Giant Surface Conductivity Enhancement in a Carbon Nanotube Composite by Ultraviolet Light Exposure

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Supporting Information

ABSTRACT: Carbon nanotube composites are lightweight, multifunctional materials with readily adjustable mechanical and electrical properties—in relevant to the aerospace, automotive, and sporting goods industries as high-performance structural materials. Here, we combine well-established and newly developed characterization techniques to demonstrate that ultraviolet (UV) light exposure provides a controllable means to enhance the electrical conductivity of the surface of a commercial carbon nanotube-epoxy composite by over 5 orders of magnitude. Our observations, combined with theory and simulations, reveal that the increase in conductivity is due to the formation of a concentrated layer of nanotubes on the composite surface. Our model implies that contacts between nanotube-rich microdomains dominate the conductivity of this layer at low UV dose, while tube-tube transport dominates at high UV dose. Further, we use this model to predictably pattern conductive traces with a UV laser, providing a facile approach for direct integration of lightweight conductors on nanocomposite surfaces.

KEYWORDS: nanocomposite, carbon nanotubes, conductivity, ultraviolet, scanning ion microscopy, microwave, cavity perturbation

INTRODUCTION

The addition of multiwall carbon nanotubes (MWCNTs) to epoxy resins produces composites with improved mechanical, thermal, and electrical properties, enabling reductions in composite component mass and opening up novel design and processing possibilities. However, as with any new material system, many barriers to implementation must be overcome before MWCNT composites can be deployed commercially. One significant impediment to the wide-scale adoption of MWCNT composites is a lack of physical understanding and predictive models governing the relationship between the structure and the physical properties of MWCNT composites. A second challenge is the development of techniques to spatially localize the properties of MWCNT composites, enabling functional elements such as carbon nanotube-based sensors, actuators, wires, and heaters to be integrated into composite components.

Previous studies have shown that the microstructure of MWCNT composites is often heterogeneous, comprising MWCNT-rich microdomains embedded in a polymer matrix. Understanding the effect of these domains on real-world material performance is complicated by the evolution of the composite surface structure under typical environmental stresses, such as UV radiation, high humidity, and elevated temperature. In one example, Petersen et al. found that UV light selectively removed epoxy matrix material, resulting in a
We prepared our samples from a commercially available epoxy resin containing predispersed MWCNTs (Zyvex) and then exposed the samples to UV light from a broadband UV lamp. A complete description of the experimental details concerning the sample fabrication and the broadband-UV light exposure conditions has been published previously. For completeness, some of these details are reproduced here along with the experimental details of all new measurements.

**Measurements.** We characterized the microstructure and nanostructure of the composite at a series of UV doses with conducting atomic force microscopy (C-AFM), scanning lithium-ion microscopy (SLIM), and transmission electron microscopy (TEM). Additionally, we measured the composite’s electrical properties with both direct current (dc) four-probe conductance measurements and a microwave cavity-perturbation technique. To support these measurements, we developed a multiscale physical model that combines molecular dynamics simulations with effective medium theory to illuminate the influence of morphology and explain the increase in surface-layer conductivity. Finally, we show that the composite’s surface may be spatially patterned by UV light, providing a means to control the surface’s conductivity independently from the conductivity of the bulk material.

**Sample Preparation.** The epoxy polymer was a stoichiometric mixture of diglycidyl ether of bisphenol A (189 equiv mass) (EPON 828, Resolution Performance Products) and an aliphatic polyetheramine curing agent (Jefamine T403, Huntsman Corporation). The cured epoxy contained a mass fraction of 3.5% MWCNT.

**RESULTS AND DISCUSSION**

**Domain Microstructure.** We imaged a micrometre-faced cross section of the composite with C-AFM (Materials), revealing micrometer-scale MWCNT-rich domains loosely connected in a conducting network (Figure 1a, left). In order to capture this microstructural information in a model, we performed image analysis (Figure S1, Supporting Information) to segment and label the MWCNT-rich domains (Figure 1a, right). On the basis of the segmented image, we computed log-normal distribution functions of the domain radii (Figure 1b) and nearest-neighbor separations (Figure 1c). Next, we computed a 3D radius distribution (Figure 1d) from the 2D radius distribution and used it to construct a 3D structural model of the composite (Supporting Information) that consisted of a neat epoxy matrix with spherical MWCNT-rich inclusions (Figure 1e) and an epoxy-rich surface layer.

