Three-dimensional architecture of carbon nanotube-anchored polymer nanofiber composite†

Nguyen Thi Xuyen,‡ Tae Hyung Kim,‡ Hong-Zhang Geng, Il Ha Lee, Ki Kang Kim and Young Hee Lee*  

Received 9th July 2009, Accepted 21st September 2009  
First published as an Advance Article on the web 25th September 2009  
DOI: 10.1039/b913762a

Carbon nanotube (CNT)-anchored polymer nanofiber mats were designed by in situ spraying of carbon nanotubes while simultaneously electrospinning polymer nanofibers. The improved conductivity of the composite mat, high catalytic current (3400 mA/cm²/mg Pt) and long term stability of the composite mat was attributed to the efficient formation of CNT bridges between nanofibers.

Carbon nanotubes (CNTs) stand out as unique materials with extraordinary electronic, mechanical, thermal, and structural properties on the microscopic scale.1–7 It has been suggested that CNTs can be combined with other materials to form hybrid or composite structures and can improve the mechanical and electrical properties of host materials.8–14 However, these approaches produce the bulk composite forms in which CNTs are embedded randomly in the host matrix. In order to fully exploit the high performance of a CNT skeleton, CNTs were well aligned to a preferred direction or stacked layer by layer, which improved, for instance, the mechanical properties of host materials by one order of magnitude.15–17  

So far, all efforts have focused on incorporating CNTs within the host matrix. Although the incorporation of a relatively small content of CNTs significantly improved the host material properties, the superb properties of CNTs have never been accessed by such approaches. For instance, the carbon nanotube/polymer composite improved the conductivity of the host polymer by an order of 1010.15–17 However, this is far from the conductivity of the CNT film, 5700 S/m.14,18 The conductivity of the composite is governed not only by the CNTs but also by the polymer matrix in this case. Although high CNT content could be used to improve the conductivity, the conductivity improvement of the composite is still generally limited by the poor dispersion of CNTs. Furthermore, the CNTs were embedded within the polymer so the high conductivity and surface properties of CNTs have never been utilized in an application.

The purpose of this paper is to design a new structure for anchoring CNTs on the surface of host polymer nanofibers so that not only electrical and mechanical properties of the host materials can be improved but also the surface properties of CNTs can be utilized. Electrospun polymer nanofibers have recently attracted interest for the application of efficient electrodes to a supercapacitor and fuel cell due to its naturally formed mat in large area.19 Here we report a simple and versatile approach that can create a free-standing and permeable mat of carbon nanotubes anchored on the surface of polymer nanofibers. Our fabrication method consists of (i) the dispersion of the thin-multiwalled carbon nanotubes (t-MWCNTs) or single-walled carbon nanotubes (SWCNTs) in solution, (ii) the preparation of a poly(amic acid) (PAA)/dimethylformamide (DMF) solution, and (iii) the incorporation of two materials by simultaneously electrospinning the PAA/DMF solution and the spray of CNTs. In contrast to conventional composite nanofibers where nanotubes are embedded in a polymeric matrix, the current approach produces a CNT-anchored nanofiber composite mat that has a three dimensional architecture. The composite morphology, interconnection, and degree of anchoring the CNTs on the polymer surfaces were controlled by the hydrophilicity/hydrophobicity of the CNT surface. This composite was further applied to a fuel cell electrode to demonstrate high performance with high current and long term stability.

Fig. 1a shows a schematic of the in situ fabricated composite of a sprayed CNT/electrospun PAA nanofiber mat. The t-MWCNTs/dichloroethane (DCE) solution was sprayed into a space between a syringe and collector in which nanofibers are formed. While PAA nanofibers were electrospun from a Taylor cone at the tip of the needle, the sprayed CNTs were expected to mix with the nanofibers. The DCE solution was immediately evaporated and, as a consequence, t-MWCNTs approached a polymer jet.

