RAPID COMMUNICATION

Three dimensional few layer graphene and carbon nanotube foam architectures for high fidelity supercapacitors

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Received 8 August 2012; received in revised form 2 October 2012; accepted 2 October 2012

KEYWORDS
Graphene;
Carbon nanotube;
Foam;
Supercapacitor;
Chemical vapor deposition

Abstract
Supercapacitors are promising alternative energy storage systems due to their relatively fast rate of energy storage and delivery. We describe a simple and scalable method to fabricate three-dimensional (3D) few-layer graphene/multi-walled carbon nanotube (MWNT) hybrid nanostructures on industrial grade metal foam foils (nickel foam) via a one-step ambient pressure chemical vapor deposition (APCVD) process. The as-grown few-layer graphene/MWNT nanocarbon foams are in the form of a homogeneous and densely packed hierarchical nanostructures and possess a very large surface area of 743 m² g⁻¹. Symmetrical electrochemical double-layer capacitors (EDLCs) of 3D hybrid hierarchical few-layer graphene/MWNT nanostructures show a high specific capacitance of 286 F g⁻¹ which leads to an energy density of 39.72 Wh kg⁻¹ and a superior power density of up to 154.67 kW kg⁻¹. Moreover, the capacitance retention of 99.34% after 85,000 charge−discharge cycles demonstrates the very high stability of the electrode architectures for supercapacitors. These merits enable the innovative 3D hierarchical few-layer graphene/MWNT foam to serve as high performance EDLC electrodes, resulting in energy storage devices with very high stability and power density.

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Introduction

The dramatically increasing consumption of fossil fuels and other natural non-renewable resources urges us to move towards alternative and renewable energy resources. With increase in renewable energy production, energy storage systems are starting to play a greater role in our everyday lives and global economy. Meanwhile, traditional energy storage devices like batteries and electrochemical capacitors (ECs) are not capable of meeting the higher demand of future systems anymore because of the relatively low power and energy density. Improving and optimizing the performance of energy storage devices has become an essential theme in recent scientific studies and research. Super-capacitors are promising alternative energy storage systems due to their relatively fast rate of energy storage and delivery. Their high power density (>10 kW kg\(^{-1}\)) and long cycle stability make them suitable for a wide variety of applications [1-9]. Typically, there are two types of ECs, one is the electrochemical double layer capacitor (EDLC), which is based on ion adsorption, and the other type is the pseudocapacitor, which operates on the principle of fast surface redox reactions [2-4,7,10-12].

The excellent chemical and physical properties of carbon materials such as high conductivity, high surface area, good corrosion resistance, excellent temperature stability, and relatively low cost, make them valuable candidates for the electrodes of electrochemical double layer capacitors, and this holds true especially for graphene and carbon nanotubes which possess the largest theoretical and experimental surface area [5,6,10,13-15]. In order to enhance the performance of the carbon nanostructure-based supercapacitors, intensive research efforts have been conducted on carbon capsules, carbon nanotubes/fibers (CNTs/CNFs), graphene and activated carbons [2,14,16-20]. The carbon hybrid nanostructure is also an intensively studied area currently, especially the growth of CNT-graphene networks by chemical vapor deposition and solution processing of graphene-CNT hybrid materials. By incorporating CNT and graphene, 3D carbon nanostructures could be developed. This novel hybrid system has been proved to possess a large surface area, unique electrical properties and has great potential for various applications, such as energy storage, biochemical sensing and 3D interconnected networks [21-26]. However, construction of 3D graphene/CNT networks is a very complicated process and these previously reported graphen/CNT hybrid systems require to be synthesized on two dimensional substrates or the use of graphene oxide platelets as a rather non-ideal substitute for graphene.

