. carbon materials [6], metal oxides [7] and conducting polymers [8], have been developed due to their important influence on the supercapacitive performance.

Graphene, a two-dimensional carbon material, is considered as a promising

candidate electrode material for supercapacitors due to its high theory surface area, excellent electrical conductivity and stable chemical properties [9, 10]. However, the graphene sheets are easy to form irreversible agglomerations due to the strong van der Waals interactions between individual graphene sheets [11-13]. This agglomeration not only decreases the surface area but also limits the access of electrolyte ions into the surface of the graphene sheets. As a result, the actual capacitance value is far lower than the theoretical one. To address this disadvantage, many efforts, including the incorporation of other nanomaterials such as carbon black (CB) [14, 15], carbon nanotube (CNT) [16, 17] and metal oxides [18, 19] among the graphene sheets, have been made. For example, Yan et al. [15] produced graphene nanosheet/CB (GNS/CB) composites, and the specific capacitance of GNS/CB (150.4 F g^{-1}) is higher than that of pure GNS (122.6 F g^{-1}) at 10 mV s^{-1} in 6 mol L^{-1} KOH. Besides, the electrochemical performance of reduced graphene oxide/CB (RGO/CB) hybrid films was investigated by Wang et al. [14], and the specific capacitance of RGO/CB hybrid film is 136.6 F g^{-1} at 0.5 A g^{-1} , which is obviously higher than that (80.0 F g^{-1}) of graphene film without CB at the same current density. It is well accepted that, for the EDLC, its charge storage mechanism is based on the electrostatic adsorption of charge separated ions on the surface of an electrode material [20-22]. Therefore, the large surface area and the porosity of electrode active materials are the basic requirements to achieve high specific capacitance. Unfortunately, due to the very low specific surface area (SSA) of CB (only $\sim 40 \text{ m}^2 \text{ g}^{-1}$ for the graphitized CB [23, 24]), the constructed graphene/CB composites behaves relatively low SSA value ($531 \text{ m}^2 \text{ g}^{-1}$

for GNS/CB [15]). Obviously, low SSA value cannot match the requirement to achieve high specific capacitance. As for metal oxides, their incorporation among the graphene sheets can highly improve the specific capacitance, but, unfortunately, will deteriorate the rate performance rapidly [10]. For instance, the specific capacitance of graphene/MnO₂ composite decreased from 210 to 74 F g⁻¹ when the scan rate increased from 2 to 100 mV s⁻¹ [25], almost 65% drop in the specific capacitance, which is due to the fact that there is not enough time to accomplish fully the redox process at high scan rate [25, 26].

Herein, we propose to introduce nanometer-sized carbide derived carbon (nano-CDC) instead of pure CNT or CB as spacer among the graphene sheets. Due to the high SSA and developed pore structure of the nano-CDC, as well as the effective prevention on the restacking of graphene sheets, the graphene/nano-CDC composite can be expected to exhibit superior supercapacitive performance.

2. Experimental

2.1 Sample preparation

2.1.1 Preparation of nano-CDC and ACDC

Nano-CDC was synthesized by chlorination of β -SiC nano-powder with a particle diameter around 60 nm at 800 °C. In addition, the prepared nano-CDC was further activated by KOH (the weight ratios of KOH/nano-CDC = 7:1), obtaining the activated nano-CDC (denoted as ACDC) sample. The more detailed chlorination and activation are presented in our previous work [22].

2.1.2 Preparation of the graphene/nano-CDC composites

Graphene oxide (GO) was prepared by a modified Hummers' method, which is detailedly described in elsewhere [27].

The stable suspension of GO (1 mg ml^{-1}) and nano-CDC (1 mg ml^{-1}) was produced by ultrasonication. Then, GO and nano-CDC were mixed at a 25% weight ratio of nano-CDC and ultrasonically dispersed for 30 min. Thereafter, 3 ml hydrazine hydrate was added to reduce the GO to the reduced graphene oxide (RGO). The mixture was magnetically stirred at room temperature over night, washed several times by deionized water, and then dried at 90°C for 12 h in vacuum, eventually constructing the G/nCDC composite.

