University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

2014

Microwave autoclave synthesized multi-layer graphene/single-walled carbon nanotube composites for free-standing lithium-ion battery anodes

Chao Zhong

University of Wollongong, cz527@uowmail.edu.au

Jia-Zhao Wang

University of Wollongong, jiazhao@uow.edu.au

David Wexler

University of Wollongong, davidw@uow.edu.au

Hua-Kun Liu

University of Wollongong, hua@uow.edu.au

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>

Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Microwave autoclave synthesized multi-layer graphene/single-walled carbon nanotube composites for free-standing lithium-ion battery anodes

Abstract

Multi-layer graphene sheets have been synthesized by a time-efficient microwave autoclave method and used to form composites in situ with single-walled carbon nanotubes. The application of these composites as flexible free-standing film electrodes was then investigated. According to the transmission electron microscopy and X-ray diffraction characterizations, the average d-spacing of the graphene-single-walled carbon nanotube composites was 0.41 nm, which was obviously larger than that of the as-prepared pure graphene (0.36 nm). The reversible Li-cycling properties of the free-standing films have been evaluated by galvanostatic discharge-charge cycling and electrochemical impedance spectroscopy. Results showed that the free-standing composite film with 70 wt% graphene exhibited the lowest charge transfer resistance and the highest charge capacity of about 303 mAh g⁻¹ after 50 cycles, without any noticeable fading.

Keywords

battery, ion, lithium, standing, free, composites, nanotube, carbon, anodes, walled, microwave, single, graphene, layer, multi, synthesized, autoclave

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Zhong, C., Wang, J., Wexler, D. & Liu, H. (2014). Microwave autoclave synthesized multi-layer graphene/single-walled carbon nanotube composites for free-standing lithium-ion battery anodes. *Carbon*, 66 (2014), 637-645.

Microwave Autoclave Synthesized Multi-layer Graphene/Single-walled Carbon Nanotube Composites for Free- standing Lithium-ion Battery Anodes

Chao Zhong,^{a*} Jia-Zhao Wang,^{a*} David Wexler,^b Hua-Kun Liu^a

^a Institute for Superconducting and Electronic Materials, University of Wollongong,
NSW 2500, Australia

^b Electron Microscopy Centre, Innovation Campus, University of Wollongong, NSW
2500, Australia

*Corresponding author.

Phone: +61-2-4298 1400, Fax: +61-2-4221 5731, E-mail: cz527@uowmail.edu.au (C. Zhong)

Phone: +61-2-4298 1478, Fax: +61-2-4221 5731, E-mail: jiazhao@uow.edu.au (J.Z. Wang)

Abstract

Multi-layer graphene sheets have been synthesized by a time-efficient microwave autoclave method and used to form composites in situ with single-walled carbon nanotubes. The application of these composites as flexible free-standing film electrodes was then investigated. According to the transmission electron microscopy and X-ray diffraction characterizations, the average *d*-spacing of the graphene-single-walled carbon nanotube composites was 0.41 nm, which was obviously larger than that of the as-prepared pure graphene (0.36 nm). The reversible Li-cycling properties of the free-standing films have been evaluated by galvanostatic discharge-charge cycling and electrochemical impedance spectroscopy. Results showed that the free-standing composite film with 70 wt% graphene exhibited the lowest charge transfer resistance and the highest charge capacity of about 303 mAh g⁻¹ after 50 cycles, without any noticeable fading.

Keywords: multi-layer graphene sheet, single-walled carbon nanotube, microwave autoclave method, flexible free-standing film, lithium-ion battery anodes

1. Introduction

Recently, flexible/bendable electronic equipment, such as roll-up displays and wearable devices, has attracted more and more attention. The development of such devices implies higher requirements on their battery systems, in which flexibility of the electrodes is essential to enable their bendable features [1-3]. Typically, the conventional lithium-ion batteries (LIBs) have electrodes containing metal substrates, which are coated with a mixture of an active material, an electrical conductor, a binder, and a solvent [4,5]. This type of electrode is not suitable for flexible or bendable batteries because the active material layer will be cracked or peeled off from the substrate during the repeated bending. Therefore, the development of flexible free-standing electrode materials is crucial for bendable and wearable batteries. Previously, our group has reported the use of single-walled carbon nanotubes (SWCNTs) to form free-standing electrodes for LIBs [6,7]. It was found that the SWCNTs could be a promising candidate due to their one-dimensional structure with a high length-to-diameter ratio. This type of electrode is lightweight, flexible, and can be fabricated easily without using a metal substrate or binder. The conductivity of the SWCNT free-standing electrode is not as good as for the conventional ones, however, due to the absence of the substrate and binder. In addition, CNT based electrodes also feature relatively low energy density owing to the limitations of double-layer charge storage, which confines charge and energy storage to only the surface of the active materials [8]. These drawbacks have seriously limited their industrial application.