At the same time, the polymer jet was stretched and split into smaller nanofibers by the high electric field applied between the emitter and collector. A series of scanning electron microscopy

† Electronic supplementary information (ESI) available: SEM images and FT-IR spectra. See DOI: 10.1039/b913762a
‡ Equal contributors.

*还有什么要交代的吗？
(SEM) images of the fabricated t-MWCNTs/PAA nanofiber composite in different magnifications are shown in Fig. 1b–d. The t-MWCNTs were uniformly decorated onto the nanofiber surface, independent of the depth of the mat. It was noted here that the t-MWCNTs were not wet enough on the PAA nanofiber surface but rather floating on the surface (Fig. 1d–e) and on the other hand, when acid-treated t-MWCNTs were sprayed together with nanofiber electrospinning similar to the previous method, the morphology of the composite mat was somewhat different. The t-MWCNTs seemed to be wet enough on the surface of the polymer nanofibers and part of the t-MWCNTs were embedded into the nanofibers, as evidenced from the tip of the t-MWCNTs (Fig. 1f, g) and also TEM images in the inset of Fig. 1g.

This distinct interfacial interaction behavior can be understood by the surface properties of carbon nanotubes and polymer nanofibers. The PAA nanofiber possesses carboxylic acid groups in PAA polymer chains in the DMF solution. When t-MWCNTs are simply dispersed in DCE solution, no functional groups (such as carboxylic acid group) are presented on the surface of the MWCNTs. Therefore, there is neither covalent (reaction) nor non-covalent (π–π stacking) attachment of the PAA polymer chain to the surface of the nanotubes. The pristine CNTs are easily phase-separated out of the PAA nanofiber surface. In spite of the unfavorable situation that CNTs are excluded from the outer surface, part of the CNTs still have a chance to be embedded into the nanofibers due to the non-equilibrium mixing processes. On the other hand, the acid-treated t-MWCNTs show adhesion, enabling them to be well grafted by polymer chains. Because the PAA polymer and the acid-treated t-MWCNTs are hydrophilic, as shown in Fig. S2,† they interact strongly with each other via hydrophilic interaction in the PAA matrix. In this case, t-MWCNTs are more likely to be embedded into the nanofibers. The composite surface becomes extremely rough (Fig. 1f, g). This was confirmed again by dispersing SWCNTs in water with sodium dodecyl sulfate (SDS) surfactant. In this case, the outer SWCNTs are functionalized by the hydrocarbon tails of the SDS surfactant and therefore become well attached to the surface of the polymer nanofibers (ESI† Fig. S1). It is noted that big bundles of long SWCNTs drove the SWCNTs to form interconnections among the nanofiber network. Thus, the macroscopic morphology of the SWCNTs case is quite different from the acid-treated MWCNTs.

Improvement of the electrical conductivity of the CNT-anchored PAA composite mat was shown in Table 1. The CNT-anchored PAA composite was stabilized and further carbonized. The PAA nanofibers were transformed into polyimide nanofibers during high temperature heat treatment while CNTs remained intact. The mean length of CNFs is usually 5–50 μm and the diameter of CNFs in composite is 200 ± 25 nm. The conductivity of the t-MWCNT-anchored CNF composite mat increased by almost twice compared to the CNF mat. This enhanced conductivity was attributed to the presence of the t-MWCNTs on the surface of the nanofibers in the mat so that the junction resistance between nanofibers was greatly reduced by the contact of highly conductive CNTs. When comparing the case of the t-MWCNTs with the case of the SWCNTs-anchored composite, the SWCNTs anchored PAA nanofiber composite mat conductivity is 18.1 S/cm, the long nanotube bundles further bridged the SWCNTs covered nanofibers. As a consequence, the conductivity of the mat was enhanced by almost six times that of the pure nanofiber mat in spite of small the CNT content. Another advantage of the CNT-anchored CNF composite can be demonstrated in the loading of Pt nanoparticles. Pt loading on nanofibers has been demonstrated previously, which allows high loading amount, uniform size of less than 3 nm, and high catalytic activity of Pt nanoparticles on the whole CNF mat. With the same loading method as shown in the schematic of Fig. 2a, the Pt loading was performed in the case of our composite. No eminent large Pt particles were visible (Fig. 2b). The Pt particles are formed on the nanofibers as well as on the nanotube surfaces (Fig. 2c). The Pt nanoparticles on the nanotube surface were uniformly distributed over the entire tubes with monodisperse sizes of ~3 nm (Fig. 2d). As a consequence, the loading amount increased by a factor of two in the case of the CNT-anchored CNF composite. This efficient loading was attributed to the additional loading on the t-MWCNT surface that is activated by the hydroxyl functional groups.