Consistent with previous studies, we found that UV light selectively removed epoxy from the nanocomposite surface, resulting in a surface layer of MWCNTs. Imaging MWCNTs embedded in an organic matrix is often challenging due to both the lack of atomic number contrast and charging artifacts associated with the poorly conducting epoxy matrix; however, we found that the surface layer of MWCNTs can be readily imaged by scanning lithium-ion microscopy (SLIM, Figure 2). In our microscope, incident lithium ions positively charge the epoxy, preventing the release of secondary electrons and was approximately 3 mm, and the samples were embedded in epoxy before facing. C-AFM measured the conductance from the AFM tip, through a percolated conducting network of MWCNTs, and down to a bottom electrode. A bias of 1 V was applied to the electrode with respect to the AFM tip potential, and the current flowing through the AFM tip was collected as the tip was scanned across the face surface in contact mode. The cantilever was model DCP11 (NT-MDT).

**SLIM.** The SLIM images were taken with a custom focused-ion-beam system that uses a recently developed lithium ion source. Images were acquired with a secondary electron detector at a beam energy of 4 kV and current of 1 pA. Images are the average of several fast scans with a total imaging time of about 60 s. Both the low current and fast scanning were needed to avoid unwanted charging artifacts.

**Electrical Characterization.** We measured the dc sheet conductance for each sample exposed to the broadband UV lamp with a four-point probe at six different locations on the sample, correcting for sample shape, contact area, and current direction. The four-point probe technique measures the dc sheet conductance, which is \( G = \sigma_{\text{bulk}}s_{\text{sample}} \) for a uniform sample (no surface layer); here, \( G \) is the sheet conductance, \( \sigma_{\text{bulk}} \) is the bulk volume conductivity, and \( s_{\text{sample}} \) is the thickness of the sample. The ac electrical properties were measured on samples that were diced into 7 mm by 3 mm by 300 \( \mu \)m coupons and performed using a microwave cavity-perturbation technique following the protocol described elsewhere. The microwave cavity-perturbation technique extracts the dielectric constant and conductivity at microwave frequencies (7.3, 8.5, 10.0, and 11.7 GHz) and is noncontact, electroless, and nondestructive.

For both dc and microwave measurements, the admittance of the surface layer is taken to be in parallel to that of the bulk. Therefore, we compute the sheet conductance of the surface layer \( (G_{\text{surface}}) \) for each UV exposed sample as

\[
G_{\text{surface}} = G_{\text{sample}} - \sigma_{\text{bulk}}s_{\text{sample}} \quad (1)
\]

where \( G_{\text{sample}} \) is the measured sheet conductance of the UV-exposed sample, \( \sigma_{\text{bulk}} \) is the bulk volume conductivity of the unexposed sample, and \( s_{\text{sample}} \) is the thickness of the UV-exposed sample (for example, the distance from the top to the bottom in Figure 1a, left). This approximation is valid when the thickness of the surface layer is much smaller than the other sample dimensions.

**Materials**

We prepared our samples from a commercially available epoxy resin containing predispersed MWCNTs (Zyvex) and then exposed the samples to UV light from a broadband UV lamp. A complete description of the experimental details concerning the sample fabrication and the broadband-UV light exposure conditions has been published previously. For completeness, some of these details are reproduced here along with the experimental details of all new measurements.

**UV Exposure.** Three UV sources were used in these experiments: a broadband UV light source, a wide-spot-size collimated UV laser, and a focused UV laser. The broadband UV light exposure (ranging from 295 to 400 nm) was performed with the with National Institute of Standards and Technology (NIST) SPHERE (Simulated Photodegradation via High Energy Radiant Exposure). The UV flux was approximately 0.5 kW m\(^{-2}\) at elevated humidity (75% relative humidity) and temperature (50 °C). This exposure was well below the glass-transition temperature of the MWCNT-epoxy samples, which was approximately 100 °C. The exposure time in the SPHERE for the most highly UV-exposed sample was 59 days, resulting in a UV dose of approximately 1.1 GJ m\(^{-2}\).

The wide-spot-size UV laser was a 364 nm Ar-ion laser with a collimated beam and a spot size of approximately 2 mm (1/e\(^2\) diameter), which allowed uniform exposure of features by a shadow mask. The maximum power density of the collimated beam was approximately 150 kW m\(^{-2}\), and the sample exposure time was approximately 1500 s, resulting in a UV dose of approximately 200 MJ m\(^{-2}\).

