Fabrication of graphene and core-shell activated porous carbon-coated carbon nanotube hybrids with excellent electrochemical performance for super-capacitors

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Abstract

Many works have demonstrated that the graphene and carbon nano-tube hybrid (RGO/CNT), synthesized by introducing CNT among graphene sheets, can exhibit improved supercapacitive performance. However, due to its relatively low specific surface area (SSA) and undeveloped pores, the introduced CNT has limited contribution to the electrochemical performance. To solve the problem, we have synthesized a hybrid (RGO/CNT@AC) of graphene and core-shell CNT@AC by introducing activated porous carbon-coated carbon nanotube (CNT@AC) among the graphene sheets.

The SSA and micropore volume of RGO/CNT@AC are greatly higher than those of RGO/CNT. Moreover, RGO/CNT@AC shows superior supercapacitive performance compared with RGO/CNT in 6 M KOH electrolyte. The highest specific capacitance is up to 193 F g^{-1} at a scan rate of 10 mV s^{-1} , much higher than that (91 F g^{-1}) of RGO/CNT. Furthermore, RGO/CNT@AC also shows obviously better rate capability (138 F g^{-1} retention at a high scan rate of 5000 mV s^{-1}) and excellent cycling stability (almost 100 % capacitance maintaining in cycling stability test). The significant improvement in supercapacitive performance of the RGO/CNT@AC hybrid should be ascribed to the abundant micropores contributed by the AC coated on the CNT surface and more diffusion paths existing between RGO sheets.

Keywords: Graphene; Carbon nanotube; Activated carbon; Supercapacitive performance

1. Introduction

Supercapacitor, a new energy storage device, has attracted considerable interest in the energy storage field, due to its high power density, rapidly charge/discharge and repeatedly cycle without significant capacitance decay, etc. [1-5]. Up to now, lots of electrode materials for supercapacitors have been investigated, such as graphene [6, 7], CNTs/graphene hybrids [8, 9], as well as conductive polymers [10-12] and activated carbon [13, 14].

Graphene, a two-dimensional one-atom-thick conductor, is promising as the electrode material for suercapacitors due to its high theory specific surface area (SSA)

of $2630 \text{ m}^2 \text{ g}^{-1}$, excellent electrical conductivity and stable chemical properties and so on [15, 16]. However, graphene sheets have an inevitable tendency to aggregation because of the strong van der Waals interactions among individual graphene sheets, which limits the accessibility of electrolyte ions and the surface area utilization [17], and, as a consequence, the capacitance value measured is far lower than the theoretical one. Previous efforts to address this problem include introducing other nanomaterials (such as acetylene black (CB) [18], CNTs [19, 20], et al.) among the graphene sheets to impede the restacking of graphene sheets. However, due to the relatively low SSA [21, 22], the CB and the CNT introduced among the graphene sheets have little contribution to the electrochemical performance. Unfortunately, this drawback cannot be effectively overcome through the introduction of CB or CNT alone because of the difficulty in constructing abundant pores on CB and CNT [23].

Obviously, introduction of porous carbon among the graphene sheets will be effective to both impede the restacking of graphene sheets and provide high SSA. J. Yan et al. constructed a sandwiched porous carbon layer@graphene hybrid by one-step pyrolysis of the mixture of graphene oxide/polyaniline and KOH, which behaves superior capacitive performance [24]. Herein, we propose another strategy that constructs porous carbon/graphene hybrids, i.e., synthesis of a RGO/CNT@AC hybrid by introducing the activated porous carbon-coated carbon nanotube (denoted as CNT@AC) instead of pure CNT among the graphene sheets. This architecture inherits the advantages of graphene and CNT (high electrical conductivity) as well as porous

carbon (huge surface area) [25]. Due to the high SSA and developed pore structure of the activated porous carbon coating (AC), more electrolyte ions diffusion pathways between graphene sheets, as well as the effective prevention on the restacking of graphene sheets by CNT@AC, the RGO/CNT@AC hybrid can be expected to exhibit superior supercapacitive performance.