In this work, we report for the first time the growth of real 3D high-quality few-layer graphene/multi-walled carbon nanotube (MWNT) hybrid hierarchical nanostructures on highly porous metal foams with arbitrary thickness via one-step ambient pressure chemical vapor deposition (APCVD). This novel 3D few-layer graphene/MWNT hybrid nanostructure foam is demonstrated to possess a very large surface area, high surface/body ratio, good permeability, stability and ductility which are highly desirable for gas sensing, catalytic and energy storage applications. We demonstrate high performance supercapacitors of long cycle stability and high energy density with the as-grown graphene/MWNT hierarchical nanostructures as high performance electrodes. There are several advantages of the 3D hybrid foam structures: (a) The CVD grown multilayer graphene layer can act as a thin layer current collector. (b) The multilayer graphene layer is also a buffer layer which facilitates the electrical connection of the MWNT to the nickel foam framework as a low resistance interface and also further enhances the connection between the MWNT bundles and the nickel foam. (c) The presence of the multilayer graphene layer also increases the stability of the CNT bundle foam electrode by preventing the alkali electrochemical activation on the nickel foam surface. (d) With the 3D backbone of the nickel foam, it is facile to obtain 3D multilayer graphene-CNT hybrid structures which dramatically increases the surface area and provides a simple and scalable approach for building 3D carbon nanostructures. (e) Minor oxidation avoids conventional alumina or other oxides buffer layer to grow this hybrid structure, which provides an effective, simple, scalable binder-free technique to prepare electrodes for supercapacitor and battery applications.

Experimental section

Growth of 3D few-layer graphene/MWNT hybrid foam nanostructure

3D few-layer graphene/MWNT foams were grown through an ambient pressure chemical vapor deposition (APCVD) method using a mixture of acetylene and hydrogen on 1.0 mm thick nickel foam, which is typically used as current collector in the battery industry (Fig. 1). Briefly, nickel foam is pre-treated with diluted acetic acid and deionized (D.I.) water to ensure the surface is completely clean and free from oxidation. Next, the nickel foam is annealed at 800 °C under ambient pressure with the flow of H\(_2\) and Ar for 45 min in order to release the residue stress in the foam, enlarge the average grain size, and also flatten the surface. After annealing, a mild reactive ion etching (RIE) O\(_2\)-plasma is applied to the annealed nickel foam for 2 min (power: 200 W, O\(_2\) flow: 50 sccm) and 2 nm Fe catalyst layer is deposited on the surface of plasma treated nickel foam by e-beam evaporation (Temescal, BJD-1800). The as-prepared nickel foam is loaded into a quartz-tube furnace chamber, heated to 750 °C under ambient pressure in an Ar/H\(_2\) (200:200 sccm) atmosphere, and annealed for 5 min. Acetylene is introduced to trigger the growth of graphene and CNTs synchronously on the nickel foam frame. After growth, the chamber is cooled to the room temperature (25 °C) at an average cooling rate of 50 °C min\(^{-1}\).

Materials characterization

The surface morphology of the 3D graphene/MWNT hybrid foam nanostructure and pristine nickel foam films are investigated by using optical microscopy, scanning electron microscopy (SEM; Leo-supra, 1550) with an X-ray energy-dispersive spectroscopy (EDS), and transmission electron microscopy (TEM; Philips, CM300) with a LaB\(_6\) cathode operated at 300 KV. For TEM imaging, the graphene/MWNT foam is ultrasonically dispersed in ethanol for 1 h and then diluted and dropped onto a TEM grid. The cross-section TEM lamella was prepared by focused ion beam (FIB) milling.

Please cite this article as: W. Wang, et al., Three dimensional few layer graphene and carbon nanotube foam architectures for high fidelity supercapacitors, Nano Energy (2012), http://dx.doi.org/10.1016/j.nanoen.2012.10.001
through Zeiss XB 1540 and the sample was lifted-out by using an Omni manipulator. A Renishaw DXR Raman spectroscopy system with a 532 nm laser (8 mW excitation power, 100x objective lens) source is used to characterize the as grown 3D graphene/MWNT hybrid nanostructure foam. Kruss Easy drop (FM 40) technique is employed to measure the contact angle of the samples. The surface area of the material was characterized on a Micromeritics ASAP 2020 surface-area with N2 gas.