The focused UV laser was a 325 nm He-Cd laser with a focused spot size of approximately 2 μm (1/e\(^2\) diameter). The maximum power density of the beam was approximately 100 MW m\(^{-2}\) inside the focused spot, and the sample exposure time was approximately 10 s, resulting in a UV dose of approximately 1 GJ m\(^{-2}\).

**C-AFM.** Samples for C-AFM were prepared by facing a cross sections of nanocomposite by ultramicrotomy. The thickness of the samples in the direction perpendicular to the face of the cross section was approximately 3 mm, and the samples were embedded in epoxy before facing. C-AFM measured the conductance from the AFM tip, through a percolated conducting network of MWCNTs, and down to a bottom electrode. A bias of 1 V was applied to the electrode with respect to the AFM tip potential, and the current flowing through the AFM tip was collected as the tip was scanned across the face surface in contact mode. The cantilever was model DCP11 (NT-MDT).
causing the epoxy regions to appear dark when observed by the secondary electron detector. In contrast, the MWCNTs appear bright because they have a conducting path to ground, allowing for the neutralization of deposited ion charge and the release of secondary electrons. Tilted cross-sectional views of freeze-fractured samples for increasing UV doses (Figure 2a) provide secondary electrons. Tilted cross-sectional views of freeze-fractured cross sections of the composite taken at increasing UV doses. Error bars represent the variation of the mean coverage that occurred when the coverage detection threshold was varied by 25%. The dashed line in (c) is a fit to a first-order exponential growth and saturation model (i.e., logistic growth), \( f(x) = a(1 + e^{-b(x-c)}) \); here, \( x \) is the UV dose, \( a = (0.87 \pm 0.01\%) \), \( b = (13.37 \pm 0.11) \text{ GJ m}^{-2} \), and \( c = (0.26 \pm 0.01) \text{ GJ m}^{-2} \), where uncertainties are determined from error propagation based on a 95% confidence interval. The solid line is the result of a numerical microerosion simulation using the 3D-microstructure model in Figure 1. (d) Mass loss of the MWCNT–epoxy as a function of ultraviolet dose, where the uncertainty was computed from the uncertainty of both the area exposed and the mass and corresponds to a single standard deviation. The dashed line in (d) is a fit to a saturated growth model, \( f(x) = a(1 - e^{-b(x-c)}) \); here, \( x \) is the UV dose, \( a = (2.15 \pm 0.02) \text{ mg cm}^{-2} \), \( b = (2.84 \pm 0.08) \text{ GJ m}^{-2} \), and \( c = (0.05 \pm 0.01) \text{ GJ m}^{-2} \), where uncertainties are determined from error propagation based on a 95% confidence interval.

indicating that UV treatment left the graphic structure of the MWCNTs largely intact. It is possible that changes to the graphic structure would be more evident for MWCNTs that were initially of higher quality. However, it is not clear how this would affect their conductivity. Indeed, UV exposure on films of single-walled carbon nanotube films has shown mixed results, with the change in conductivity dependent on initial tube quality and surface chemistry as well as the environmental conditions of exposure. Future work will explore higher quality MWCNTs to test this observation. However, we speculate that higher quality MWCNTs may show an even larger enhancement in the surface conductivity.

While there is substantial evidence that the MWCNT domains collapse into a densified layer on the surface, we do not have a complete understanding of the mechanism behind this collapse. Despite our lack of complete knowledge, we can speculate about the possible mechanisms of the collapse. One key point is that as the epoxy matrix is removed by the UV light, the surface of the epoxy must recede past each MWCNT...
that is released. We hypothesize that the MWCNTs are attracted to the epoxy surface as it recedes past them, pulling them along with the receding surface. There are several possible mechanisms that could contribute to an attractive force between the receding epoxy surface and the MWCNTs, including (but not limited to) van der Waals forces, water capillary forces, and electrostatic forces. We speculate that it is unlikely that mutually attractive forces between the MWCNTs alone are sufficient to collapse the MWCNT domains, as similar (uncollapsed) aggregates occur in MWCNT powders. Thus, the mechanical, chemical, and electrostatic interactions between the MWCNTs and the receding epoxy surface are likely key factors in the collapse.