Graphene has outstanding properties, such as nontoxicity, chemical and thermal tolerance, electrical conductivity, and mechanical hardness. Such properties suggest a wide range of industrial applications, including adsorbents, catalyst supports, thermal

transport media, structural and electronic components, batteries/capacitors, and even applications in biotechnology [9 - 14]. Based on this idea, hybrid structures constructed by placing SWCNTs among graphene planes through covalent C-C bonding were reported to overcome the above-mentioned problems for CNTs [15-18]. Wang et al. reported using graphene film directly as a free-standing electrode for lithium-ion batteries [19]. After only the initial cycle, however, the capacity dropped down to 100 mAh g⁻¹ (current density: 50 mA g⁻¹). The poor Li cycling property is mainly owing to the restacking of graphene layers during the fabrication process, which indicates that the arrangement of the layered structure for stacks of graphene sheets is closely related to their electrochemical performance. Recently, Fan's group reported a three-dimensional composite powder material that consists of CNTs and graphene sheets [20]. The unique sandwich structure of this composite endows it with high-rate transportation of electrolyte ions and electrons throughout the electrode matrix and therefore increases the material's conductivity. Based on this idea, we designed and fabricated free-standing graphene-carbon-nanotube anodes for bendable Li-ion batteries. Embedding graphene with SWCNTs through a lamination process to prepare the free-standing electrode has the following advantages: 1) the sandwich structure of the graphene-carbon-nanotube composite will prevent the graphene sheets from being restacked during the electrode fabrication process [21]; 2) the layered graphene sheets that are integrated into the composite will form a conductive matrix, so that the film's conductivity will be improved [20].

The free-standing composite electrodes of graphene-carbon nanotube were fabricated using as-prepared graphene, which was synthesized by using a time-efficient microwave autoclave method. The effects of the reaction temperature on the graphene

characteristics were explored to help us to select the optimum graphene precursor for making the free-standing graphene-carbon nanotube electrodes. In order to investigate the graphene properties in the composite film, the graphene weight ratio was also varied for comparison.

2. Experimental

2.1 Synthesis: The multi-layer graphene sheets were prepared by using a microwave autoclave method. Graphite oxide (GO) was synthesized from natural graphite powder (Fluka) by a modified Hummers method, as reported elsewhere [22,23]. 60 mg of the as-prepared GO was added into 200 mL 0.02 M HCl solution, followed by 2 hours ultrasonication to make a homogeneous suspension. 150 mg NaOH and 3 mL $\text{H}_4\text{N}_2\cdot\text{H}_2\text{O}$ were then added to the solution, followed by 10 min stirring. The solution was then transferred into sealed Teflon vessels (25 mL each) and reacted at different temperatures (120 °C, 150 °C, and 180 °C) for 5 min using a Milestone Microsynth Microwave Labstation (Germany). In an alkaline medium, hydrazine hydrate can serve as a reducer, and therefore, the GO was reduced to multi-layer graphene sheets (MLG) during this process. The black products were washed repeatedly with de-ionized water and dried at 100 °C in a vacuum oven overnight. The products were designated MLG-1, MLG-2, and MLG-3, respectively (see Table 1).

The free-standing MLG-SWCNT composite films were fabricated through vacuum filtration of a suspension of MLG-SWCNT composite. To synthesize the composite material in situ, SWCNTs (purchased from Hipco™) and Triton X-100 were added to de-ionized water and ultrasonicated for 2 h. After that, the suspension was mixed with the as-prepared GO, which was then subjected to the same conditions and procedures

as were applied in the synthesis of MLG (with 180 °C selected as the reaction temperature). Before proceeding to the vacuum filtration, a poly(vinylidene) fluoride (PVDF) membrane was wetted in a 50:50 v/v deionized water to ethanol solution for 30 minutes. The MLG-SWCNT composite suspension was then passed through the wetted PVDF filter in a filtration cell under a positive pressure to produce a free-standing mat of the MLG-SWCNT composite. Subsequently, the resultant composite mat was washed with de-ionized water and then peeled off from the PVDF filter after drying overnight in a vacuum oven at 60 °C. By using this method, three MLG-SWCNT composite films were fabricated with MLG weight percentages of 30, 50, and 70 wt%, which were designated as MLG-SWCNT-1, MLG-SWCNT-2, and MLG-SWCNT-3, respectively (see Table 2).