2. Experimental

2.1. Sample preparation

2.1.1 Preparation of graphene oxide (GO) powders

Graphene oxide (GO) powders were obtained by a modified Hummers' method as described in literatures [19, 26]. In brief, 2 g graphite and 1 g NaNO₃ were added into a 250 ml flask filled with 46 ml H₂SO₄ (98 %) in ice bath under stirring. Next, 6 g KMnO₄ was slowly added to the solution over about 1 h, and, in the mean time, the ice bath was used to keep the temperature of the solution below 10 °C. After adding KMnO₄, the ice bath was removed and the solution was heated to 50 °C, followed by a slowly addition of 80 ml deionized water. And then temperature of the solution was raised to 90 °C and maintained for 30 min. Next 60 ml deionized water with 10 vol. % H₂O₂ was added to the solution until the reaction was terminated. The resultant solution was centrifuged and washed by 10 wt. % HCl and deionized water to completely remove the impurities, and, finally, dried at 60 °C for 12 h to obtain the GO powders.

2.1.2 Preparation of activated porous carbon coated carbon nanotube (CNT@AC)

0.05 g nitric acid-treated CNT (20 ~ 40 nm in diameter, obtained from the Shen-

zhen Nanotech Co. Ltd. of China) with 2.5 g glucose was added into 100 ml deionized water and ultrasonically dispersed for 3 h. Then, the resultant mixture was put into Teflon-sealed autoclave with a fill rate of 80 %. After 15 h hydrothermal treatment at 190 °C, the produced black powders were further carbonized in a tube furnace at 800 °C for 2 h in argon atmosphere, thus obtaining a core-shell pristine carbon-coated CNT composite (denoted as CNT@PC).

The as-prepared CNT@PC was activated by KOH at 800 °C for 1 h in argon atmosphere. Thereafter, the activated sample was immersed in 10 wt. % HCl solution, then washed to neutral and dried at 100 °C for 10 h, thereby achieving core-shell activated porous carbon-coated CNT composite (CNT@AC).

2.1.3 Preparation of graphene/CNT@AC hybrids (RGO/CNT@AC)

GO powder was added into 50 ml deionized water and dispersed by ultrasonication for 1 h. Then, the obtained CNT@AC was mixed with GO with a weight ratio of 2 : 8 and ultrasonically dispersed for 2 h. Thereafter, 5 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 by deionized water until to neutral, and then dried at 60 °C for 12 h, eventually constructing the graphene/CNT@AC hybrid (RGO/CNT@AC).

To probe into the effect of KOH amount, the as-prepared CNT@PC were activated by using different weight ratios of KOH to CNT@PC (0 : 1, 2 : 1, 4 : 1, 6 : 1 and 8 : 1), and the corresponding RGO/CNT@AC hybrids are denoted as

RGO/CNT@PC, RGO/CNT@AC-2, RGO/CNT@AC-4, RGO/CNT@AC-6 and RGO/CNT@AC-8, respectively.

RGO/CNT hybrid was also prepared by mixing the pristine CNT (without AC coating) and the RGO in the same way. For comparison, the CNTs with equal quantity were added in the RGO/CNT and the RGO/CNT@AC hybrids. In addition, the amount of the estimated RGO as well as CNT and porous carbon in the RGO/CNT@AC hybrids was list in the supplementary material.

2.2. Characterization

The morphologies and microstructure of the samples were observed using a Hitachi S-4800 field emission scanning-electron microscopy (SEM) at 15 kV and a JEM-2010 transmission electron microscopy (TEM) at 200 kV. X-ray diffraction (XRD) patterns between 10 (2θ) and 60 (2θ) degrees were collected by Rigaku D/MAX-2500 powder diffractometer with Cu-K α radiation ($\lambda=0.154$ nm) operated at 40 kV and 200 mA. Gas adsorption/desorption analysis was done in the V-Sorb 2800TP surface area and pore distribution analyzer (Gold APP Instruments Corporation, China) with N₂ as adsorbent at 77 K. Prior to analysis, samples were degassed in vacuum at 200 °C for 8 h. The SSA, according to BET (Brunaure, Emmet and Teller) theory and nanopore volume, was calculated by using t-plots based on the N₂ sorption isotherm. Pore size distributions were calculated using the Horvath-Kawazoe method and assuming a slit-pore model.