The graphene/ACDC composites (G/ACDC) were also prepared in the same way, and the G/ACDC composites with different ACDC content (25, 45 and 65 wt.%) were denoted as G/ACDC-25, G/ACDC-45 and G/ACDC-65, respectively. In addition, the RGO without nano-CDC was also synthesized by above described method.

2.2 Characterization

The morphology and microstructure of the samples were observed by scanning electron microscopy (SEM, Hitachi S4800, Japan) and transmission electron microscopy (TEM, JEOL JEM-2010, Japan). X-ray diffraction (XRD) patterns between 10 and 70 (2θ) degrees were collected by Rigaku D/MAX-2500 powder diffractometer with Cu-K α radiation ($\lambda=0.154 \text{ nm}$) operated at 40 kV and 200 mA . Raman scattering was performed on a Raman spectrometer (Renishaw) by using Ar^+ laser ($\lambda=514.5 \text{ nm}$). The N_2 adsorption and desorption analysis was performed at 77 K using the ASAP 2020 instrument (Micromeritics). Prior to analysis, all the samples

were degassed in vacuum at 200 °C for 8 h. The SSA and micropore volume were calculated by Brunauer-Emmett-Teller (BET) method and t-plot method, respectively. The pore size distribution was determined by non-local density functional theory (NLDFT). The electrical conductivity of samples was measured by the four-point probe technique (ST-2722 powder resistivity tester, Suzhou Jingge Electronic Co. Ltd.).

2.3 Preparation of electrode and electrochemical measurement

The electrochemical investigations were carried out in a symmetrical two-electrode cell with a cellulose separator (TF4030, NKK). The working electrodes were prepared as follows: A slurry consisting of 80 wt.% active materials, 10 wt.% carbon black and 10 wt.% PTFE (60 wt.% suspension in water) binder was smeared into nickel foam and dried in vacuum at 120 °C for 10 h. Thereafter, the electrode was pressed at a pressure of 10 MPa. The active area of the electrode is 1 cm². The loading mass of active materials is about 1 mg cm⁻² for each electrode used in this work. 6 mol L⁻¹ KOH solution was used as electrolyte. The electrochemical performances of all samples were characterized by cyclic voltammograms (CV) in a potential range of 0 ~ 0.9 V at different scan rates of 5~5000 mV s⁻¹, galvanostatic charge/discharge tests with cutoff voltage of 0 ~ 0.9 V and electrochemical impedance spectroscopy (EIS) in the frequency range between 10 mHz and 100 kHz at open circuit potential. The CV and EIS measurements were performed on CHI650D electrochemical workstation. The galvanostatic charge/discharge and long life tests were carried out on potentiostat/galvanostat (CT2001A, Land, Wuhan, China). Energy density (E, Wh

kg^{-1}) and power density ($P, \text{W kg}^{-1}$) were calculated from the CV curves at different scan rates using the following equations [10, 13, 28, 29]: $E = 1/2 CV^2$ and $P = E/t$. Where, C is the specific capacitance of one electrode (F g^{-1}), V is the applied voltage range and t is the discharge time (s).

3. Results and discussion

3.1. Structure and morphology of the G/nCDC composites

Fig. 1. XRD patterns of RGO, nano-CDC and G/nCDC.

The XRD patterns of RGO, nano-CDC and G/nCDC are presented in **Fig. 1**. It can be observed that the XRD pattern of RGO exhibits a dominant diffraction peak around 22.4° , corresponding to the graphite-like structure (002) [30]. Nano-CDC shows a broad peak at around 22.6° , corresponding to the diffuse scattering from disordered amorphous carbon, indicating the amorphous nature of nano-CDC. As for the G/nCDC composite, its diffraction peak at about 23° becomes weaker and broader in comparison to that of nano-CDC, which can be attributed to the combined effect of

diffuse scattering from both RGO and nano-CDC. This result suggests that the structure of RGO in the G/nCDC composite becomes more amorphous relative to that of the pristine RGO, which also confirms that the graphite-like structure, which occurs in RGO, is not formed in the G/nCDC composite, and the self-stacking of RGO has been impeded due to the introduction of nano-CDC.