2.2 Characterization: The products were characterized by using X-ray diffraction (XRD; GBC MMA) with Cu K α radiation, as well as field emission scanning electron microscopy (FE-SEM; JEOL 7500) and transmission electron microscopy (TEM; JEOL 2011 200 keV). TEM samples were prepared by dispersion of ground samples onto holey carbon support film. Raman spectroscopy was conducted to further investigate the materials, using a JOBIN YVON HR800 Confocal Raman system with 632.8 nm diode laser excitation on a 300 lines mm⁻¹ grating at room temperature. The conductivity measurements were performed on a JANDEL RM3 four-point probe instrument. The as-prepared free-standing films were used to fabricate the electrodes, using CR 2032 coin-type cells, which were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) by stacking the anodes with a porous polypropylene separator and a lithium foil counter and reference electrode. The electrolyte used was 1 M LiPF₆ in a 50:50 (v/v) mixture of ethylene carbonate and dimethyl carbonate. The

cells were galvanostatically discharged and charged within a voltage window of 0.01-3.0 V (vs. Li/Li⁺) at a current density of 30 mA g⁻¹ and a temperature of 20 °C. The discharge capacities are based on the total amount of free-standing electrode. An Ametek PARSTAT 2273 electrochemistry workstation was used to perform the electrochemical impedance spectroscopy (EIS; ac amplitude 5 mV, frequency range 100 kHz – 0.01 Hz).

3. Results and Discussion

To investigate the morphology of the MLG synthesized at different reaction temperatures, field emission scanning electron microscope (FESEM) images were collected, as shown in Figure 1. The images reveal a curled morphology consisting of rippled structures for each sample. Comparing Figure 1(a), (b), and (c), a trend towards more nanosized thin wrinkled structures was observed when the reduction temperature was increased. This phenomenon could possibly be due to the minimization of surface energy [24]. Oxygen-containing functional groups on the GO were reduced by hydrazine hydrate during the reaction. At higher temperature, this reaction proceeds faster (e.g. MLG-3 at 180 °C compared to MLG-1 at 120 °C). GO reduced at 180 °C lost more oxygen-containing groups from its surface, which made it less stable. Therefore, these surface-stress-induced strains led to the formation of the observed wrinkled structures.

The rippled and crumpled structures of the MLG samples were further revealed by high resolution TEM (HR-TEM), and the images are shown in Figure 2. The stacked structure of the nanosheets in the cross-sections of MLG can be clearly observed. Interestingly, the MLG prepared at the temperatures of 120, 150, and 180 °C showed

a trend in average d -spacing values of 0.43, 0.40, and 0.36 nm, respectively. This trend can be attributed to the degree of GO reduction, as the introduction of oxygen-containing functional groups (such as hydroxyl and epoxide) results in an increase in the d -spacing of GO compared to graphite [25]. As mentioned previously, over a range of reduction temperatures and pressures, GO can form a series of graphene–graphene-oxide transition states. The types and quantities of the oxygen-containing functional groups on the surface of the graphene can be varied. In the reaction, elevating the temperature could make the reduction reaction proceed further, which means that more oxygen-containing functional groups are lost from the surface of the GO within a certain reaction time. Therefore, with fewer supporting oxygen groups on their surfaces, the d -spacing of the graphene interlayers is decreased.

In the in-situ synthesis of the graphene–carbon-nanotube composites, the optimum reduction temperature in the microwave autoclave reaction was determined to be 180 °C. This was based on the following considerations. As mentioned in the introduction, the arrangement of the graphene layered structure is crucial for its electrochemical performance [19]. As a result, multi-layer graphene sheets with curled or wrinkled morphologies are favourable during the fabrication of free-standing films. With such morphologies, different arrangements of layers can be provided to prevent the multi-layer graphene sheets from restacking, and the space between graphene layers is also enlarged, so that the SWCNTs can be sandwiched into the layers more easily. On the other hand, although the larger d -spacing of the MLG-1 sample (around 0.43 nm) may be of benefit for the accommodation of lithium ions, the sample contains more residual oxygen-containing groups, which will affect the electrochemical performance, resulting in higher irreversible capacity due to the reaction between the oxygen-

containing groups and the lithium ions [26,27]. Taking all the above factors into consideration, 180 °C was selected as the best reduction temperature for the in situ synthesis of the composite.

