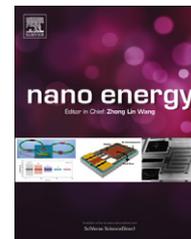




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RAPID COMMUNICATION

In situ synthesis of graphene/single-walled carbon nanotube hybrid material by arc-discharge and its application in supercapacitors



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KEYWORDS

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Abstract

Aiming to the synthesis of graphene/single-walled carbon nanotube (SWNT) hybrid materials, an arcing-discharge method for an efficient and large-scale production has been developed. Furthermore, the performance of supercapacitors using this graphene/SWNT hybrid has been studied, which gives a remarkable result with the specific capacitance of ~ 350 F/g at 2.7 V and an energy density of ~ 68 Wh/kg in the standard industry organic electrolyte system.

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Introduction

Both one and two dimensional nano carbon materials, carbon nanotube (CNT) and graphene have inspired tremendous interest due to their unique physical and chemical properties [1–7]. Their hybrid materials, if carefully designed and prepared, might generate some synergistic and more exciting performance than the individual materials. Dimitrakakis, et al. proved that CNTs and graphene sheets can be combined to form a novel 3D nanostructure which is suitable for the hydrogen storage or using as the active material in

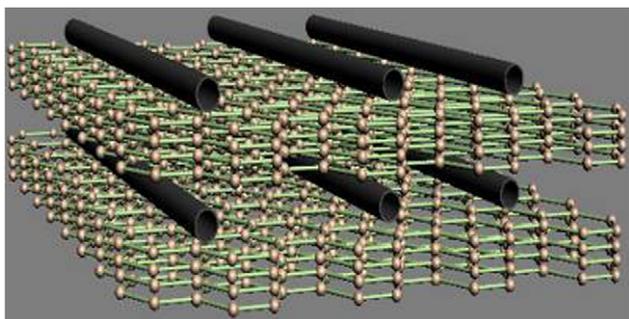
supercapacitors [8]. As it is well known that in the bulk state, graphene sheets intend to re-stack together due to the strong π - π interaction. Thus, the theoretical high surface area and other properties of graphene could not be fully materialized for some applications such as the active material in supercapacitors. It is expected that if highly conducting CNTs are used as the spacers, the hybrid structure with graphene (Scheme 1), where the combined excellent properties of both these two nano carbon materials can work together, would be ideal for such supercapacitor applications where both high surface and conductivity are needed. We have reported that using a hybrid process, such a material using graphene oxide (GO) and CNTs has been developed and shows an excellent supercapacitor performance [9]. Some other hybrid structures of CNTs with graphene sheets have been

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also fabricated, using a solution process [10], or growing CNTs on graphene sheets by chemical vapor deposition [11-13]. Nevertheless, these fabrication processes are complex, and more importantly, the graphene materials in these hybrid materials are all from GO. Obviously, using GO as the graphene material for such hybrid materials has been limiting their performance due to the abundant defects on GO sheets and low conductivity.

Arc-discharge is a powerful technique to make carbon materials, and is believed to be one of the most efficient techniques for large-scale synthesis of the as-prepared SWNTs product [14,15]. Recently, arc-discharge has been employed to prepare graphene sheets with advantages of large-scale and fewer defects [16,17]. Obviously, it is highly demanded and also a great challenge to develop a method to generate a hybrid material of these two materials simultaneously with few defects. Part of the reason is due to its extremely fast process of the arcing method. In this work, we wish to report a highly efficient and large-scale arc-discharge process for the in situ synthesis of such a graphene/SWNT hybrid for the first time. The hybrid was prepared where the SWNTs were grown in between or entwined around the graphene sheets (Figures 1 and 2), forming a network. Furthermore, due to its intrinsic and



Scheme 1 The illustration of the hybrid materials with SWNTs grown in between the graphene sheets, forming a unique network carbon nano material, with both SWNTs and graphene grown in situ and with fewer defects than other methods.

engineered structure and properties, the supercapacitors fabricated using this material gave the best performance (~ 350 F/g) reported so far for pure carbon materials.