Fabrication and measurements of supercapacitor cells

As-prepared few-layer graphene/MWNT foam is sectioned with equal areas and soaked with 6 M KOH aqueous at 80 °C to activate the surface of the foam nanostructures. A two-electrode measurement technique was employed for the electrochemical measurements, where the two pre-treated carbon nanostructure foams are assembled into a sandwich structure with a porous membrane (Celgard 3501), which functions as a separator. In this work, aqueous electrolyte (6 M KOH) is used as the electrolyte. The packaging of the supercapacitor cell is conducted in an Ar atmosphere glove box at room temperature (Labconco). The two electrodes of the packaged cell are connected to an electrochemical analyzer (Gamry Reference 600™) with an alligator clip. Cyclic voltammetry (CV), chronopotentiometry (charge-discharge (CD)), and electrochemical impedance spectroscopy (EIS) were conducted to evaluate the performance of the supercapacitors. Cyclic voltammetry scans were performed with a voltage window of 1 V in the range 0-1 V at scan rates ranging from 2.5 mV s⁻¹ to 500 mV s⁻¹. The charge-discharge measurements are conducted under different current densities and the stability test is obtained at a current density value of 21.33 mA cm⁻². Potentiostatic EIS measurements were performed between 0.1 Hz and 1 MHz with amplitude of 10 mV.

Results and discussion

Growth of 3D few-layer graphene/MWNT foam nanostructure

The growth of graphene/MWNT foam nanostructure is proposed and the scheme is illustrated in Fig. 1a. The process involves three steps: First, a mild anisotropic reactive ion etching (RIE) O2 plasma treatment is applied to the nickel foam to form a nickel oxide layer on the nickel foam frame and roughens the surface of the nickel frame. The nickel oxide layer serves as a buffering layer minimizing the formation of undesired Ni3C by inhibiting the diffusion of carbon into the nickel foam [27]. Next, a layer of iron catalyst (thickness 2 nm) is deposited on the surface of nickel foam by e-beam evaporation. Since the e-beam evaporation is an isotropic technique, only the top surface of the nickel frames are covered with the Fe catalyst. After O2 plasma oxidation, the samples are loaded to a thermal chemical vapor deposition (CVD) tube furnace and acetylene and hydrogen are introduced to grow the 3D graphene/MWNT nanostructures on the surfaces of the nickel foam backbone. The surface roughness and oxide layer after reduction by H2 annealing will generate fine growth islands for CNTs and the water from the reduction will facilitate the CNTs growth as well. Optical micrographs of inch-scale pristine nickel foam, as grown 3D few-layer graphene foam (without deposition of Fe catalyst) and few-layer graphene/MWNT nanostructure from identical growth condition are shown in Fig. 1b. A scanning electron microscope (SEM) micrograph of the pristine nickel foam is shown in Fig. 1c to demonstrate that the porosity level is around 120 pores per inch (PPI) and the average grain size of nickel is 10-20 μm.

We successfully controlled the loading mass of carbon hybrid nanostructures with various growth time, catalyst amount and carbon source concentration. The mass of loading...
trend with respect to the growth time demonstrates the loading mass is proportional to the growth time (Supporting Information Fig. S1). It is important to note that the loading mass in this work is the weight change of the sample measured before and after APCVD growth.

SEM images in Fig. 2a and b indicates the topside morphology of graphene/MWNT nanostructures at different magnifications on nickel foam. Randomly oriented and densely packed surface morphology of the as-grown MWNT structures are grown on nickel foam which is commonly used as the current collector for energy storage devices (Fig. 1b). The average diameter of the as grown MWNT is around 20 nm which can be roughly measured from the high magnification SEM image (Fig. 2b). Iron catalysts, circled light spots in Fig. 2b, were confirmed with Energy Dispersive Spectroscopy (EDS) (Fig. S2), suggesting a tip-growth mechanism of the MWNT. The dense and homogeneous graphene/MWNT network structure possesses a very large active area that is desirable for supercapacitor electrodes, which is also beneficial for loading of pseudo capacitive oxides like MnO2, RuO2, etc. To verify the surface area, we conducted surface area characterization on a Micromeritics ASAP 2020 surface-area with N2 gas. The measurement was conducted on the sample right after growth and no sample activation was applied, and the as-synthesized sample was directly degassed at 230°C for 48 h under vacuum prior to the measurement. The sample exhibits a type II adsorption isotherm typical of materials of permanent microporosity (Supporting Information Fig. S3). The Langmuir and Brunauer-Emmett-Teller (BET) surface areas were found to be 743 and 497 m²/g, respectively. The obtained data is lower than the theoretical graphene surface area (2630 m²/g) but higher than values for MWNT (400 m²/g) as reported before [4,28]. The high porosity and relatively high surface area suggest this type of few-layer graphene/MWNT hybrid foam structure is an excellent candidate for the electrodes of energy storage devices.