Figure 3 shows FE-SEM images of the as-fabricated MLG-SWCNT free-standing films synthesized at 180 °C. Figure 3(a) presents a photograph of a typical free-standing film (MLG-SWCNT-3) fabricated by vacuum filtration, which is round in shape and about 3.4 cm in diameter. The average thicknesses and mass densities of the as-fabricated MLG-SWCNT samples are summarized in Table 2 for comparison. It can obviously be found that with increasing graphene ratio from 30 to 70 wt% in the composite, the thickness of the film is decreased from 115 to 78 μm , and the mass density is increased from 0.336 to 0.495 g cc^{-1} . Hence, it can be concluded that graphene can be used to efficiently increase the mass density of the CNT films. Figure 3(b) and (c) shows top views of the composite films, and the amount of MLG is clearly seen to increase upon increasing the MLG to SWCNT weight ratio from 3:7 (Figure 3(b)) to 7:3 (Figure 3(c)). A FE-SEM cross-sectional image of sample MLG-CNT-3 is presented in Figure 3(d). It can be clearly seen that the SWCNTs are uniformly wrapped on/in between the curled graphene sheets. An image that was taken from a 45° view of the film (Figure 3(e)) delivers a further interpretation of such morphology. The upper and lower halves of the image present the surface and the cross-section of the composite film, respectively. It can be clearly observed that carbon nanotubes are present at the broken edge, where the stacked graphene can also be clearly identified. By using the 15-point Brunauer–Emmett–Teller (BET) N_2 adsorption method, the specific surface areas of the as-prepared free-standing composite samples MLG-SWCNT-1, MLG-SWCNT-2, and MLG-SWCNT-3 were

measured to be 949.9, 655.8, and 524.5 m² g⁻¹, respectively. It is clear that the sample with higher graphene content showed a relatively lower specific surface area value. This may benefit the electrochemical performance by minifying the initial irreversible capacity [28,29].

The X-ray diffraction (XRD) patterns obtained from MLG-3 and MLG-SWCNT-3 composite are presented in Figure 4, together with those of the as-prepared GO and the pristine graphite. The diffraction peak around 26.4° for graphite (Figure 4(a)) has completely disappeared in the graphite oxide pattern, and a broad peak has arisen at $2\theta = 10.9^\circ$ (Figure 4(b)), indicating the successful oxidation of raw graphite to graphite oxide [30]. In Figure 4(c), the diffraction peaks at $2\theta = 24.4^\circ$ and 43.2° can be attributed to graphite-like (002) and (100) structure, respectively [31,32]. By using Bragg's law, it can be calculated that the *d*-spacing for MLG-3 is 0.364 nm ($2\theta = 24.4^\circ$), which is larger than that for the pristine graphite (0.335 nm). This value matches very well with the average *d*-spacing measured from HR-TEM that is shown in Figure 2(b). Interestingly, calculations showed that the *d*-spacing for MLG-SWCNT-3 composite (Figure 4(d)) would be as high as 0.407 nm ($2\theta = 21.8^\circ$). This may be because during the in situ reduction process, the SWCNTs could embed themselves into the graphene oxide layers and thus enlarge the interlayer spacing of the multi-layer graphene sheets [33].

The MLG-SWCNT-3 sample was also investigated by TEM and HR-TEM imaging. Figure 5(a) reveals that the sample is composed of carbon nanotubes embedded in crumpled graphene sheets. The inset selected area electron diffraction pattern obtained from the dotted circled region reveals reflections consistent with the

presence of both graphene and CNTs with larger d -spacing. HR-TEM of the parallel fringes associated with graphene (Figure 5(b)) indicated d -spacings of around 0.41 nm, consistent with the results obtained by XRD (0.407 nm). XRD provides information on average d -spacing, while the TEM images only illustrate a small area of the sample, and local variations in the graphene d -spacings are expected. Furthermore, because 200 keV electrons are known to result in some damage to the graphene morphology, the d -spacing measurements obtained in both this Figure and Figure 2 can at best be seen as semiquantitative.