Material and methods

Synthesis of graphene/SWNT hybrid

Briefly, we tested a series of catalyst from a mixture of NiO and Y_2O_3 with 4.2:1 atom Ni:Y and different amount of carbon atom. The consumable anodes were 120 mm in diameter and prepared by mixing the ground catalyst with the carbon source materials on a procedure as described in the literature [15]. Direct current (DC) arc-discharge was carried out in a home-made water-cooled stainless steel chamber filled with a mixture of H_2 and He at a pressure of ~ 530 Torr. Different ratios of H_2 and He ranging from 5 to 50 vol% H_2 and direct currents of 90 to 150 A were tested. The discharge voltage was kept around 30 V by controlling the distance between the two electrodes. The optimized conditions for the composite production are 12.5 vol% H_2 with 4.2:1:189.6 atom Ni:Y:C at 120 A. In a typical run, tens of grams of graphene/SWNT hybrid can be generated in minutes. The catalyst was removed by refluxing the hybrid in the boiling 2.6 M HNO_3 for 24 h, and then the hybrid was washed repeatedly by de-ionized water till a pH value reach 7.

Fabrication of supercapacitor

The supercapacitor test cells were fabricated with the two-electrode configuration. The graphene/SWNT hybrid was activated first by KOH (6:1 mass KOH:hybrid). KOH/hybrid mixtures were heated at $850^\circ C$ for 4 h in a horizontal tube furnace and then cold down. The temperature was ramped from room temperature to $850^\circ C$ at $5^\circ C/min$. The mixtures were washed repeatedly by de-ionized water till a pH value reach 7. The electrodes were made of the activated graphene/SWNT hybrid, combined with 5 wt% conductive carbon black as conductive additive and 5 wt% polyvinylidene fluoride as binder. The two electrodes were separated

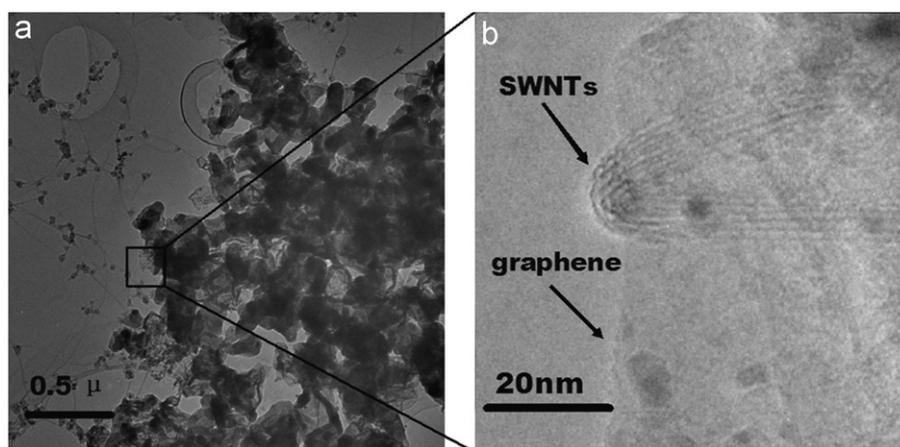


Figure 1 (a) Low- and (b) high-magnification TEM images of graphene/SWNTs hybrid produced under the condition of Ni/Y/C=4.2:1:189.6 ratio and with $\sim 12.5\%$ (v/v) H_2 in the buffer gas. The arrows indicate SWNTs bundle entwining around the graphene and the edge of graphene sheets.