2.3. Preparation of electrode and electrochemical measurement

The electrochemical investigations were carried out in a symmetrical two-electrode cell with a cellulose separator. The working electrodes were prepared as follows: a slurry of consisting 80 wt. % active substance, 10 wt. % carbon black and 10 wt. % polytetrafluoroethylene (PTFE) binder was smeared into nickel foam and dried in vacuum at 120 °C for 10 h. The loading mass of the electrode is around 2 mg with an area of 1 cm². A 6 M KOH solution was used as electrolyte. Cyclic voltammograms (CVs) and electrochemical impedance spectroscopy (EIS) were collected on CHI650D electrochemical workstation. The galvanostatic charge/discharge tests were carried on potentiostat/galvanostat (CT2001A, Land, Wuhan, China).

3. Results and discussion

Fig. 1 shows the electron microscopy of CNT, CNT@PC and CNT@AC, respectively. It can be deduced from Fig. 1a and b that approximately 30 nm thick pristine carbon is uniformly coated on the CNT surface, constructing a core-shell structured CNT@PC. After KOH activation, the surface of the carbon coating on CNT becomes highly rougher (Fig. 1c), which can be attributed to the etching of carbon caused by the KOH activation [27]. TEM observation of CNT@AC demonstrates that CNT is completely covered by a uniform AC coating (Fig. 1d), and the structure of AC is mainly composed of disordered carbons (Fig. 1e and f).

Fig. 1. SEM images of (a) CNT, (b) CNT@PC, (c) CNT@AC; TEM images of (d) the low-resolution, (e) and (f) the high-resolution of CNT@AC

Fig. 2 presents the SEM images of RGO and RGO/CNT@AC, respectively. The coplanar alignment of RGO becomes layered aggregates (Fig. 2a) due to the strong van der Waals interactions among graphene sheets, indicating a lower electrolyte-accessible surface area. After the introduction of CNT@AC, the graphene sheets become more crumple and dispersive (Fig. 2b), suggesting the achievement of impedance on the restacking of graphene sheets.

Fig. 2. SEM images of (a) RGO and (b) RGO/CNT@AC

Fig. 3 displays the XRD patterns acquired from CNT, CNT@PC, CNT@AC, RGO, RGO/CNT@PC and RGO/CNT@AC-6, respectively. Four diffraction peaks, a

strong peak at $2\theta = 26^\circ$ (002), two weak peaks at $2\theta = 43^\circ$ and 44.5° (10), and a broad peak at $2\theta = 22^\circ$, respectively, are visible in the XRD pattern of CNT. For CNT@PC, except for the diffraction peak at $2\theta = 22^\circ$, all the other peaks become significantly weaker, which should be attributed to the carbon coating on the CNT surface. As for CNT@AC, it exhibits a stronger diffraction peak at $2\theta = 26^\circ$ but a weaker peak at $2\theta = 22^\circ$ compared with CNT@PC, suggesting a relatively more ordered carbon structure. In addition, RGO displays an obviously broad diffraction peak at about $2\theta = 23^\circ$. As for RGO/CNT@PC and RGO/CNT@AC-6, however, this peak becomes dramatically weaker, suggesting the enlargement of the space among graphene sheets due to the introduction of carbon-coated CNT and thus the achievement of the effective prevention on the restacking of graphene layers.

Fig. 3. XRD patterns of CNT, CNT@PC, CNT@AC, RGO, RGO/CNT@PC and RGO/CNT@AC-6

Nitrogen adsorption/desorption analysis of CNT@PC and CNT@AC-6 was carried out, and the obtained results are shown in **Fig. 4**. The SSA of CNT@AC-6, which is calculated from Fig. 4a, is up to $1808 \text{ m}^2 \text{ g}^{-1}$, almost 4 times as high as that of

CNT@PC ($495 \text{ m}^2 \text{ g}^{-1}$), suggesting that KOH activation to the carbon coating on CNT leads to the dramatic increase in the SSA of CNT@AC.