To further study the as-prepared samples, Raman spectroscopy was performed, and the spectra are shown in Figure 6. From Figure 6(a), the intensities of the D and G bands of each spectrum (at 1330 cm^{-1} and 1580 cm^{-1} , respectively) can be measured as I_D and I_G , respectively. The I_D/I_G values for the MLG-1, MLG-2, and MLG-3 samples were calculated as 1.90, 1.86, and 1.70, respectively. It is obvious that I_D/I_G decreases with increasing reaction temperature. The decrease in the I_D/I_G ratio is ascribed to the decrease in the number and/or the size of sp^2 clusters [34]. In the experiment, the oxygen functional groups in the GO sheets were removed by the chemical reduction, and the size of the conjugated G network (sp^2 carbon) that was re-established was smaller than the original one. Therefore, the I_D/I_G ratio can be a good measure of the degree of reaction, which further proves that the reduction proceeds further with increasing reaction temperature. In Figure 6(b), which was obtained from the composite sample MLG-SWCNT-3, all the Raman features typical of CNTs are observed: the tangential modes (G-band) with the G^- and G^+ parts at 1554 cm^{-1} and 1593 cm^{-1} , respectively, the D-band at $\sim 1306\text{ cm}^{-1}$, and the radial breathing mode (RBM) band in the lower frequency range below 290 cm^{-1} .

To investigate the electrochemical performance of the free-standing electrodes, Nyquist plots for electrodes made of pure SWCNTs and MLG-SWCNT composites after 5 cycles were compared, as shown in Figure 7. To maintain uniformity, electrochemical impedance spectroscopy (EIS) was performed on the working electrodes in the fully charged state. All the plots display a semicircular loop in the high to medium frequency region and a sloped line in the low-frequency region. According to the results obtained, an equivalent circuit, shown as the inset in Figure 8, was proposed to fit the impedance spectra, which includes the electrolyte resistance (R_s), a constant phase element (CPE), the charge transfer resistance (R_{ct}), and the Warburg impedance (Z_w). The intercept on the Z real axis in the high frequency region corresponds to the resistance of the electrolyte (R_s). The diameter of the semicircle gives the charge-transfer resistance (R_{ct}), which is related to the charge transfer through the electrode/electrolyte interface. The inclined line in the low frequency region represents the Warburg impedance (Z_w), which is associated with the solid-state diffusion of Li ions in the electrode materials [35,36]. It can be observed in the Figure that the diameter of the semicircle decreases with higher graphene content in the film electrode. Therefore, it can be assumed that the interparticle resistance of the electrode is suppressed by the addition of graphene, and consequently, the composite film made with 70 wt% graphene (MLG-SWCNT-3) has the lowest charge-transfer resistance. By using a four-point probe instrument, the conductivity of MLG-SWCNT-1, MLG-SWCNT-2, and MLG-SWCNT-3 were measured to be 39.1, 74.6, and 114.5 S cm⁻¹, respectively. This result further proves that with higher graphene content, the composite shows improved conductivity.

Figure 8(a) presents the discharge and charge curves for the 1st and 50th cycles for the pure SWCNT, MLG-SWCNT-1, and MLG-SWCNT-3 electrodes. It can be observed that the first discharge capacities of the three electrodes were 1109, 980, and 950 mAh g⁻¹, while the first charge capacities were 204, 219, and 293 mAh g⁻¹, respectively. The first cycle coulombic efficiencies for the electrodes made from SWCNTs, MLG-SWCNT-1, and MLG-SWCNT-3 were calculated as 18.4%, 22.3%, and 30.8%, respectively. The low coulombic efficiency is due to the large irreversible capacities in the initial cycle. The results demonstrated that the sample with lower graphene content exhibited larger initial irreversible capacity. This phenomenon matches the BET results very well and could be possibly owing to the larger specific surface area which led to the irreversible formation of more solid electrolyte interphase (SEI) layers [28,29]. To identify all of the electrochemical reactions in the initial cycle, cyclic voltammetry (CV) was conducted on the cells with MLG-SWCNT-1 and MLG-SWCNT-3, respectively, at ambient temperature in the 0.0-3.0 V range and a scan rate of 0.1 mV s⁻¹ (Figure 8(b)). Li metal was used as the counter and reference electrode. It is obvious that a peak is observed at 0.62 V for both of the curves, which can be attributed to the irreversible formation of solid electrolyte interface (SEI) layer [XXX]. It is also noticeable on MLG-SWCNT-1 figure that there are two peaks in the cathodic process at 1.11 V and 1.59 V, respectively, which represents the irreversible reaction with the surface functional groups [XXX]. Figure 8(c) shows a comparison of the cycling behaviour of the three samples. In the 50th cycle, a reversible charge capacity of about 187 mAh g⁻¹ is observed for the electrode made of pure SWCNTs, which is 91.7% of the capacity in the 1st charge. In comparison, the electrode made from MLG-SWCNT-3 shows the highest reversible charge capacity of 303 mAh g⁻¹ after 50 cycles without any fading. It is also noticeable in the first 10 cycles that the

coulombic efficiency of the MLG-SWCNT-3 sample is also among the best. The capacity density shown in Table 2 yields a further interpretation of the electrochemical performance of the free-standing electrodes. It can be obviously found that the capacity density of MLG-SWCNT-3 is over 80% higher than that of the MLG-SWCNT-1 sample.