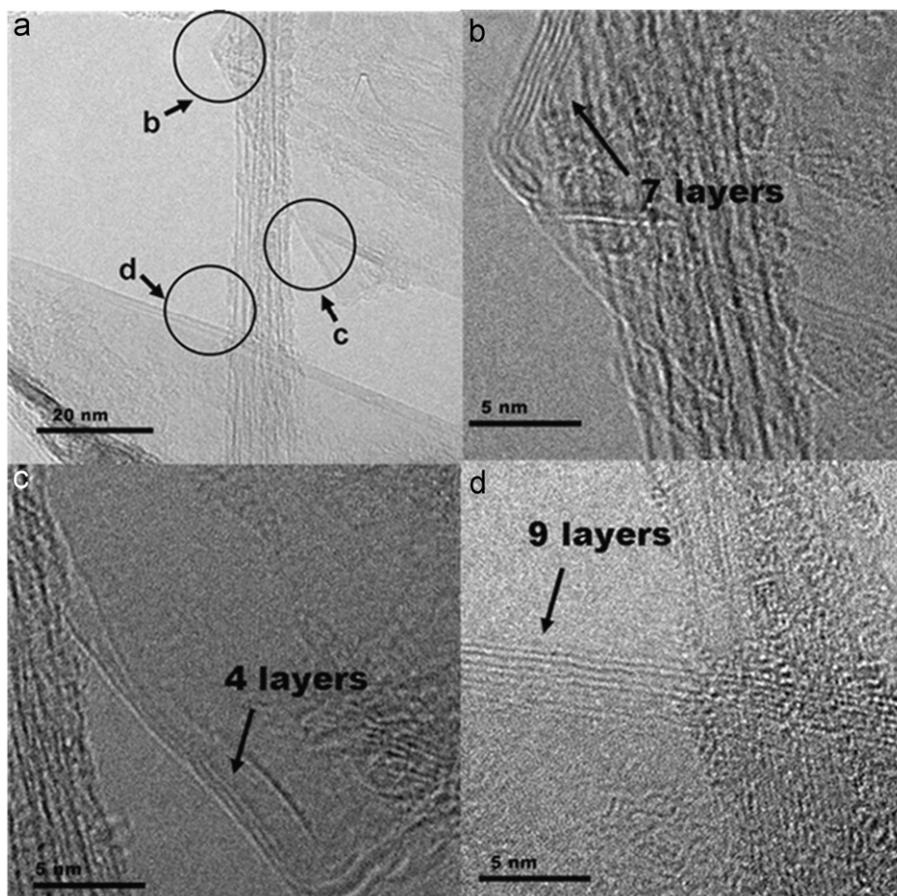


Figure 2 HRTEM images of graphene/SWNTs hybrid produced under the condition of Ni/Y/C=4.2:1:189.6 ratio and with ~12.5% (v/v) H₂ in the buffer gas. The SWNTs connect two individual graphene sheets, forming a network (a). (b)-(d) show the graphene sheets consist of seven (b), four (c), and nine (d) layers.

by a thin ion-porous separator (NKK[®] TF48-40) film in the TEA BF₄/AN electrolyte.

Instruments and methods

Transmission electron microscopy (TEM) images were obtained using a Tecnai 20 at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-3500N scanning electron microscope at an accelerating voltage of 20 kV. Raman spectra were measured with a Renishaw inVia Raman spectrometer using laser excitation at 514.5 nm. The surface area measurements were measured with a JWGB BK122F. Electrical measurements were carried out, and the data were collected with a Keithley SCS 4200. Cyclic voltammetry (CV) was performed with a LK98B II microcomputer-based electrochemical analyzer. The galvanostatic charge discharge was carried out with a supercapacitor tester (Arbin Instrument, USA). The energy density is calculated according to Eq. (1):

$$E_{density} = \frac{C \int_{t_0}^{t_1} V(t) dt}{3.6t} \quad (1)$$

where $E_{density}$ stand for energy density and C is the specific capacitance, V is the voltage during the discharge; t is the total time of discharge; t_0 is the start time of discharge while t_1 is the end time.