Fig. 4. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution curves of CNT@PC and CNT@AC-6

Fig. 5 presents the nitrogen adsorption/desorption isotherms and pore size distributions of RGO/CNT, RGO/CNT@PC and RGO/CNT@AC-6. It can be deduced from Fig. 5a that the SSA of RGO/CNT, RGO/CNT@PC and RGO/CNT@AC-6 is $344 \text{ m}^2 \text{ g}^{-1}$, $421 \text{ m}^2 \text{ g}^{-1}$ and $1871 \text{ m}^2 \text{ g}^{-1}$, respectively. The RGO/CNT@AC hybrid behaves a dramatically higher SSA. Therefore, it can be expected that RGO/CNT@AC will exhibit higher capacitance, since high SSA will be beneficial to offer more accessible surface for electrolyte ions. In addition, the hysteresis loops in the relative pressure region between 0.4 and 1.0 suggest the presence of mesopores for all the samples. Larger hysteresis loop means more mesopores. Obviously, RGO/CNT@PC exhibits a largest volume of mesopores. As for RGO/CNT@AC-6, its markedly larger nitrogen adsorption volume relative to RGO/CNT@PC and RGO/CNT at low pressure (P/P_0) suggests a more developed microporous structure, which is evidenced by the pore size

distributions presented in Fig. 5b. Undoubtedly, higher SSA and more developed porous structure, which are mainly contributed by the porous CNT@AC, will enable the RGO/CNT@AC hybrids to show superior supercapacitive performance.

Fig. 5. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution curves of RGO/CNT, RGO/CNT@PC and RGO/CNT@AC-6

To disclose the effect of KOH amount on the pore structure, **Table 1** lists the detailed porosity characteristics of RGO/CNT and RGO/CNT@AC hybrids where the carbon coating on CNT was activated by different amounts of KOH. As can be seen, the KOH amount has significant effect on the porosity characteristics of RGO/CNT@AC. For example, as the KOH amount increases, the SSA and the micropore volume of the RGO/CNT@AC hybrids increase firstly and then decrease. The highest SSA ($1871 \text{ m}^2 \text{ g}^{-1}$) and the largest micropore volume ($0.71 \text{ cm}^3 \text{ g}^{-1}$) are obtained when the weight ratio of KOH to CNT@PC is up to 6 : 1 (RGO/CNT@AC-6). In any case, however, all of the RGO/CNT@AC samples show greatly higher SSA and larger micropore volume than those of RGO/CNT and RGO/CNT@PC.

Table 1. Porosity characteristics of RGO/CNT and RGO/CNT@AC hybrids where the carbon coating on CNT was activated by different amounts of KOH

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	P_{micro} (nm)	P_{meso} (nm)
RGO/CNT	344	0.03	0.48	0.84	4.05
RGO/CNT@PC	421	0.11	1.26	0.81	4.12
RGO/CNT@AC-2	799	0.27	0.87	0.83	3.96
RGO/CNT@AC-4	1196	0.41	0.65	0.86	3.88
RGO/CNT@AC-6	1871	0.71	0.24	0.86	4.15
RGO/CNT@AC-8	982	0.34	1.06	0.85	3.93

S_{BET} : Specific surface area determined by BET method.

V_{micro} : Micropore volume calculated using the t-plot method.

V_{meso} : Mesopore volume calculated BJH adsorption cumulative volume.

$P_{\text{micro}}, P_{\text{meso}}$: Micropore and Mesopore value obtained from BJH desorption dV/dD pore volume plot.

In order to evaluate the electrochemical performances of the obtained RGO/CNT@AC hybrids, cyclic voltammogram (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) measurements were employed in 6 M KOH solution at ambient temperature. All the CV curves were measured at various scan rates ranging from 10 to 5000 mV s^{-1} within a potential range of 0 ~ 1 V. The specific capacitances of RGO, CNT@AC-6 and RGO/CNT@AC-6, calculated

