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High-surface-area and high-porosity conductive nanostructures

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Anchoring multiwalled carbon nanotubes to polymeric nanofibers produces conductive nanostructures with high surface area and high porosity.

Electrospun polymeric nanofibers have vast potential for the support and deposition of other materials on their surfaces due to their large surface area, high porosity, and significant number of interfiber connections. Nonwoven mats of these nanofibers are used in various applications, from biodegradable scaffolds for stem cell growth, to potential pH sensors, semiconductive and piezoelectric materials, drug liberation systems, and energy-storage materials.[1–4] Depositing other materials onto these mats can lead to new hybrid systems or to novel nanocomposites with optimal architecture, improved properties, and new functionalities.

A wide variety of nanomaterials can be deposited on the mats, with multi-walled carbon nanotubes (MWCNTs) being among the most promising. These nanotubes combine unique electrical, chemical, and mechanical properties with a large surface area. They have a wide range of uses, including in sensors and actuators, as reinforcement material, and as catalysts in chemical reactions. The MWCNT surface can also be chemically modified to give specific targets and functionalities. In such cases, the key is to ensure that, after functionalization, the interaction area between the MWCNTs and the environment is maximized. For example, if functionalized MWCNTs are used as sensors, maximizing their surface area would increase detection efficiency.[5] If used as fillers in nanocomposites, achieving the best possible contact area with the polymeric matrix will improve stress transfer between the polymer and the MWCNTs.[6] One way to maximize the surface area is to coat electrospun nanofibers with MWCNTs. However, the coating process can be hampered by strong interactions between the MWCNTs, resulting in poor dispersion in solvents, for example.

In this work, we focused on overcoming such difficulties to produce conductive nanostructures made of electrospun, nonwoven mats of nanofibers of polyamide 6 (PA6) and MWCNTs.[7]

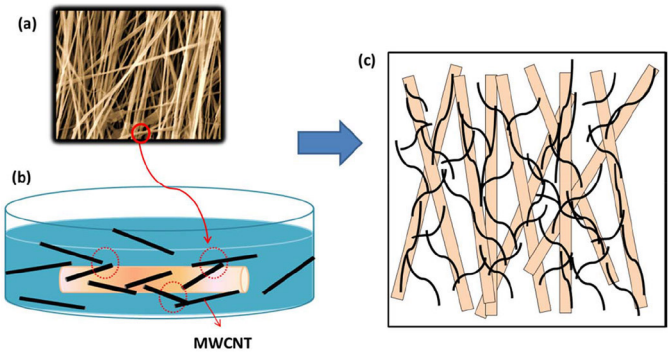

Figure 1. *(a) Electrospun polyamide 6 (PA6) nanofibers. (b) Immersion of the nanofibers in a surfactant solution containing multi-walled carbon nanotubes (MWCNTs) with a carboxyl (COOH) functionality: $MWCNT_{COOH}$. (c) Conductive mats with a stable and interconnected $MWCNT_{COOH}$ network anchored to the nanofibers.*

We anchored MWCNTs to the PA6 nanofibers using a surfactant solution, with three experimental steps: see Figure 1. First, we added a carboxyl group to the MWCNTs to give $MWCNT_{COOH}$. Next, we electrospun PA6 with $MWCNT_{COOH}$ to produce nanofibers of $PA6/MWCNT_{COOH\,(x)}$, where x is the mass fraction of $MWCNT_{COOH}$ in the nanofiber.[2] Finally, we immersed the $PA6/MWCNT_{COOH}$ electrospun mats in a solution containing a nonionic surfactant (Triton X-100) and $MWCNT_{COOH}$. We then confirmed the efficiency of the functionalization using UV spectroscopy.