Results and discussion

Synthesis of graphene/SWNT hybrid materials

The hybrid material was synthesized by the simple arcing method with a similar setup as that in the synthesis of SWNTs and graphene individually reported earlier [15,16], but with different catalysts and buffer gas controlling parameters. While it was observed that certain amounts with different quality of the hybrid materials of graphene/SWNT can be produced in a wide range of catalyst/carbon ratios when hydrogen gas was presented in the buffer gas (Figure 1, Figure S1, Figure S2, see Supplementary), the optimized graphene/SWNT hybrid was generated at the condition of 4.2 atom Ni: 1 atom Y: 189.6 atom C with ~12.5% (v/v) H₂ in the buffer gas.

Figure 1 shows the TEM images of the hybrid produced under the optimized condition of 4.2 atom Ni: 1 atom Y: 189.6 atom C with ~12.5% (v/v) H₂ in the total buffer gas. The image in Figure 1a clearly shows the presence of SWNTs (on the left part of the image), graphene (on the right part) and the hybrid of the two. The SWNTs bundles in Figure 1b are entwining around the graphene, which indicates that the SWNTs bundles are well contacted with the graphene sheets. The connection could be Wan de Walls force or π - π stacking or chemical bonding where further study is needed.

The SEM image (see Supplementary Figure S3) also supports the hybrid structure that the SWNTs grow in between or wind with the graphene sheets, forming a network.

More structure details of the hybrid are shown in Figure 2: The high-resolution TEM (HRTEM) images show scrolled edges of the graphene, and the number of graphene layers can be clearly distinguished [17]. Figure 2a are the SWNTs, connecting two individual graphene sheets, forming a network. Figure 2b~d show the graphene sheets consist of seven (b), four (c), and nine (d) layers. The thickness distribution of the graphene is not as uniform as the former result in literature for the production condition is slightly changed [17]. More HRTEM images in the Supplementary (Figure S4, S5) show the networks formed by SWNTs and graphene sheets, and the number of graphene layers.

Interestingly, we noticed that the H₂ percentages in the buffer gas and catalyst loadings have great impact on the ratios of graphene/SWNT in the hybrid products. Figure 3 shows the TEM images of graphene/SWNT hybrids produced at different concentrations of H₂ in the mixed buffer gas ranging from 5 to 50 vol% (a-d, H₂ concentration being 5, 12.5, 25, 50 vol%, respectively) with the same content of catalyst (4.2 atom Ni: 1 atom Y: 189.6 atom C). As shown in Figure 3a, with the presence of 5 vol% H₂, only SWNTs were observed and no graphene was visible. While with 12.5% H₂ loading, roughly half

of the products were SWNTs and the others were graphene sheets. With more H₂ loading, as shown in Figure 3c and d, there were less and less visible SWNTs but more and more graphene sheets observed from TEM images.

These results have also been verified by Raman spectroscopy studies. Figure 4 show the Raman results of the hybrid products generated under different amounts of catalyst or different ratios of H₂/He. Figure 4a shows the Raman spectra of three graphene/SWNT hybrids, obtained at the present of 12.5 vol% H₂ but using different catalyst loading: the optimized amount of catalyst (4.2 atom Ni: 1 atom Y: 189.6 atom C), double of the optimized amount of catalyst (4.2 atom Ni: 1 atom Y: 94.8 atom C) and half of the optimized amount of catalyst (4.2 atom Ni: 1 atom Y: 379.2 atom C), respectively. As it can be seen from Figure 4a, the peaks in the region (100-375 cm⁻¹), corresponding to the A_{1g} radial breathing mode (RBM) of SWNTs [18], become weaker and weaker with the decreasing amount of catalyst. Simultaneously, the inset shows clearly that the peaks at ~2700 cm⁻¹ of the products exhibit blue shift with the decreasing of the amounts of catalysts. This indicates that less SWNTs but more graphene were generated, since the 2D peak of graphene is located around 2720 cm⁻¹ and that for SWNTs is around 2672 cm⁻¹ [18]. Also, this is expected as we reported before that only graphene could be generated