Fig. 2. SEM images of RGO (a) and G/nCDC (b) (nano-CDCs are exemplarily marked by ellipses).

Fig.2 exhibits SEM images of RGO and G/nCDC. Obviously, the individual graphene sheets in RGO have been densely restacked agglomerated due to the van der Waals interactions between the layers of graphene (Fig. 2a). As for the G/nCDC composite, the graphene sheets become more crumpled and loose, which should be ascribed to the introduction of nano-CDC among the graphene sheets (Fig. 2b). Further TEM observation also clearly exhibits that lots of nano-CDCs are distributed among the graphene sheets (**Fig. 3**).

Fig. 3. TEM images of (a) RGO and (b) G/nCDC (nano-CDCs are marked by arrows).

The SAED patterns are inset in the corresponding figures.

The selected area electron diffraction (SAED) patterns of pure RGO and RGO in G/nCDC are shown in Fig. 3a and b (the inset). The diffraction rings with different radius correspond to the (002), (100), (004) and (110) planes of graphite, respectively. It can be seen that the brightness of diffraction rings for (002), (100) and (110) planes in pure RGO is relatively higher than that of (004) plane, corresponding to the low crystalline graphitic structure, which can be attributed to the self-stacking of RGO. As for RGO in G/nCDC, the weaker diffraction ring for (002) and the disappeared diffraction ring for (004) suggest that the graphitic structure is not formed and the self-stacking of RGO is impeded due to the introduction of nano-CDC. Therefore, it can be deduced that this architecture of the G/nCDC composite is evidently more favorable for the access of electrolyte ions into the surfaces of the graphene sheets and nano-CDCs.

Fig. 4. Raman spectra of RGO, nano-CDC and G/nCDC.

The Raman spectra of RGO, nano-CDC and G/nCDC are shown in **Fig. 4**. It can be seen that all of RGO, nano-CDC and G/nCDC possess two obvious characteristic peaks at 1350 cm^{-1} and 1595 cm^{-1} , corresponding to the disorder-induced D band and graphite G band, respectively. The intensity ratio of D band to G band (I_D/I_G) indicates the degree of disorder and defects in carbon materials. The I_D/I_G ratios of RGO, nano-CDC and G/nCDC are 0.92, 1.42 and 1.23, respectively. Compared with the initial I_D/I_G ratio of pure RGO, the increased I_D/I_G ratio of G/nCDC indicates that the structure of G/nCDC composites become more disorderly, which is consistent with the analysis of XRD.

3.2. Pore structure of G/nCDC and G/ACDC

The low-temperature N_2 adsorption/desorption isotherms and pore size distributions of RGO and nano-CDC are shown in **Fig. 5**. It can be observed from Fig. 5a that RGO barely adsorbs N_2 at low relative pressure (P/P_0) and exhibits a typical IV type nitrogen adsorption/desorption isotherms at relative pressure $P/P_0 = 0.4 \sim 1.0$, suggesting that there exists some mesopores and few micropores [16]. These