Scanning electron microscopy (SEM) revealed that only a small amount of $MWCNT_{COOH}$ attached to nanofibers composed solely of PA6: see Figure 2(a). However, far more $MWCNT_{COOH}$ from the surfactant dispersion attached to nanofibers comprising PA6 and $MWCNT_{COOH}$: see Figure 2(b) and (c). We also measured the electrical conductivity of some of the samples, with and without the coating treatment, and after an immersion time of 24 hours: see Table 1. The noncoated nanofibers had an electrical insulating behavior,

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Table 1. *DC volumetric conductivity of PA6 nanofiber mats with MWCNTs with COOH functionality.*

Sample	Immersion time (hours)	DC volumetric conductivity (S/m)
PA6/MWCNT$_{COOH\,(0)}$	0	$9.0 \times 10^{-12} \pm 1.2 \times 10^{-12}$
PA6/MWCNT$_{COOH\,(0)}$	24	$1.0 \times 10^{-4} \pm 0.2 \times 10^{-4}$
PA6/MWCNT$_{COOH\,(3)}$	0	$3.0 \times 10^{-12} \pm 0.8 \times 10^{-12}$
PA6/MWCNT$_{COOH\,(3)}$	24	$2.1 \times 10^{-2} \pm 1.1 \times 10^{-2}$
PA6/MWCNT$_{COOH\,(5)}$	0	$9.9 \times 10^{-11} \pm 6.5 \times 10^{-11}$
PA6/MWCNT$_{COOH\,(5)}$	24	$5.0 \times 10^{-2} \pm 3.2 \times 10^{-2}$
PA6/MWCNT$_{COOH\,(10)}$	0	$1.5 \times 10^{-12} \pm 0.3 \times 10^{-12}$
PA6/MWCNT$_{COOH\,(10)}$	24	$2.5 \times 10^{-2} \pm 0.9 \times 10^{-2}$

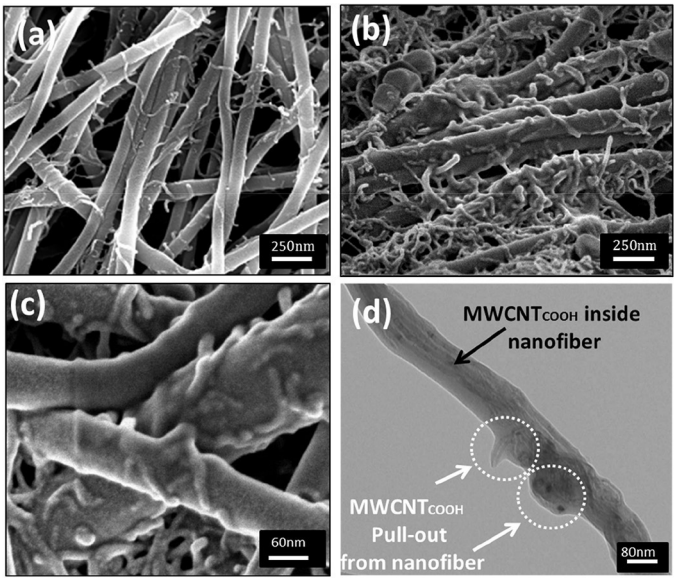

Figure 2. *Scanning electron microscope images of MWCNT-coated electrospun mats: (a) PA6/MWCNT$_{COOH(0)}$; (b, c) PA6/-MWCNT$_{COOH(10)}$; (d) Transmission electron microscopy of a nanofiber showing MWCNT$_{COOH}$ both inside and pulling out from the nanofiber.*

with conductivities of 10^{-12}S/m, but no improvement in conductivity even with MWCNT$_{COOH}$ inside the nanofibers. However, coating composite nanofibers with MWCNT$_{COOH}$ dramatically increased electrical conductivity, to 10^{-2}S/cm. We credit the improved conductivity to the formation of a stable MWCNT$_{COOH}$ percolated network, resulting from MWCNT$_{COOH}$ leaving the solution to anchor to the PA6/MWCNT$_{COOH}$ nanofibers. The anchoring is possible due to MWCNT$_{COOH}$ inside the PA6 nanofibers poking out to form anchorage points to which the MWCNT$_{COOH}$ from the solution can attach: see Figure 2(d).

In summary, by anchoring functionalized MWCNTs to nanofibers made from both PA6 and MWCNTs, we have achieved conductive nanostructures with a high surface area and high porosity. These nanostructures have potential as gas sensors, for example. Therefore, the next steps will be to test these materials as sensors and to electrospin other polymers such as poly(aniline) and poly(pyrrole).

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