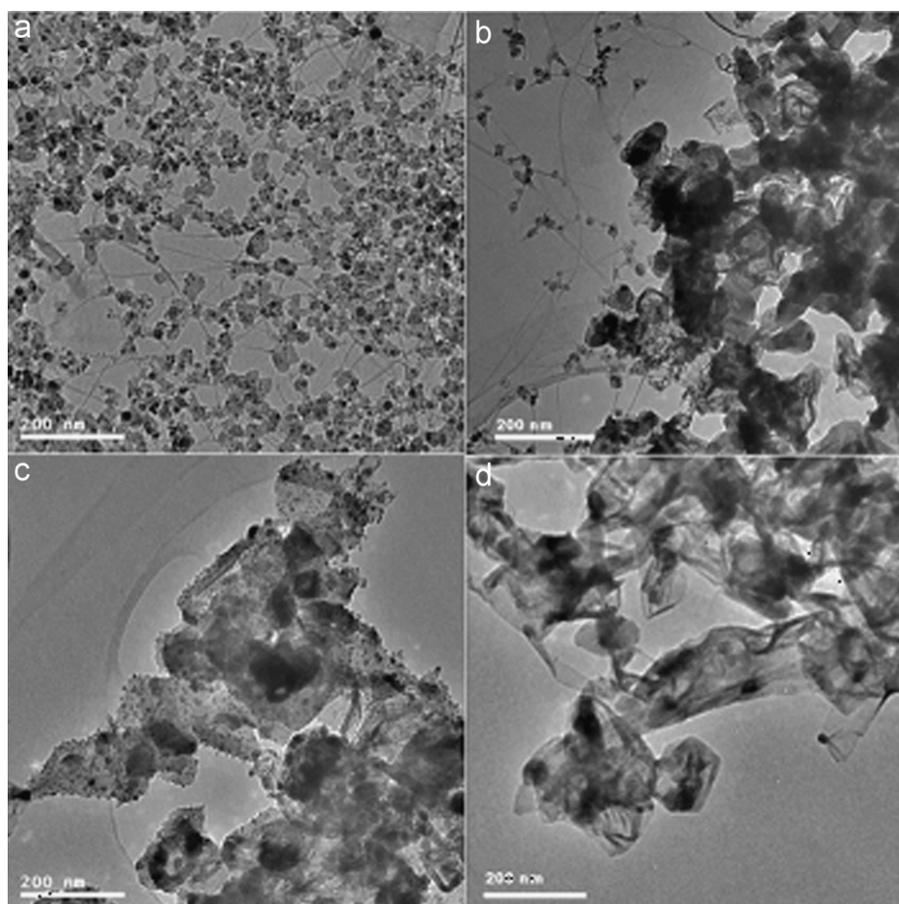


Figure 3 (a)-(d) the TEM images of graphene/SWNT hybrids obtained from different concentrations of H₂ in the mixed buffer gas ranging from 5 to 50 vol% (a-d, H₂ content being 5, 12.5, 25, 50 vol%, respectively) under the optimized catalyst condition of 4.2 atom Ni: 1 atom Y: 189.6 atom C. It can be seen that SWNTs become less and graphene become more as the concentration of H₂ increasing.