mesopores may be caused by the overlapped regions due to the folded and crumpled graphene sheets [21]. However, nano-CDC adsorbs N_2 at low relative pressure (P/P_0) largely, indicating the existence of large amount of micropores, which agrees well with the result of pore size distribution (Fig. 5b). The more detailed porosity characteristics of RGO and nano-CDC are listed in **Table 1**. The SSA for nano-CDC is $1531 \text{ m}^2 \text{ g}^{-1}$, obviously higher than those of some other nanometer-sized carbon materials (such as, CB [24], onion-like carbon [31] and CNT [32]). Therefore, it can be deduced that the incorporation of nano-CDC among the graphene sheets will provide more accessible surface for electrolyte ions. Fig. 5a also shows the low-temperature N_2 adsorption/desorption isotherms of the G/nCDC composite. It can be seen that G/nCDC adsorbs more N_2 than RGO at low relative pressure (P/P_0), indicating the existence of more micropores due to the introduction of nano-CDC. Furthermore, in comparison to the isotherms of RGO, a larger hysteresis loop for G/nCDC suggests more mesopores (Fig. 5b), which demonstrates that the restacking of graphene sheets has been effectively impeded by nano-CDCs. As expected, G/nCDC behaves a markedly higher SSA value ($890 \text{ m}^2 \text{ g}^{-1}$) than that of RGO ($279 \text{ m}^2 \text{ g}^{-1}$). This SSA value of G/nCDC is also significantly higher than that of the RGO/CB composite ($531 \text{ m}^2 \text{ g}^{-1}$) synthesized by a similar preparation route [15]. In addition, benefiting from the micropore property of nano-CDCs, the G/nCDC composite also exhibits an obvious increase in the total pore volume and micropore volume compared with RGO (Table 1). Therefore, higher SSA and more developed pore structure may suggest that G/nCDC will behave superior supercapacitive

performance than RGO.

Fig. 5. (a) Low-temperature N₂ adsorption/desorption isotherms of RGO, nano-CDC and G/nCDC, (b) pore size distributions of RGO, nano-CDC and G/nCDC, (c) Low-temperature N₂ adsorption/desorption isotherms of ACDC and G/ACDC, (d) pore size distributions of ACDC and G/ACDC.

In Fig. 5 and Table 1 are further presented the low-temperature N₂ adsorption/desorption isotherms and porosity characteristics of the ACDC and G/ACDC composite samples. Compared with the pristine nano-CDC, ACDC behaves a significantly higher SSA of up to 2265 m² g⁻¹ and more mesopores with a pore size of 2~5 nm, which, undoubtedly, are contributed by the KOH activation [22]. As for the same content of introduced nano-CDC (25 wt.%), the synthesized G/ACDC composite exhibits a much higher SSA (1089 m² g⁻¹) than G/nCDC (890 m² g⁻¹)

(Table 1). In addition, it can be deduced from Fig. 5b and d that there exists more mesopores at the pore size from 2 to 5 nm for G/ACDC by comparison to G/nCDC, which should be attributed to the hierarchical pore structure of ACDC. Obviously, the pore structure of the introduced nano-CDC affects markedly the SSA and pore size distribution of graphene/nano-CDC composite. That is to say, the SSA and pore size distribution of the graphene/nano-CDC composite can be effectively tuned by the introduced nano-CDC.

Table 1 Porosity characteristics of different samples

Sample	$S_{\text{BET}}^{\text{a)}}$ ($\text{m}^2 \text{g}^{-1}$)	$V_{\text{total}}^{\text{b)}}$ ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{micro}}^{\text{c)}}$ ($\text{cm}^3 \text{g}^{-1}$)
RGO	279	0.43	0.01
nano-CDC	1531	1.13	0.44
ACDC	2265	2.12	0.46
G/nCDC	890	0.85	0.19
G/ACDC	1089	0.96	0.22

^{a)} Specific surface area was calculated by BET method;

^{b)} Total pore volume; ^{c)} The volume of micropores;

3.3. Electrochemical performance of G/nCDC and G/ACDC

The CV curves of RGO, G/nCDC and G/ACDC are measured and shown in **Fig. 6**. The scan rates for all CV tests were in the range of 5 ~ 5000 mV s^{-1} . The symmetrically rectangular-like shapes for all these CV curves at low scan rates imply an electric double-layer capacitance behaviour. Compared with RGO, G/nCDC and G/ACDC both show higher specific capacitance at the same scan rate, which can be ascribed to the effective impediment on the agglomeration of graphene sheets and