To further characterize the nanostructure change of the free-standing electrode before and after cycling, a morphological study was conducted on the MLG-SWCNT-3 electrode after 50 cycles and the SEM images are shown in Figure 9. Comparing to the free-standing electrode before cycling (see Figure 3(c-e)), it retained a similar surface morphology and no obvious crack can be found. From the enlarged image shown in Figure 9(b), SWCNTs and graphene sheets can be clearly identified from the sandwiched structure. This is a solid evidence to demonstrate the structural stability of the MLG-SWCNT-3 electrode, and this is also one of the reasons why good cycling behaviour was observed.

The improvements in the physical and electrochemical performance can be attributed to 1) the expansion in the d -spacing of the composite material, which may deliver additional sites for accommodation of lithium ions [33]; 2) the improved electronic conductivity of the composite electrodes contributed by the graphene conductive matrix [20]; and 3) the increased mass density, which could be another important reason. Based on the above results, it can be concluded that the MLG-SWCNT composite film with 70 wt% graphene content has the most outstanding electrochemical performance in terms of cycling stability and capacity density. Using the free-standing MLG-SWCNT composite anode for coupling with a promising free-

standing cathode for assembly of the whole bendable cell will be demonstrated in our future work.

4. Conclusions

Multi-layer graphene sheets were synthesized by using a time-efficient microwave autoclave method at different reaction temperatures. The optimised graphene powder was selected to form a composite in situ with single-walled carbon nanotubes to fabricate flexible free-standing films. The free-standing composite film with 70 wt% graphene exhibited the lowest charge transfer resistance and the highest charge capacity of about 303 mAh g⁻¹ after 50 cycles. The good Li cycling performance can be attributed to 1) the improved electronic conductivity of the electrodes due to the higher mass density and reduced thickness of the electrode; 2) sufficient ionic conductivity contributed by the unique sandwich structure with efficient conductive paths; and 3) the enlarged average *d*-spacing, which contributes additional sites for the accommodation of lithium ions.

Acknowledgments: Financial support provided by an Australian Research Council (ARC) Discovery Project (DP 0987805) is gratefully acknowledged. Many thanks also go to Dr. Tania Silver for critical reading of the manuscript. This research used equipment located at the UOW Electron Microscopy Centre and funded by Australian Research Council grants LE0882813 and LE0237478.

Table 1. Preparation conditions and physical properties of the synthesized multi-layer graphene sheets.

<i>Sample name (pure graphene)</i>	<i>Synthesis temperature (°C)</i>	<i>Reaction time (min)</i>	<i>d-space value (nm)</i>
MLG-1	120	5	0.43
MLG-2	150	5	0.40
MLG-3	180	5	0.36

Table 2. Physical properties of multi-layer graphene sheet–single-walled carbon nanotube composite films.

<i>Sample name (composite film)</i>	<i>MLG ratio in composite (wt%)</i>	<i>Film thickness (μm)</i>	<i>Density (g/cc)</i>	<i>Capacity density at 2nd cycle (mAh/cc)</i>
MLG-SWCNT-1	30	115	0.336	90.72
MLG-SWCNT-2	50	95	0.406	113.68
MLG-SWCNT-3	70	78	0.495	163.35

Figure 1. FE-SEM images of the graphene synthesized by microwave autoclave at the reaction temperatures of (a) 120 °C, (b) 150 °C, and (c) 180 °C.

Figure 2. HR-TEM images of multi-layer graphene sheets synthesized using a microwave autoclave method at the reaction temperatures of (a) 120 °C, (b) 150 °C, and (c) 180 °C. The average interlayer d -spacings were estimated from measurements of sets of approximately parallel fringes, as indicated on the figure panels.

Figure 3. (a) Photograph of MLG-SWCNT-3 film; FE-SEM images of MLG-SWCNT composite films, with the ratio of graphene content (b) 30 wt%, and (c) 70 wt%; (d) and (e) cross-sectional FE-SEM images of MLG-SWCNT-3 film.