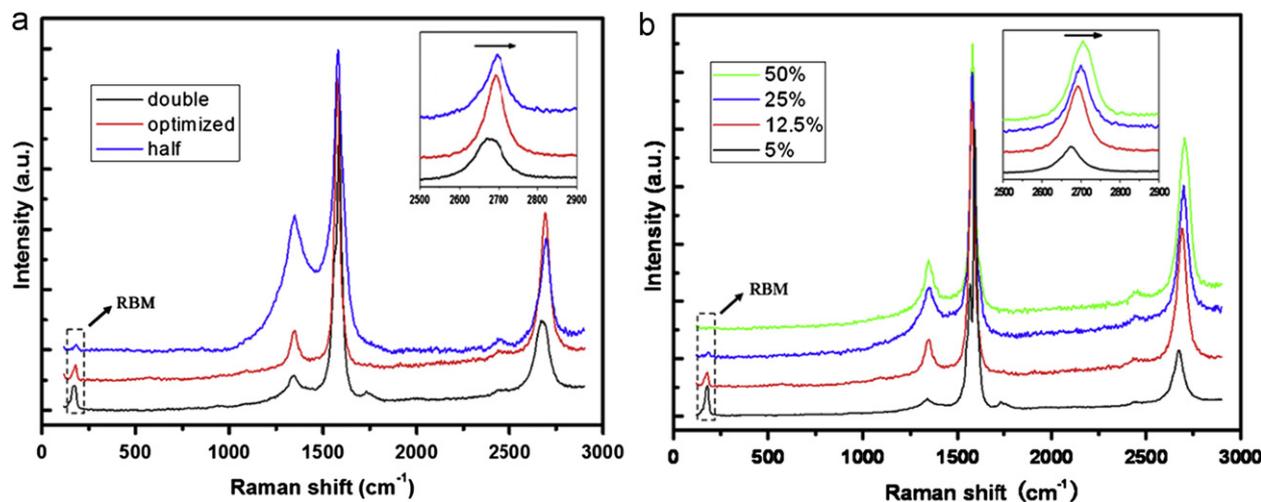


Figure 4 (a) Typical Raman spectra of the products obtained under the H_2 loading of 12.5 vol% H_2 at different catalyst loadings: the optimized amount of catalyst (4.2 atom Ni: 1 atom Y: 189.6 atom C), double of the optimized amount of catalyst (4.2 atom Ni: 1 atom Y: 94.8 atom C) and half of the optimized amount of catalyst (4.2 atom Ni: 1 atom Y: 379.2 atom C). The decreasing intensity of the RBM peaks with the mass reduction of catalyst indicates the decreasing amount of the SWNTs while the blue shift of the 2D band shows the growing amount of graphene. (b) Typical Raman spectra for the products from different ratios of H_2 in the buffer gas (H_2 concentrations being 5, 12.5, 25, and 50 vol%, respectively) with a catalyst loading of 4.2 atom Ni: 1 atom Y: 189.6 atom C. The decreasing intensity of the RBM peaks with the increasing partial pressure of H_2 indicates the decreasing amount of the SWNTs while the blue shift of the 2D band shows the growing amount of graphene.

when no catalyst is used [17]. Figure 4b is the Raman spectra of the products with different ratios of H_2 in the buffer gas but with the same amount of catalyst (4.2 atom Ni: 1 atom Y: 189.6 atom C). The concentration of the H_2 in the H_2/He mixture was varying from 5 to 50 vol%. It shows clearly that the RBM peaks of SWNTs is becoming weaker and weaker with the H_2 content increasing, while the 2D peaks of graphene is getting stronger and more blue-shift as shown in the inset. All these indicate that more graphene but less SWNTs were generated with H_2 increasing.

Mechanism of graphene/SWNT hybrid formation

In the synthesis of graphene/SWNT hybrid, the formation of the SWNTs and graphene are expected to be two independent processes. The formation of SWNTs follows the vapor-liquid-solid mechanism. In this mechanism, the SWNTs grow from the oversaturated metal carbon liquid alloy at a lower temperature due to the decreased solubility of carbon [19]. For the graphene, the graphite evaporates in the center of the arc, forming carbon cluster, and then H_2 in the buffer gas can connect with the edge of the carbon cluster which minimize the formation of nanotubes and thus graphene is generated [20]. There is no need of catalyst for the formation of the graphene but the hydrogen or other reactive gas is necessary. Thus, the amount of the catalyst and the concentration of H_2 in the mixed buffer gas are the two key factors for growing graphene and SWNTs together.

The amount of the catalyst is important to the SWNTs production in the hybrid, the more catalyst the more seeds for the formation of SWNTs. A proper amount of the catalyst (4.2 atom Ni: 1 atom Y: 189.6 atom C) is thus expected to generate the proper amount of seeds for the SWNTs, and leaving the other carbon atoms to form graphene. With the growing amount of the catalyst, the seeds for the growing of

the SWNTs become more and leaving fewer carbon atoms for the formation of the graphene, so there will be more SWNTs and less graphene sheets to be generated.