more developed pore structure contributed by the nano-CDC. More interestingly, due to the higher SSA and developed hierarchical pore structure of ACDC, the G/ACDC composite shows better supercapacitive performance than RGO and G/nCDC. For example, at a scan rate of 5 mV s^{-1} , the specific capacitance of G/ACDC is up to 184 F g^{-1} , higher than those of RGO (70 F g^{-1}) and G/nCDC (149 F g^{-1}). Moreover, it can be observed that increasing the scan rate leads to a gradual change in the CV shapes of the three samples. The shape of CV curves for RGO is obviously distorted when the scan rate is up to 1000 mV s^{-1} . But, for G/nCDC and G/ACDC, they both can keep a relatively typical rectangle shape in CV curve even at 5000 mV s^{-1} . Comparatively, G/ACDC exhibits the best rate performance. Its specific capacitance can still sustain 87 F g^{-1} at 5000 mV s^{-1} , corresponding to a capacitance retention ratio of 47%, much higher than those of RGO (9 F g^{-1} , 13%) and G/nCDC (37 F g^{-1} , 25%). These results indicate that the incorporation of ACDC among the graphene sheets is beneficial to the achievement of superior supercapacitive performance for the graphene/nano-CDC composite, since ACDC can contribute more accessible surface and fast transport channel for electrolyte ions.

Fig. 6. CV curves of RGO (a), G/nCDC (b) and G/ACDC (c) at different scan rates in 6 mol L⁻¹ KOH solution.

3.4. Effect of the introduced ACDC content

As discussed above, G/ACDC behaves better supercapacitive performance than G/nCDC. Next, we will systematically probe into the effect of the introduced ACDC content so as to achieve the optimal electrochemical performance for the G/ACDC composite. The low-temperature N₂ adsorption/desorption isotherms and pore size distributions of the G/ACDC composites having different content of ACDC are measured (**Fig. S1**), and their more detailed porosity characteristics are listed in **Table 2**. As the ACDC content increases, the G/ACDC composite possesses larger volumes of micropores and mesopores, thus resulting in higher SSA values. The corresponding SSA values of G/ACDC-25, G/ACDC-45 and G/ACDC-65 are 1089, 1465 and 1594 m² g⁻¹, respectively.

Table 2 Porosity characteristics of G/ACDC composites

Sample	$S_{\text{BET}}^{\text{a)}}$ ($\text{m}^2 \text{g}^{-1}$)	$V_{\text{total}}^{\text{b)}}$ ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{micro}}^{\text{c)}}$ ($\text{cm}^3 \text{g}^{-1}$)
G/ACDC-25	1089	0.96	0.22
G/ACDC-45	1465	1.32	0.28
G/ACDC-65	1594	1.89	0.31

^{a)} Specific surface area was calculated by BET method;

^{b)} Total pore volume; ^{c)} The volume of micropores;

Fig. 7a shows the dependence of the specific capacitance of the G/ACDC composites and the introduced ACDC content at a scan rate of 5 mV s^{-1} . As the ACDC content increases, the specific capacitance of G/ACDC first increases, reaching the maximal value of 195 F g^{-1} at the ACDC content of 45 wt.%, and then trends to decrease. Obviously, the G/ACDC composite having a ACDC content of 45 wt.% (G/ACDC-45) exhibits the highest specific capacitance. Furthermore, the rectangle-like shape of CV curve at a scan rate of 5000 mV s^{-1} implies that G/ACDC-45 as an electrode material for supercapacitors also exhibits superior rate capability (**Fig. S2a**). This rate performance is comparable to that of CNT film with hydrogen treatment [33], but the specific capacitance of G/ACDC-45 is markedly higher. In addition, it is worth noting that, though G/ACDC-65 possesses the relatively highest SSA of $1594 \text{ m}^2 \text{g}^{-1}$ (Table 2), it behaves a poorer capacitive performance (Fig. 6 and **Fig. S2b**). This may be ascribed to the excess introduction of ACDC among graphene sheets. As mentioned above, although ACDC behaves a SSA value up to $2265 \text{ m}^2 \text{g}^{-1}$, its specific capacitance is only 141 F g^{-1} . As the introduced ACDC content increases, the contribution of ACDC to the overall capacitive performance of the G/ACDC composite will become larger. As a consequence, the

excess introduction of ACDC among graphene sheets doesn't lead to superior capacitive performance. However, in any case, all the G/ACDC composites behave higher specific capacitances compared with RGO and the G/nCDC composites.