Figure 4. X-ray diffraction patterns for the as-prepared (a) graphite, (b) graphite oxide, (c) MLG synthesized at 180 °C, and (d) MLG-SWCNT with graphene content of 70 wt%.

Figure 5. MLG-SWCNT-3: (a) bright field TEM image and selected area electron diffraction pattern (inset) obtained from circled region located over hole in carbon support film, (b) HR-TEM image of graphene region with indicated d -spacing obtained by averaging spacings between marked parallel fringes.

Figure 6. Raman spectra of (a) MLG, and (b) MLG-SWCNT-3 composite materials.

Figure 7. Impedance plots for free-standing electrodes made from pure SWCNTs and MLG-SWCNT composites. The inset is the equivalent circuit used to interpret the data.

Figure 8. (a) Discharge and charge curves for selected cycles for SWCNT and MLG-SWCNT composite electrodes; (b) voltammogram of MLG-SWCNT-3 at a scan rate of 0.1 mV s^{-1} ; (c) cycling behaviour of electrodes made from pure SWCNT film, composite film with 30% MLG (MLG-SWCNT-1), and composite film with 70% MLG (MLG-SWCNT-3) at a current density of 30 mA g^{-1} ;

Figure 9. SEM images of the MLG-SWCNT-3 electrode after 50 cycles.

References

- [1] Gwon H, Kim H, Lee KU, Seo D, Park YC, Lee Y, et al. Flexible energy storage devices based on graphene paper. *Energy Environ Sci* 2011;4:1277-83.
- [2] Hu. L, Mantia FL, Wu H, Xie X, McDonough J, Pasta M, et al. Lithium-ion textile batteries with large areal mass loading. *Adv Energy Mater* 2011;1:1012-7.
- [3] Xu G, Zheng C, Zhang Q, Huang J, Zhao M, Nie J, et al. Binder-free activated carbon/carbon nanotube paper electrodes for use in supercapacitors. *Nano Research* 2011;4(9):870-81.
- [4] Tarascon JM, Armand M. Issues and challenges facing rechargeable lithium batteries. *Nature* 2001;414:359-67.
- [5] Aricò AS, Bruce P, Scrosati B, Tarascon J, Schalkwijk WV. Nanostructured materials for advanced energy conversion and storage devices. *Nat Mater* 2005;4:366-77.
- [6] Ng SH, Wang J, Guo ZP, Chen J, Wang GX, Liu HK. Single wall carbon nanotube paper as anode for lithium-ion battery. *Electrochim Acta* 2005;51:23-8.
- [7] Chew SY, Ng SH, Wang J, Novak P, Krumeich F, Chou SL, et al. Flexible free-standing carbon nanotube films for model lithium-ion batteries. *Carbon* 2009;47:2976-83.
- [8] Byon HR, Gallant BM, Lee SW, Shao-Horn Y. Role of oxygen functional groups in carbon nanotube/graphene freestanding electrodes for high performance lithium batteries. *Adv Funct Mater* 2013;23:1037-45.
- [9] Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, Stach EA, et al. Graphene-based composite materials. *Nature* 2006;442:282-6.
- [10] Guo SJ, Dong SJ, Wang EK. Three-dimensional Pt-on-Pd bimetallic nanodendrites supported on graphene nanosheet: facile synthesis and used as an advanced nanoelectrocatalyst for methanol oxidation. *ACS Nano* 2010;4(1):547-55.
- [11] Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, et al. Superior thermal conductivity of single-layer graphene. *Nano Lett* 2008;8(3):902-7.