Fig. 2c shows the underside view of the as grown graphene/MWNT foam. We can see the presence of MWNT on the edges of the nickel frame while no MWNT on the underside of the nickel frame. Raman spectra recorded from the graphene region located at the underside of the graphene/MWNT foam (Fig. 2d black curve) further confirms the absence of MWNT. The presence of the G peak at 1581 cm⁻¹, the 2D peak at 2709 cm⁻¹ and the G/2D ratio indicate the typical Raman characteristics for few-layer graphene (FLG) sheets, which is similar to those reported for CVD grown graphene layers [29–34]. No D band is observed at 1360 cm⁻¹ due to the high quality of the as grown structures. Raman spectra features collected from the dark regions of few-layer graphene/MWNT nanostructures foam (topside of foam) are in good agreement with the MWNT Raman spectra, which clearly shows the presence of the intense D band centered around 1380 cm⁻¹, the intensity of which is relatively higher compared to that of the G band centered around 1570 cm⁻¹ (Fig. 2d red curve) [35]. The 2D band for MWNT centered at ~2700 cm⁻¹ is a single peak which is similar to that of graphene. The presence of the intense D band in the spectrum is associated with defects of the MWNT. The absence of MWNT on the backside is attributed to the isotropic manner of deposition by the e-beam evaporation which only deposits iron catalysts on the topside of the nickel foam frame. We further confirmed this phenomenon via Energy Dispersive Spectroscopy (EDS) analysis (Fig. S3 a and b). No Fe presence was observed on the underside (Fig. S3a). The selective coverage of the MWNT dramatically decreased the mass loading and increased the active material utilization which is desirable for supercapacitor applications. Furthermore, full coverage of CNTs on both sides may be valuable for...
other applications and it can be also achieved by simply doing growth using identical conditions by using samples with catalyst nanoparticles deposited on both sides.

Transmission electron microscopy (TEM) was employed to further confirm the existence of graphene layers under MWNT and the quality of the carbon nanotubes. The TEM samples were prepared by using an ethanol-sonication method to peel as grown few-layer graphene/MWNT nanostructures off the nickel foam surface. Graphene sheets were broken and peeled off from the nickel backbone during ultra-sonication process, therefore, small graphene fragments are attached to the MWNT (Fig. 3a). The average diameter of the as-grown carbon nanotubes have a diameter of around 15-20 nm with a wall thickness of about 15-20 layers and inner diameter around 5 nm as determined by direct high resolution (HR) TEM imaging (Fig. 3b), which is in accordance with the SEM observations (Fig. 2b). In the same sample we observed a relatively large area graphene film consisting of regions with different thickness (Fig. S4a). The variation in the number of the graphene layers as revealed in Fig. S4a is due to the process of peeling of the graphene film from the nickel substrate during preparation for TEM imaging. The graphene layers on nickel foam are quite uniform and continuous which is verified by the SEM imaging of the underside view of the graphene/MWNT foam (Fig. 2c). This is also confirmed in a control sample of few-layer graphene only, where uniform film on nickel foam is grown without depositing iron catalyst (Supporting Information Fig. S5). The edges of few-layer graphene films tend to fold back which allows obtaining a cross-sectional view of the film in the TEM and the number of graphene layers can be determined. In our case, the few-layer graphene film consists of 7-10 graphene layers as counted from the HRTEM micrograph (Fig. 3c). Though the oxide layer from the plasma pre-treatment functions fairly well to inhibit the diffusion of too much carbon into the nickel, after reduction in the hydrogen environment during the growth the total exposure time to carbon source is still relatively longer compared to the previously reported experiments of growth of single-layer graphene films on either flat nickel substrate or nickel foam [8,36–38]. Raman spectroscopy has confirmed that the graphene under layer in the graphene/MWNT foam nanostructure is predominantly multilayer rather than single layer. This is desirable to have in our work since for energy storage devices multilayer graphene film tends to provide better bonding between MWNT and nickel foam. Furthermore the multilayer graphene is capable of holding together the whole structure way better facilitates the formation of a three dimensional interconnects by etching the nickel away [37,38]. HRTEM and cross-sectional bright field TEM images were used to confirm there is a direct connection between few-layer graphene and MWNTs. Fig. S6 shows a few-layer graphene film at the nickel-carbon interface with an average thickness of about 5 nm.