Fig. 7. (a) Specific capacitances of G/ACDC composites as a function of ACDC content at 5 mV s⁻¹ in 6 mol L⁻¹ KOH solution, (b) Specific capacitances of RGO and the G/ACDC composites at different scan rates from 5 to 5000 mV s⁻¹.

Fig. 7b shows the relation curves of specific capacitance and scan rates of RGO and the G/ACDC composites. It can be found that the specific capacitances decrease with the increase of scan rate in a range of 5 ~ 5000 mV s⁻¹. As for the capacitance retention, however, all the G/ACDC composites exhibit markedly higher capacitance retention than RGO at the same scan rate. For example, as the scan rate increases to 5000 mV s⁻¹, the capacitance retentions of G/ACDC-25, G/ACDC-45 and

G/ACDC-65 are 47%, 67% and 65%, respectively, all obviously higher than that of RGO (13%). Interestingly, at the same scan rate of 500 mV s^{-1} , the specific capacitance and capacitance retention of G/ACDC-45 are 167 F g^{-1} and 86%, respectively, both higher than those of the RGO/CB composites electrode (118 F g^{-1} , 67%) reported in the literature [15]. Obviously, this significant improvement in the specific capacitance and rate performance benefits from higher SSA, more developed hierarchical pore structure and effective impediment on the restacking of graphene sheets contributed by ACDC.

Fig. 8. (a) EIS plots, (b) equivalent circuit and (c) Bode phase angle plots of the RGO and G/ACDC composites.

Fig. 8a presents the EIS plots of the RGO and the G/ACDC composites, and the

corresponding equivalent circuit is shown in Fig. 8b. All samples can be simulated by this equivalent circuit, which offers an effective tool to understand the intrinsic mechanism of electrode materials [34, 35]. In the low frequency region of EIS plots, the linear parts of all the samples tend to be vertical lines, indicating a nearly ideal capacitive behavior of EDLCs. In the high frequency region, the intercept of the semicircle with the real axis represents the equivalent series resistance (ESR), including the ionic resistance of electrolyte, the intrinsic resistance of active material and the interfacial resistance between the electrode and the current collector [36]. It can be estimated that the ESR values of all G/ACDC composites are around 0.41 ohm, which is lower than that of RGO (0.58 ohm). In addition, a semicircle can be observed on the EIS plots of all samples and the radius of semicircle corresponds to the charge transfer resistance (R_{CT}) at the electrode/electrolyte interface [37]. RGO has the highest R_{CT} value (4.6 Ω) than the others, and the R_{CT} decreases with increasing the ACDC content, indicating that the ions of electrolyte can move in the pore structure of G/ACDC composite electrodes more easily (**Table S1**). The intersection of the projection of the linear parts to the real axis in the EIS plot represents the total internal resistance (TIR) [37, 38]., The TIR value, an important factor that affects the rate performance of supercapacitors, is the sum of ESR, R_{CT} and the internal distribution of the electrolyte resistance values in the pore matrix. The TIR values of RGO, G/ACDC-25, G/ACDC-45 and G/ACDC-65 are 8.46, 0.91, 0.76 and 0.59 ohm, respectively. The highest TIR value of the RGO electrode can be ascribed to its lowest electrical conductivity value (275 S m⁻¹, **Table 3**), since poor electrical conductivity

means the increase in the interfacial contact resistance between electrode materials and current collector and the motion resistance of electrolyte ions in the electrode materials [21]. As displayed in **Table 3**, ACDC exhibits relatively higher electrical conductivity, therefore, its incorporation among the RGO sheets can increase the electrical conductivity of the G/ACDC composite and thus reduce the internal resistance of the composite electrode.