**Surface Coverage Measurements.** We quantified the growth of the surface MWCNT layer by binarizing the SLIM images (Figure S2) and computing the fraction of the surface covered by MWCNTs at each UV dose (Figure 2c). To capture this surface coverage behavior in our conductivity model, we performed a microerosion simulation on our 3D structural model. The simulation progressed through the removal of neat-epoxy voxels from the simulated surface (Figure 1e) using the experimentally measured epoxy removal rate for the MWCNT–epoxy composite (Figure 2d). The microerosion simulation enables us to estimate how much epoxy is removed from the surface while accounting for the nonuniform etch rate of the surface, which is caused by the MWCNT domains. The effect of the nonuniform etch rate has been observed experimentally as an increasing surface roughness with increasing UV dose.7 In our microerosion simulation for the highest UV dose (1.1 GJ m⁻²), the average etch depth was approximately 4 μm, although 10 μm pits in the surface were quite common (Figure 1e). The surface coverage calculated from the microerosion simulation (Figure 2c) and simulated images of the surface (Figure S4) were both in good agreement with the experiment, leading us to conclude that the bulk microstructure and epoxy removal rate are the primary factors in determining the UV-dose dependence of MWCNT surface coverage.

**DC and Microwave Electrical Surface Measurements.** To quantify electrical conductivity, we performed dc four-point probe measurements and microwave cavity perturbation measurements10 at each UV dose (Materials section). The four-point probe measurements of the unexposed sample yielded a bulk-volume conductivity of σ bulk ≈ 2 mS m⁻¹, while the microwave measurements in combination with self-consistent effective medium theory16 enabled us to estimate the conductivity within the MWCNT-rich domains to be σ domain ≈ 2 S m⁻¹ (Supporting Information). The 3-orders-of-magnitude difference between the bulk volume conductivity and the domain conductivity provides evidence that the clustering of MWCNTs into discrete domains severely limits the bulk volume conductivity.

After characterizing the bulk properties of the unexposed sample, we used a parallel admittance circuit model (eq 1, Supporting Information) to estimate the conductivity of MWCNT-rich domains with varying degrees of densification (Figure S9). We employed the conductivity data from our simulations in combination with two-phase mixture theory16 to model the surface layer conductivity as a function of UV dose (Supporting Information). We found that for low UV doses (from 0.0 to 0.3 GJ m⁻²) the conductivity data were consistent with a three-dimensional transport model (d = 3, in eq 1, Supporting Information) that incorporated varying domain conductivity but maintained a constant MWCNT-domain volume fraction (Figure 3, region I). In this regime, the densification of MWCNTs in near-surface domains serves to increase the domain conductivity. However, the change in MWCNT-domain volume fraction is negligible because the exposed MWCNTs form isolated islands (Figure 2b at 0.2 GJ m⁻²), leaving the electrical connectivity between domains unchanged. For larger UV doses (from 0.3 to 1.1 GJ m⁻²) the densified MWCNT-rich domains on the surface begin to connect, and the conduction mechanism is dominated by the electrical percolation of the concentrated-MWCNT surface layer. In this regime, the conductivity follows a two-dimensional transport model (d = 2, in eq 1, Supporting Information) that incorporates both changing domain conductivity and changes in the surface coverage (Figure 3, region II).
Although the above simulations serve to elucidate the mechanisms behind the increased surface conductivity, they are somewhat arduous to perform. As an alternative to the simulations above, we suggest a relatively simple scaling relation that applies in the high-UV-dose limit, that is, once the surface layer is fully densified and completely covers the bulk. This scaling relation is given by $\sigma_{\text{surface}} \sim \sigma_{\text{domain}} AD$, here, $\sigma_{\text{domain}}$ is the conductivity of the MWCNT domains in the bulk, $A$ is the length-to-diameter ratio of the nanotubes, and $D$ is the densification ratio of the domains, which may be computed as the ratio of the diameter of the domains in the bulk to the thickness of a densified domain after epoxy removal (Supporting Information). This scaling relation predicts a surface conductivity of approximately $1 \text{kS m}^{-1}$ for our system, which is consistent with the measured conductivity at the highest UV dose. Although this scaling relation applies to a surface uniformly covered by MWCNTs, it is equally valid for patterned UV exposure, as long as the smallest feature of the UV-exposed pattern is larger than the typical MWCNT domain size. We note that both temperature and humidity are interesting processing variables that may potentially provide additional controls to dynamically tune the enhancement of the surface conductivity and mechanisms of action.