Hydrogen in the buffer gas can react with the edge of the carbon cluster, which minimize the formation of nanotubes and other close carbon structures [16]. So, with the proper concentration of the H_2 (12.5% (v/v) H_2 in the total buffer gas), both significant or similar amount of SWNTs and graphene can be generated simultaneously. When more hydrogen is applied, more graphene but less SWNTs would be generated.

Thus, when both optimized parameters of catalyst and H_2 loading are applied, as indicated with the results from the optimized conditions above, roughly similar amounts of SWNTs and graphene are generated simultaneously and a graphene/SWNT hybrid with fewer defects is yielded.

Supercapacitor studies of graphene/SWNT hybrid materials

The products were used as the supercapacitor electrode material. The supercapacitor test cells were fabricated with the two-electrode configuration as detailed in the experimental part. Briefly, the electrodes were made of the activated graphene/SWNT hybrid, combined with 5 wt% conductive carbon black as the conductive additive and 5 wt% polyvinylidene fluoride as the binder. The two electrodes were separated by a thin ion-porous separator film in the TEA BF_4/AN electrolyte to form the supercapacitor device for testing.

To accelerate the testing for more charging/discharging cycles, the device performance data were taken once every 5 cycles (cycle1, 6 and so on) using a 0.5 A/g charge to 2.7 V and 0.1 A/g discharge in the TEA BF_4/AN electrolyte, and all other cycles (cycle 2,3,4,5 and so on) were run at an accelerated rate of 1 A/g [21]. While, the conductivity

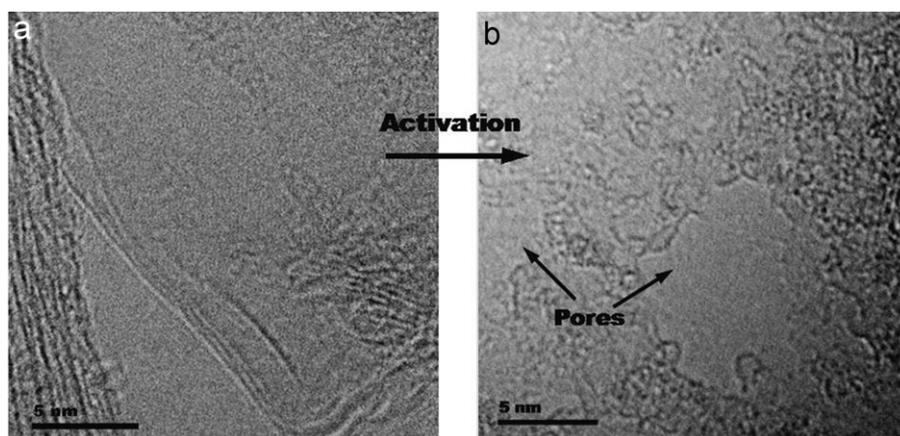


Figure 5 The HRTEM images before (a) and after (b) activation. The graphene in (a) shows a smooth surface and (b) demonstrates the porous morphology after activation. The arrow in (b) shows the pores caused by the activation.

(273 S/m) is much better than that of the commercial activated carbon used for supercapacitors. For example, the conductivity of commercial nanoporous carbon RP-20 (Kuraray Chemical Co.) is ~ 4 S/m. But, the specific capacitance for the pristine hybrid material is only ~ 30 F/g. So, the Brunauer-Emmett-Teller (BET) surface area was checked and found it was low as only ~ 65 m²/g, which is obviously low for a high performance supercapacitor electrode material.