The Bode phase angle plots of RGO and G/ACDC composites are shown in Fig. 8c. It can be observed that the phase angle for these samples becomes larger with increasing the ACDC content. The phase angle of RGO, G/ACDC-25, G/ACDC-45 and G/ACDC-65 is 82.4°, 87.3°, 87.9° and 88.6° at 0.01 Hz, respectively, which is close to that of ideal capacitor (90°), suggesting a good double layer capacitive behavior [39].

Table 3 Conductivity of RGO, ACDC and the G/ACDC composites.

Samples	RGO	G/ACDC-25	G/ACDC-45	G/ACDC-65	ACDC
Conductivity (S m ⁻¹)	275	403	454	487	613

The Ragone plot of energy density against power density is shown in **Fig. 9**. It can be seen that the energy density of the RGO electrode drops rapidly at high power density, while all the G/ACDC composite electrodes show improved energy density with little degradation even at higher power density. The G/ACDC-45 electrode delivers a highest energy density of 21.9 Wh kg⁻¹ at a power density of 219 W kg⁻¹,

and can still remain 14.7 Wh kg^{-1} even at a power density of 146 kW kg^{-1} . As a contrast, the energy density of the RGO electrode is only 7.9 Wh kg^{-1} at a power density of 80 W kg^{-1} , and the energy density quickly drops to 1 Wh kg^{-1} as the power density increases to 10 kW kg^{-1} . Moreover, the obtained energy density of G/ACDC-45 (21.9 Wh kg^{-1}) is also higher than those of RGO/CB ($\sim 18.7 \text{ Wh kg}^{-1}$) and graphene/onion-like carbon ($\sim 17.9 \text{ Wh kg}^{-1}$) at the same potential range in aqueous electrolytes [15, 40].

Fig. 9. Ragone plots of RGO and the G/ACDC composites based supercapacitors in 6 mol L^{-1} KOH solution.

The cycling stability is a most important criterion for the supercapacitor. **Fig. 10** shows the result of long-term cyclic charge/discharge test of G/ACDC-45 at a current density of 1 A g^{-1} . The charge/discharge curve of G/ACDC-45 shows a highly symmetric triangle shape (inset in Fig. 10), which is the characteristic of the double layer charge storage mechanism, in agreement with the results of CV tests. At the beginning of cycling, a slight increment in the specific capacitance is observed. This increase is presumed to be a gradual increase in the effective charge storage sites caused by the continuous diffusion of the electrolyte ions into the electrode during

cycling [41]. As the cycling continues, the specific capacitance of G/ACDC-45 is quite stable over the entire cycle numbers, and almost 100 % or more specific capacitance can be remained even after 10000 cycles, indicating excellent cycling stability, which is important for the practical application.

Fig. 10. The long-term cyclic charge/discharge test of G/ACDC-45 at a current density of 1 A g^{-1} . The inset in Fig. 8 is the charge/discharge curves of G/ACDC-45.

4. Conclusions

The graphene/nano-CDC composites have been prepared by introducing the nanometer-sized carbide-derived carbon among the RGO sheets. Compared with RGO, the composite behaves higher SSA, more developed pore structure and thus superior supercapacitive performance. The pore structure of the introduced nano-CDC markedly affects the SSA, pore size distribution and the electrochemical performance of the graphene/nano-CDC composite. When the KOH-activated nano-CDC, which possesses higher SSA and more developed hierarchical pore structure, is incorporated among the RGO sheets, the resultant G/ACDC composite exhibits superior supercapacitive performance. The highest specific capacitance of this composite can

reach 195 F g^{-1} at a scan rate of 5 mV s^{-1} , a 179% improvement by comparison to RGO. Even at the scan rate of 5000 mV s^{-1} , the cyclic voltammogram curve of the G/ACDC composite can still keep a relatively typical rectangle shape and the capacitance retention can maintain 67% (130 F g^{-1}), approximately 5 times higher than those of RGO. Therefore, the superior specific capacitance, excellent power performance and outstanding cycling stability suggest a great potential of the G/ACDC composite as an electrode material for supercapacitors.

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