from CV curves shown in Fig. 6a , are 59 F g^{-1} , 93 F g^{-1} and 193 F g^{-1} , respectively. This result shows that the incorporation of CNT@AC among RGO sheets can greatly improve the capacitive performance of the hybrid electrodes due to the improvement in enhancing the electron-electrolyte transports and decreasing kinetic difficulties for both charge transfer and ions transport through the electrode. From the CV curves of RGO/CNT, RGO/CNT@PC and RGO/CNT@AC-6 (Fig. 6b), it is clear that RGO/CNT@AC-6 shows best capacitive performance at a scan rate of 10 mV s^{-1} , corresponding to a specific capacitance up to 193 F g^{-1} , a high energy density around 97 Wh Kg^{-1} , which is greatly higher than those of RGO/CNT (91 F g^{-1} , 46 Wh Kg^{-1}) and RGO/CNT@PC (100 F g^{-1} , 50 Wh Kg^{-1}). Obviously, this significant improvement in the specific capacitance of RGO/CNT@AC-6 can be ascribed to the higher SSA and more developed pore structure contributed by KOH activation to the carbon coating on CNT. In addition, the specific capacitances of RGO/CNT, RGO/CNT@PC and RGO/CNT@AC-6 show a decrease trend as the scan rate increases (Fig. 6c), which is due to the fact that the charge diffusion cannot match the rapid increase in the scan rates [28]. However, RGO/CNT@AC-6 can always exhibit markedly higher capacitance at the same scan rates. Even at a scan rate of 5000 mV s^{-1} , the CV curve of RGO/CNT@AC-6 can keep a rectangular-like shape (Fig. 6d) and its specific capacitance can still sustain 138 F g^{-1} , corresponding to a capacitance retention ratio of 72 %, evidently higher than those of RGO/CNT (23 F g^{-1} , 25 %) and RGO/CNT@PC (49 F g^{-1} , 49 %) (Fig. 6c), suggesting that the RGO/CNT@AC hybrid can also exhibit supe-

rior rate performance. This result is interesting, which may mean that the RGO/CNT@AC hybrid possesses more favorable architecture for the transport of the electrolyte ions than RGO/CNT.

Fig. 7 shows a schematic illustration of the ion diffusion behavior for RGO/CNT and RGO/CNT@AC. Owing to the developed porous structure in the AC coating on CNT, RGO/CNT@AC can provide more diffusion paths existing between RGO sheets than RGO/CNT, which will eventually facilitate the rapid transport of the electrolyte ions.

Fig. 6. (a) CV curves of RGO, CNT@AC-6 and RGO/CNT@AC-6 at $10 mV s^{-1}$, (b) CV curves of RGO/CNT, RGO/CNT@PC and RGO/CNT@AC-6 at $10 mV s^{-1}$, (c) the dependences of specific capacitance of RGO/CNT, RGO/CNT@PC, and

RGO/CNT@AC-6 on the scan rate of CVs from 10 to 5000 mV s^{-1} , (d) CV curves of RGO/CNT, RGO/CNT@PC, and RGO/CNT@AC-6 at 5000 mV s^{-1}

Fig. 7. Schematic illustration of the ions diffusion behavior for RGO/CNT and RGO/CNT@AC

To further investigate the effect of KOH amount on the supercapacitive performance, the CVs of the RGO/CNT@AC hybrids where the carbon coating on CNT was activated by different amounts of KOH were measured and shown in **Fig. 8**. It can be seen that the specific capacitances of RGO/CNT@AC hybrids are heavily dependent upon the KOH amount. As the KOH amount increases, the specific capacitances of the RGO/CNT@AC hybrids at the scan rate of 10 mV s^{-1} first increase, reaching the maximal value of 193 F g^{-1} at the 6 : 1 weight ratio of KOH to CNT@PC (RGO/CNT@AC-6), and then trends to decrease (Fig. 8a). This result can be explained by the SSA measurements. Since for the EDLC, charge storage mechanism is based on the electrostatic adsorption of charge separated ions on the surface of an electrode material [29], it is reasonable that the RGO/CNT@AC hybrid having larger surface area can acquire higher specific capacitance. In any case, however, all the RGO/CNT@AC samples show significantly higher specific capacitances in comparison with RGO/CNT, suggesting that introducing CNT@AC instead of pure CNT

among the graphene sheets is effective for the achievement of superior capacitive performance. In addition, as the scan rate increases, the specific capacitances of RGO/CNT@AC hybrids show a decrease trend (Fig. 8b). However, the fact that the RGO/CNT@AC hybrids always exhibit evidently higher capacitances than RGO/CNT at the same scan rates implies that introducing CNT@AC among the graphene sheets is also beneficial for the improvement of rate performance.