**Patterning Experiments.** To demonstrate the potential for patterning the conducting layer, we performed two experiments using UV-laser exposure. First, we used a wide-spot-size (approximately $2 \text{ mm}^2$), collimated UV laser (364 nm) and a shadow mask to pattern a wire on the nanocomposite surface (Figure 4a,b). Although the UV-laser dose was only $(222 \pm 9) \text{ MJ m}^{-2}$ for the patterned wire, the resulting surface coverage was comparable to that obtained at a dose of $(450 \pm 30) \text{ MJ m}^{-2}$ from the broadband-UV lamp. We attribute the higher epoxy etch rate for the UV laser to heating caused by the high power density of the UV laser (approximately $150 \text{kW m}^{-2}$) compared to the broadband UV lamp (approximately $500 \text{ W m}^{-2}$). Taking $(450 \pm 30) \text{ MJ m}^{-2}$ as an effective UV dose for the UV-laser patterned wire, we estimate the thickness of the wire to be $(159 \pm 50) \text{ nm}$ (Figure S8b) and the conductivity of the surface layer to be $(99 \pm 21) \text{ S m}^{-1}$ (Figure 3), resulting in a predicted resistance of $(86 \pm 32) \text{k}\Omega$. Four-probe current–voltage $(I–V)$ measurements of the $0.2 \text{ GJ m}^{-2}$ wire showed Ohmic behavior (Figure 4c) with a resistance of $(48.1 \pm 0.2) \text{k}\Omega$, which is both consistent with the prediction and significantly lower than the resistance of a control device $(809.6 \pm 0.5) \text{k}\Omega$ that was not exposed to UV light (Figure 4c).

In the next patterning experiment, we scanned a focused laser (325 nm) across the nanocomposite surface to write the NIST logogram (Figure 4d), testing a more complex pattern. The local intensities of the broad- and focused UV-laser exposures were approximately 3 and 6 orders of magnitude larger, respectively, than the broadband-UV lamp source used for the quantitative conductivity studies described in Figures 2 and 3. Despite this significant difference in the UV-exposure time scale and wavelength spectrum, the resistance measurements and SLIM images indicate that UV-laser patterning causes an increase in the surface conductivity that is comparable to a much slower blanket exposure, providing a broad range of processing conditions that predictably tune the conductivity.

**CONCLUSIONS**

In this investigation, we examined a system where UV light selectively removed epoxy matrix material from a composite surface, causing the MWCNT-rich domains near the surface to densify and form an electrically well-connected surface layer. For our system, the resulting concentrated MWCNT layer increased the surface conductivity of the composite by over 5 orders of magnitude, spanning the range from 2 to $1 \text{kS m}^{-1}$. To describe this behavior, we developed a 3D microerosion simulation technique that predicts MWCNT surface coverage based on microstructure and epoxy removal rate and proposed a simple scaling relation that predicts the surface conductivity after UV exposure. Taken together, these advances enable features of predetermined conductivity to be written on the surface of a nanocomposite by simply exposing it to UV light.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b04522.

Details of image processing algorithms and techniques used to characterize the domain structure based on C-AFM data and to quantify the surface coverage based on SLIM images; it also includes C-AFM images of cross sections of MWCNT–epoxy samples at various UV doses, details of the microstructure model and microerosion simulations, details of the Raman spectroscopy mapping to measure the G-D ratio of the surface compared to the bulk, details of the dc and microwave cavity perturbation data used to quantify the electrical properties of the epoxy control samples and the MWCNT–epoxy samples, a more detailed description of the two-phase conductivity model and the conductivity scaling relation, transmission electron microscopy images used to measure the surface layer thickness, and details of the molecular dynamics simulations of the...
nanostructure, morphology, and conductivity of the MWCNTs during domain densification (PDF)

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Notes
The authors declare no competing financial interest.

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REFERENCES

(8) The full description of the procedures used in this article requires the identification of certain commercial products and their suppliers. The inclusion of such information should in no way be construed as indicating that such products or suppliers are endorsed by NIST or that they are necessarily the best materials, instruments, software or suppliers for the purposes described.


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