Supercapacitors based on 3D graphene/MWNT foam nanostructures

The nickel foam frame functions as a current collector for the EDLC, the backbone of the few-layer graphene/MWNT
foam nanostructure, and also serves as protection for the active materials loaded in the framework. Supercapacitors based on few-layer graphene/MWNT foam nanostructure electrodes were fabricated according to the schematic process flow illustrated in the supporting information Fig. S7, which includes two equal area few-layer graphene/MWNT foam nanostructure electrodes spaced apart by a porous separator. Cyclic voltammetry for few-layer graphene/MWNT foam nanostructure supercapacitors were conducted at scanning rates between 2.5 mV s\(^{-1}\) and 500 mV s\(^{-1}\) within a voltage window of 0–1.0 V in 6 M potassium hydroxide (KOH) aqueous electrolyte solution. The interaction between electrode and electrolyte is critical for the performance of supercapacitor devices since the surface wettability of the electrode is known to influence the interfacial state of the carbon surface and its double-layer properties, such as point of zero charge, electrical contact resistance, adsorption of ions (capacitance), and self-discharge characteristics [6]. For a porous film electrode with a thickness around 1 mm the electrode-electrolyte interaction is even more significant. To study the effect of surface wettability to specific capacitance and to avoid introducing other undesired contaminations, we pre-treat the as-grown graphene/MWNT foam nanostructure with 6 M KOH aqueous solution at 80 °C for 1 h to mildly activate the surface properties of the carbon nanostructure to make it hydrophilic. This KOH aqueous pre-treatment is less harsh than the high temperature activations of carbon structures but it is expected to show the true performance of the few-layer graphene/MWNT foam nanostructure hybrid foam nanostructure supercapacitors were conducted at scan rates between 2.5 mV s\(^{-1}\) and 500 mV s\(^{-1}\) with different current densities in a voltage window of 0–1 V. The nearly rectangular shape and the absence of peaks of oxidation and reduction for all scan rates suggest the SCs based on this type of carbon foam structure has small equivalent series resistance, high rate handling capability and excellent electrochemical performance. Moreover, the CV curves exhibit nearly mirror-image current response on voltage reversal, indicating a good reversibility [40]. The maximum specific capacitance value of 269.79 F g\(^{-1}\) is obtained for the few-layer graphene/MWNT foam nanostructure at the scan rate of 5 mV s\(^{-1}\), which is much higher (~120% more) than that for self-assembled graphene/carbon nanotube hybrid films [41]. The specific capacitance tends to decrease with increasing scan rates because of the relative long diffusion length for the porous foam structure and an increase of the ion transport related resistance (Fig. 5b). Specific capacitance values at scan rates under the scan rate of 100 mV s\(^{-1}\) maintain more than 80% of the initial value, indicating process stability, repeatability, and superior performance of the supercapacitor [11,13,41].

Cyclic voltammetry measurements were conducted on control samples based on pristine nickel foam and graphene/nickel foam respectively to rule out their effects on the final specific capacitance (Fig. 5c and Fig. S8). The measurements verified that the areal capacitance effects from the nickel foam and the graphene foam are negligible. The low capacitance value of the graphene/nickel heterostructure is due to the low total surface area of the as grown graphene sheet compared to that of densely packed MWNT.

Chronopotentiometry measurements were conducted to further evaluate the electrochemical performance of the graphene/MWNT foam nanostructure supercapacitors. The galvanostatic charge–discharge test was performed with different current densities in a voltage window of 0–1 V. The near linear and symmetric charge and discharge curves suggest a very good capacitive performance with a rapid I–V response for our device (Fig. 5d). The specific capacitances at different current densities are calculated through equation

\[
C_s = \frac{Z_l}{m \cdot \Delta V \cdot S}
\]

where \(C_s\) is the specific capacitance, \(Z_l\) is the integrated area of the CV curve, \(m\) is the mass of the active materials of one electrode, \(\Delta V\) is the voltage window, and \(S\) is the scan rate. After the pre-treatment with 6 M KOH aqueous solution, the specific capacitance of the few-layer graphene/MWNT foam is improved by 320% (increases from 55 F g\(^{-1}\) to 233 F g\(^{-1}\)) at a scanning rate of 50 mV s\(^{-1}\) (Fig. 4a). The contact angle is decreased from 142° to 18° after the activation of the carbon nanostructure surface, which further indicates that the surface wettability is significantly enhanced (as shown in Fig. 4b and c).