Table 1 List of the electrical conductivity, the CNT content, the Pt loading amount, and the Pt nanoparticle average size determined by the XRD of [111], [200], [220] peaks of different kinds of CNT/CNF composite mats.

<table>
<thead>
<tr>
<th>Samples</th>
<th>CNTs content (wt%)</th>
<th>Conductivity (S/cm)</th>
<th>Pt loading amount (wt%)</th>
<th>Pt size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNFs</td>
<td>—</td>
<td>3.1</td>
<td>20</td>
<td>2.9 ± 0.4</td>
</tr>
<tr>
<td>t-MWNTs/CNFs</td>
<td>50–65</td>
<td>6.13</td>
<td>40</td>
<td>3 ± 0.6</td>
</tr>
</tbody>
</table>

Fig. 3 shows the cyclic voltammetric (CV) curves for the catalytic activity of the Pt nanoparticles applied to a direct methanol fuel cell. The Pt-CNT-anchored CNF sample exhibits an oxidation current of up to 3400 mA/cm2/mg Pt (Fig. 3a). One significant difference in the CV curve of the t-MWCNT-anchored CNF from the pure CNF sample is that it did not reveal an increased background current during oxidation. The pure CNF sample showed high upshift current during oxidation. This shift has been attributed to the formation of micropores during the carbonization process in CNFs that contributed to the capacitance in the CV curve. However, in
the case of the t-MWCNT-anchored CNF composite, it is conjectured that the mesopore formation could be affected by the high thermal conductivity of carbon nanotubes and, therefore, a different distribution of micropores and mesopores in the composite can be expected. The net catalyst efficiency can be obtained by subtracting this capacitance contribution. Keeping this in mind, the improvement of the catalytic efficiency of the t-MWCNT-anchored CNF composite was prominent compared to the pure CNF mat, which will be discussed in the next paragraph. This improvement was again realized by the formation of the three-dimensional architecture of the t-MWCNT-anchored CNF composite. Since methanol oxidation involves many intermediate steps and forms many intermediate species, it is necessary to have mesopores to support the mass transport of such species. The detailed formation of micropores and mesopores by the presence of anchored CNTs on the CNFs will be further investigated.

Another advantage of the CNT-anchored nanofiber composite mat is the long term stability of the catalytic current. Fig. 3b represents the stability of the catalytic current. A voltage of 0.6 V was applied to the working electrode to record the current as a function of time. The absolute current density of the t-MWCNT-anchored CNF composite mat was 1.7 times higher than that of the pure CNF mat which is the highest of all reported values. Moreover, the current density of the t-MWCNT-anchored CNF composite mat decayed only by 30% after 600 s while the pure CNF mat decayed 90% after 100 s. The improved stability was attributed to the efficient formation of a three-dimensional architecture that reduced the junction resistance between the nanofiber skeletons.

A method of designing an efficient three-dimensional architecture has been demonstrated in which highly conductive CNTs are anchored on the surface of a polymer nanofiber mat. Further application of the composite mat in loading Pt nanoparticles and methanol fuel cell demonstrated that not only improving the loading amount of the Pt nanoparticles was realized but also the maximum catalytic current was obtained with long term stability. This is attributed to the efficient conducting channel that is formed to transport electrons and an appropriate mesopore formation in the carbon nanofiber mat.