To improve the performance of our graphene/SWNT hybrid, we have activated the hybrid materials by KOH [22]. The KOH reacted with the carbon atoms at the surface of carbon materials, generating nanoscale pores [22] (Figure 5), therefore, the surface area result of the activated hybrid was improved to ~ 190 m²/g by BET method and ~ 300 m²/g by the Barrett-Joyner-Halenda (BJH) method. The conductivity after the activation does not change too much and still has ~ 259 S/m, which is still much better than that of the commercial carbon RP-20. The supercapacitor devices based on the new activated hybrid material were tested again under similar condition. But, for the first few cycles, specific capacitance is still as low as ~ 70 F/g. Surprisingly, the specific capacitance of hybrid did not decrease as expected for most results in literatures, but actually increased dramatically with more cycles. As it shows in Figure 6, after 6700 cycles, the specific capacitance increased to ~ 300 F/g and became stable around 350 F/g with an energy density of ~ 68 Wh/kg [12]. A typical galvanostatic charge/discharge curve with a specific capacitance of 381 F/g is shown in Figure S 6a and a typical CV curve at the scan rate 1 mV/s shows a specific capacitance of 339 F/g (Figure S 6b). The little fluctuation of the graph in Figure 6 is caused by the room temperature variation with the day and night alternation [23]. There has been reported that “electro-activation” could cause capacitance to increase [24,25]. It is believed that due to the unique structure of graphene/SWNT hybrid, during the charging/recharging process, the interfacial wetting ability was improved. Furthermore, the channel or pore (both size and volume) for electrolyte ions to pass is improved due to the intercalation between both the graphene layers and SWNT/graphene structures. After enough electro-activation charging cycles, the electrolyte ions can fully access the hybrid material and the specific capacitance become stable. The structures of the electrode materials after 8000 cycles were tested by HRTEM (Figure S7). Interestingly, a more

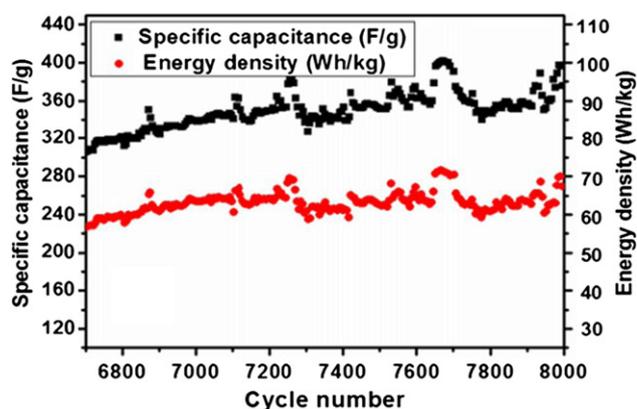


Figure 6 The cycling test results of the specific capacitance at 0.5 A/g charge and 0.1 A/g discharge. The specific capacitance grows from ~ 70 F/g to ~ 300 F/g and become stable around 350 F/g at 2.7 V (the black line) with an energy density (the red line) of ~ 68 Wh/kg in the TEA BF₄/AN electrolyte. The little fluctuation of the graph in Figure 6 is caused by the room temperature variation with the day and night alternation.

porous morphology and the fewer-layer structure of graphene were observed, which could be caused by the intercalation of the electrolyte ions. Note that for our hybrid materials, the surface area by BET method is ~ 190 m²/g, but the surface area by BJH method is ~ 300 m²/g. It is reported that this difference indicates that our hybrid materials have more negative curvature regions, which requires electro-activation to fully achieve their best capacitance performance [26].

Conclusions

We have developed a simple method for synthesizing the hybrid of SWNTs and graphene by an arc discharge method. With the increasing of the amount of catalyst or the decreasing concentration of H₂, the ratio of SWNTs increases and graphene decreases in the hybrid. With the optimized condition, a hybrid with about similar amount of graphene and SWNTs could be generated in only one step on large scale. The supercapacitor based on this material gave a specific capacitance of ~ 350 F/g and an energy density of

~68 Wh/kg in the TEA BF₄/AN electrolyte system. Thus, it is expected this material could be a good candidate for supercapacitor and other applications.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2012.07.001>.

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