Fig. 5a presents the CV behavior of the as-grown 3D graphene/MWNT hybrid foam nanostructure under different scan rates. The nearly rectangular shape and the absence of peaks of oxidation and reduction for all scan rates suggest the SCs based on this type of carbon foam structure has small equivalent series resistance, high rate handling capability and excellent electrochemical performance. Moreover, the CV curves exhibit nearly mirror-image current response on voltage reversal, indicating a good reversibility [40]. The maximum specific capacitance value of 269.79 F g\(^{-1}\) is obtained for the few-layer graphene/MWNT foam nanostructure at the scan rate of 5 mV s\(^{-1}\), which is much higher (~120% more) than that for self-assembled graphene/carbon nanotube hybrid films [41]. The specific capacitance tends to decrease with increasing scan rates because of the relative long diffusion length for the porous foam structure and an increase of the ion transport related resistance (Fig. 5b). Specific capacitance values at scan rates under the scan rate of 100 mV s\(^{-1}\) maintain more than 80% of the initial value, indicating process stability, repeatability, and superior performance of the supercapacitor [11,13,41].

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\[
C_s = \frac{Z_l}{m \cdot \Delta V \cdot S}
\]

where \(m\) is the carbon mass of one electrode, \(i\) is the discharge current and \(\Delta V / \Delta t\) is the slope of the discharge.
The as calculated specific capacitances under different current densities between 1.78 mA cm\(^{-2}\) and 21.33 mA cm\(^{-2}\) are shown in Fig. 5e. The highest specific capacitance of 286 F g\(^{-1}\) (slightly higher than the one calculated from the CV curve) is obtained at the current density of 1.78 mA cm\(^{-2}\). This demonstrates the superior capacitive performance of this few-layer graphene/MWNT foam architecture\[20\].

To further evaluate the performance of the graphene/MWNT hybrid foam nanostructures for the electrodes of EC, we calculated the energy density (\(E\)) and power density (\(P\)) based on the chronopotentiometry measurement results of our device. The energy density (\(E\)) and power density (\(P\)) are calculated by using equations:

\[ E = \frac{1}{2} C_s (\Delta V)^2 \]  

\[ P = \frac{E}{t} \]

where \(t\) is the total time of discharge, \(C_s\) is the specific capacitance value from charge-discharge curves, and \(\Delta V\) is the potential range which is 1.0 V for aqueous electrolyte normally. The few-layer graphene/MWNT foam electrode shows a three-dimensional architecture for high fidelity supercapacitors.

Please cite this article as: W. Wang, et al., Three dimensional few layer graphene and carbon nanotube foam architectures for high fidelity supercapacitors, Nano Energy (2012), http://dx.doi.org/10.1016/j.nanoen.2012.10.001
performance with a high energy density of 39.72 Wh kg\(^{-1}\) at 3.74 kW kg\(^{-1}\) which gradually reduces to 25.78 Wh kg\(^{-1}\) at 154.67 kW kg\(^{-1}\). These results are better compared to the previously reported systems like graphene films, MnO\(_2\) nanowire/graphene, single-wall carbon nanotubes (SWNTs), MWNT, vertically aligned MWNT, polyaniline (PANI), polypyrrole (PPy), Poly(ethylenedioxythiophene) (PEDOT), activated carbon monolith and activated carbon-manganese dioxide hybrid capacitor (Fig. 5f) [1,17,40-46]. Fig. 5f shows the Ragone plot of the energy density (E) versus power density (P) values of different supercapacitor systems in detail. The E and P values are based on the mass of the active materials of the electrodes. The maximum energy density of 39.72 Wh kg\(^{-1}\) and the highest power density of 154.67 kW kg\(^{-1}\) in aqueous electrolyte resulting in superior performance compared to other types of electrochemical capacitor systems, suggest that this graphene/MWNT foam nanostructure is a good candidate for future electrochemical capacitor and battery electrodes.