Characterizations

For transmission electron microscope (TEM) analysis, the prepared Pt-loaded carbon nanofiber mat was ground into small fragments. This powder was dissolved in ethanol and sonicated in a bath-type sonicator (Power sonic 505, Hwashin) for a minute or less to get individually dispersed nanofibers. This solution was then dropped onto a carbon TEM grid and dried in a vacuum furnace. The high-resolution TEM (JEOL, JEM2010F, 200 kV) was used to observe the composite morphology. A scanning electron microscope (SEM, JEOL JSM6700F) was used to observe the morphology of the Pt-loaded carbon nanofibers. Thermogravimetric analysis (TGA) was used to measure the amount of Pt in the carbon nanofiber mat under an air environment. To measure the activity of the catalyst, the samples were ground and dispersed in isopropanol by sonication and then a certain amount was dropped on a glassy carbon electrode that was 4 mm in diameter. The measurement of catalytic activity was performed in 1 M CH3OH/0.5 M H2SO4. The methanol/sulfuric acid solution was bubbled with N2 gas for 30 min to remove molecular oxygen before measurement. The voltage was scanned from −0.225 V to +1.15 V vs Ag/AgCl KCl 3.5 M using differential pulse voltammetry (pulse height; 3 mV, pulse width; 1 ms.

Experimental

Synthesis of the carbon nanotube-anchored polymer nanofiber composite mat

The arc discharge singlewalled carbon nanotubes (SWCNTs) and thin-mutiwalled nanotubes (t-MWCNTs) purchased from Hanhwa Nanotech Co. Ltd were used in this study. The diameter of the SWCNTs ranged from 1.2 to 1.5 nm with a wide range of length distributions (5–20 nm). The diameter ranges of the t-MWCNTs were 10–20 nm with a length distribution (1–10 nm). The pristine SWCNTs with a concentration of 0.5 mg/ml and sodium dodecyl sulfate (SDS) (Sigma–Aldrich) of 3 mg/ml were dissolved in deionized water and sonicated in a bath type sonicator (Power sonic 505) at 400 W for 10 hours. The pristine t-MWCNTs of 0.5 mg/ml were dispersed in dichloroethane (DCE) with the same sonications as the SWCNTs. In addition, the CNTs were refluxed in strong acid (HNO3:H2SO4 = 1: 3) for 3 hours at 120 °C. The CNT solution was then neutralized with deionized water until pH = 7. The solution was further centrifuged at 10 000 rpm for 15 min. The supernatant CNT solution was used for the composite.

The synthesis of poly(americ acid) (PAA)—a polyamide precursor—was done similarly to the previous report. Electrospinning of the PAA nanofiber mat and spraying the carbon nanotube solution were performed simultaneously in the close chamber. The spray of the CNTs was directed to the space between the syringe and the collector in which the nanofiber is formed. When the combined electrospinning–spray process was terminated, in the case of the SWCNTs/polymer nanofiber composite, the mat was immersed into deionized water for 5 minutes to remove the surfactant (this process was not necessary in the case of t-MWCNTs) and dried in a dry oven at 100 °C for an hour. Then, the composite mat was stabilized in the oven and became a carbon nanotube/polyimide (PI) nanofiber composite mat, which was further carbonized into a carbon nanotube/carbon nanofiber composite mat. The stabilization and carbonization processes were performed similarly to the previous report. The CNT loading amount was 50–65 wt% before carbonization. After carbonization of the composite, the composite was functionalized by 5M H2SO4 solution for three days. Pt-loading on this composite was then done by following the method in the previous work. Pt-loading was conducted on samples of t-MWCNT/PI nanofiber composite mat. It was noted that the form of the mat remained intact throughout the whole process.

7824 | J. Mater. Chem., 2009, 19, 7822–7825
step height; 0.5 mV, step time; 100 ms) at room temperature. Scanning was conducted until the curve was saturated to a stable state.

Acknowledgements

This work was supported by the STAR-faculty project and World Class University (WCU) project from Ministry of Education and Science and Technology, and in part by the KOSEF through CNNC at SKKU.

References