- [12] Schedin F, Geim AK, Morozov SV, Hill EW, Blake P, Katsnelson MI, et al. Detection of individual gas molecules adsorbed on graphene. *Nat Mater* 2007;6:652-5.
- [13] Gilje S, Han S, Wang M, Wang KL, Kaner RB. A chemical route to graphene for device applications. *Nano Lett* 2007;7(11):3394-8.
- [14] Liu Z, Robinson JT, Sun X, Dai H. PEGylated nano-graphene oxide for delivery of water insoluble cancer drugs. *J Am Chem Soc* 2008;130(33):10876-7.
- [15] Zhao MQ, Liu XF, Zhang Q, Tian GL, Huang JQ, Zhu W, Wei F. Graphene/single-walled carbon nanotube hybrids: one-step catalytic growth and applications for high-rate Li-S batteries. *ACS Nano* 2012;6:10759-69.
- [16] Zheng Q, Zhang B, Lin X, Shen X, Yousefi N, Huang ZD, Li Z, Kim JK. Highly transparent and conducting ultralarge graphene oxide/single-walled carbon nanotube hybrid films produced by Langmuir–Blodgett assembly. *J Mater Chem* 2012;22:25072-82.
- [17] Wu Y, Zhang T, Zhang F, Wang Y, Ma Y, Huang Y, Liu Y, Chen Y. In situ synthesis of graphene/single-walled carbon nanotube hybrid material by arc-discharge and its application in supercapacitors. *Nano Energy* 2012;1:820-7.
- [18] Zhao MQ, Zhang Q, Huang JQ, Tian GL, Chen TC, Qian WZ, Wei F. Towards high purity graphene/single-walled carbon nanotube hybrids with improved electrochemical capacitive performance. *Carbon* 2013;54:403-11.
- [19] Wang C, Li D, Too CO, Wallace GG. Electrochemical properties of graphene paper electrodes used in lithium batteries. *Chem Mater* 2009;21:2604-6.
- [20] Fan Z, Yan J, Zhi L, Zhang Q, Wei T, Feng J, et al. A three-dimensional carbon nanotube/graphene sandwich and its application as electrode in supercapacitors. *Adv Mater* 2010;22:3723-8.
- [21] Wang JZ, Zhong C, Chou SL, Liu HK. Flexible free-standing graphene silicon composite film for lithium-ion batteries. *Electrochem Commun* 2010;12:1467-70.

- [22] Hummers WS, Offeman RE. Preparation of graphitic oxide. J Am Chem Soc 1958;80:1339.
- [23] Kovtyukhova NI, Ollivier PJ, Martin BR, Mallouk TE, Chizhik SA, Buzaneva EV, et al. Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. Chem Mater 1999;11:771-8.
- [24] Sridhar V, Jeon J, Oh I. Synthesis of graphene nano-sheets using eco-friendly chemicals and microwave radiation. Carbon 2010;48(10):2953-7.
- [25] McAllister MJ, Li J, Adamson DH, Schniepp HC, Abdala AA, Liu J, et al. Single sheet functionalized graphene by oxidation and thermal expansion of graphite. Chem Mater 2007;19:4396-404.
- [26] Guo P, Song H, Chen X. Electrochemical performance of graphene nanosheets as anode material for lithium-ion batteries. Electrochem Commun 2009;11:1320-4.
- [27] Xing W, Dahn JR. Study of irreversible capacities for Li insertion in hard and graphitic carbons. J Electrochem Soc 1997;144(4):1195-201.
- [28] Cao F, Guo Y, Zheng S, Wu X, Jiang L, Bi R, et al. Symbiotic coaxial nanocables: facile synthesis and an efficient and elegant morphological solution to the lithium storage problem. Chem Mater 2010;22:1908-14.
- [29] Beguin F, Chevallier F, Vix-Guterl C, Saadallah S, Bertagna V, Rouzaud JN, Frackowiak E. Correlation of the irreversible lithium capacity with the active surface area of modified carbons. Carbon 2005;43:2160-7.
- [30] Zhang Y, Guo L, Wei S, He Y, Xia H, Chen Q, et al. Direct imprinting of microcircuits on graphene oxide film by femtosecond laser reduction. Nano Today 2010;5:15-20.
- [31] Zhong C, Wang J, Chen Z, Liu H. SnO₂-graphene composite synthesized via an ultrafast and environmentally friendly microwave autoclave method and its use as a superior anode for lithium-ion batteries. J Phys Chem C 2011;115:25115-20.

- [32] Wakeland S, Martinez R, Grey JK, Luhrs CC. Production of graphene from graphite oxide using urea as expansion–reduction agent. *Carbon* 2010;48(12):3463-70.
- [33] Yoo E, Kim J, Hosono E, Zhou H, Kudo T, Honma I. Large reversible Li storage of graphene nanosheet families for use in rechargeable lithium ion batteries. *Nano Lett* 2008;8(8):2277-82.
- [34] Tallant DR, Parmeter JE, Siegal MP, Simpson RL. The thermal stability of diamond-like carbon. *Diamond Relat Mater* 1995;4:191-9.
- [35] Li Y, Li J. Carbon-coated macroporous $\text{Sn}_2\text{P}_2\text{O}_7$ as anode materials for Li-ion battery. *J Phys Chem C* 2008;112:14216-9.
- [36] Wang JZ, Chen J, Konstantinov K, Zhao L, Ng SH, Wang GX, et al. Sulphur-polypyrrole composite positive electrode materials for rechargeable lithium batteries. *Electrochim Acta* 2006;51:4634-8.