Long cycling life is also one of the most critical factors for the application of supercapacitor electrodes. A test sequence of 85000 charge-discharge cycles for our graphene/MWNT foam electrode supercapacitor was carried out with a current density of 21.33 mA cm\(^{-2}\) (Fig. 6a). After 85000 cycles, over 99.34% capacitance was maintained without obvious aging or performance degradation which demonstrates the excellent electrochemical performance of this type of electrode material for the application of practical energy storage devices [2,20,47,48]. The near identical CV characteristics even after 80000 cycles suggests our supercapacitor can recover its original performance after long-term storage (Fig. S9). The slight capacitance enhancement of the device in the first several thousands of cycling is due to the increased effective interfacial area between few-layer graphene/MWNT nanostructure and electrolyte with the increase of reaction time [49]. We believe the KOH activation may also play a role in this enhancement which is based on a similar principle as shown in Fig. 4. This self-strengthening effect also helps to stabilize the device for long term running and offers a better option for the applications of the foam material for supercapacitor electrodes.

Potentiostatic electrochemical impedance spectroscopy (EIS) measurements were performed after 1st, 13000th, 26000th, 85000th cycles to evaluate the internal resistance change during the cycling charge-discharge test. The EIS Nyquist plots show a near linear and vertical characteristic and a series of constant spectra with an identical equivalent series resistance around 3 Ω for the EIS measurements after 1st, 13000th, and 26000th cycles, which further demonstrate an exceptional electrochemical cycling stability of our graphene/MWNT foam nanostructure electrodes (Fig. 6b). The excellent cycling performance achieved in our graphene/MWNT nanostructure system can be attributed to the electrochemical stability of the active material. In addition, the graphene layer helps the connection of MWNT on the nickel foam. An insignificant right shifting characteristic (ESR shifts from 3 Ω to 5.5 Ω) of the EIS measurement over 85000 cycles is due to the increase of the internal resistance. The prolonged 45° Warburg slope is associated with the ion diffusion and transport resistance. The diffusion and transport impedance depends on the frequency of the potential perturbation and also the travel path. Since the parameters are identical for all of EIS measurements at selected cycling, the prolonged Warburg slope may be due to the fouling of the diffusion path [50]. After 80000 cycles ionic transport pathway became more tortuous, resulting in the diffusion phenomena more pronounced. The more resistive ionic transport led to the additional capacitive loop and the Warburg impedance, respectively. Since the potential perturbation and also the travel path. Since these parameters are identical for all of EIS measurements at selected cycling, the prolonged Warburg slope may be due to the fouling of the diffusion path [50].

Conclusion

We have demonstrated a novel 3D hierarchical few-layer graphene/MWNT hybrid foam nanostructure by ambient pressure chemical vapor deposition. This type of new nanocarbon architecture offers a facile, scalable and low cost approach for supercapacitor and battery applications. The low density (normally <500 g m\(^{-3}\)), excellent ductility, high

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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.2012.10.001.

References

in summer 2010. His area of expertise include materials synthesis and processing, De Novo carbon nanostructures and their applications in energy storage devices, III-V semiconductor nanowires synthesis, characterization and device fabrication.

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Miroslav Penchev, received his MS and Ph.D. degree in Electrical Engineering from University of California, Riverside, in October 2009 and June 2012, respectively. During his graduate studies at University of California, Riverside, under the supervision of Prof. Mihrimah Ozkan and Prof. Cengiz S. Ozkan, he conducted research in the area of nanostructured materials synthesis, including inorganic nanowires, graphene, and graphene-CNT hybrid materials. His research interests include applications of nanostructured materials in gas sensing and energy storage devices.

Isaac Ruiz is a Ph.D. student of Electrical Engineering (EE) at the University of California (USA) with Dr. Mihrimah Ozkan as his advisor, since 2010. He received his B.S. in Physics from San Diego State University (USA) in May 2010. At the University of California Riverside he has been engaged in the synthesis of carbon nanomaterials and their applications. The carbon nanomaterials range from graphene and carbon nanotubes to hybrid carbon nanostructures. Applications for these materials have included solar cells, batteries, supercapacitors and gas sensors.

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