Fig. 8. (a) CV curves of RGO/CNT@AC hybrids at 10 mV s⁻¹, (b) the dependences of specific capacitance of RGO/CNT@AC hybrids on the scan rate of CVs from 10 to 5000 mV s⁻¹

Fig. 9 shows galvanostatic charge/discharge curves of the RGO/CNT@AC hybrids in 6 M KOH electrolyte. All the charge/discharge curves exhibit almost symmetrical isosceles lines, which are the characteristic of electric double layer capacitance, in well agreement with the experimental results from CV tests. Furthermore, the curve of RGO/CNT@AC-6 shows longer charge/discharge time than the other samples indicating a highest specific capacitance value.

Fig. 9. The galvanostatic charge/discharge at 0.5 A g^{-1} curves of RGO/CNT@AC hybrids

Electrochemical impedance spectroscopy (EIS) is used to analyze the characteristic frequency response of the RGO/CNT@AC hybrids, and the corresponding AC impedance spectra (Nyquist plots) in 6 M KOH electrolyte are shown in **Fig. 10**. The imaginary part of the impedance spectra at low frequencies represents the capacitive behavior of the electrode and approaches a 90° vertical line in an ideal capacitor [30]. Therefore, the fact that all the Nyquist plots of the RGO/CNT@AC hybrids lean towards the imaginary axis in the low frequency region suggests a good double layer capacitive behavior. In the high frequency region, larger semicircle represents higher charge transfer resistance, and a larger x-intercept represents higher equivalent series resistance. Obviously, among all the RGO/CNT@AC hybrids, RGO/CNT@AC-6 behaves lowest charge transfer resistance and equivalent series resistance.

Fig. 10. The Nyquist plots of RGO/CNT@AC hybrids in 6M KOH electrolyte (the inset shows expanded high-frequency region of Nyquist plots)

Cycling stability is a most important criterion for supercapacitor. In order to evaluate the long-term cycling stability of the RGO/CNT@AC hybrids, the CV curves were measured for 6000 cycles at the scan rate of 50 mV s^{-1} in 6 M KOH electrolyte, and the results are shown in **Fig. 11**. It is observed that, for the RGO/CNT@AC hybrids where the carbon coating on CNT was activated by different amounts of KOH, their specific capacitances are quite stable over the entire cycle numbers, and almost 100 % specific capacitance can be remained even after 6000 cycles, indicating excellent cycling stability, which is significant for the practical application. At the beginning of cycling, a slight increment in the specific capacitance is observed. This increase is presumed to be the continuous activation occurring in the electro-active material caused by diffusion of electrolyte ions inside the electrode during cycling [31, 32]. So the samples RGO/CNT@AC-4 and -6 with higher SSA and more developed pores can show more evident increase in the specific capacitance at the early circulation.

Fig. 11. Cycling stability of RGO/CNT@AC hybrids and RGO/CNT at 50 mV s⁻¹ in 6 M KOH electrolyte

4. Conclusion

A RGO/CNT@AC hybrid composed of graphene and core-shell CNT@AC is fabricated by incorporation of CNT@AC among the graphene sheets. The SSA and micropore volume of the RGO/CNT@AC hybrid, strongly effected by the amount of KOH used for activating the carbon coating on CNT, are both significantly higher than those of RGO/CNT. Compared with RGO/CNT, RGO/CNT@AC exhibits better electrochemical performances, such as higher specific capacitance, superior rate capability and excellent cycling stability, presenting great potential for practical application as an electrode material for supercapacitors. The present work shows that the introduction of CNT@AC instead of CNT among the graphene sheets can be considered as an effective route to impede the restacking of graphene sheets, acquire high SSA and developed micropores and thus achieve excellent supercapacitive performance.

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