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Synthesis of ZnO nanoarrays on carbon fibers using combined atomic layer deposition and hydrothermal methods

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Jingyu Wang[1], **Binbin Weng**[2,4], **Preston Larson**[3] **and Yingtao Liu**[1,4]

[1] School of Aerospace & Mechanical Engineering, University of Oklahoma, Norman 73019, United States of America
[2] School of Electrical and Computer Engineering, University of Oklahoma, Norman 73019, United States of America
[3] Samuel Roberts Noble Microscopy Laboratory, University of Oklahoma, Norman 73019, United States of America
[4] Authors to whom any correspondence should be addressed.

E-mail: yingtao@ou.edu **and** binbinweng@ou.edu

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Abstract

The paper presents the synthesis and characterization of zinc oxide (ZnO) nanoarrays on carbon fiber fabrics using the combined atomic layer deposition (ALD) and hydrothermal methods. A conformal ZnO seed layer was first synthesized using the ALD method on carbon fiber surfaces, then characterized by field emission scanning electron microscope (FESEM). ZnO nanoarrays were grown on the carbon fibers using the hydrothermal method. The morphology of ZnO nanoarrays in the form of nanowires and nanorods was controlled by adjusting hydrothermal synthesis parameters, including the concentration of chemical reagents and solution temperature. The FESEM characterization showed that the synthesized ZnO nanowires and nanorods had a wurtzite structure and uniformity distributed on the surface of carbon fibers. The length to diameter ratios of the ZnO nanoarrays were controlled between 44 and 270. The thermogravimetric analysis tests showed that the growth of ZnO nanoarrays added about 10% additional weight to the carbon fibers.

1. Introduction

Recently light-weight structural composite materials have attracted significant attention due to their high strength-to-weight ratio, corrosion resistance, and design flexibility [1]. Integrating nanomaterials and nanostructures within conventional fiber reinforced composites provides a promising approach to improve composite properties. Carbon felt and carbon nanotubes have been synthesized on continuous structural fiber fabrics [2, 3]. Vertically aligned zinc oxide (ZnO) nanowires have been synthesized on natural fibers, such as cotton fibers [4–6] and jute fibers [7], and synthetic fibers, such as poly(acrylonitrile) fibers [8] and polyester fibers [9]. In particular, structural fibers, including carbon fibers [10–12] and aramid fibers [13–15] with vertically aligned nanowires, can result in advanced composite materials with enhanced mechanical properties due to the increased interfacial area between fiber and polymer matrix. Additionally, the piezoelectric properties of ZnO nanowires can also lead to load sensing functions for *in situ* structural health monitoring and prognostics in complex composite structures [16–19].

Most current approaches to growing ZnO nanoarrays on carbon fiber fabrics are based on the dip-coating method that can only attach ZnO seeds to substrates by weak van der Waals forces in a wet chemical environment [2–9]. In addition, considering the strong hydrophobic properties and the cylindrical shape of the carbon fibers, it is challenging to deposit ZnO seeds in a good uniformity, conformity, and controlled crystal orientation using the dip-coating method.

In recent years, an emerging technique called atomic layer deposition (ALD) has become popular because it offers advantages, such as high degree of conformity, atomic-scale thickness controllability, perfect stoichiometric uniformity, low impurity contamination, and low growth temperature [20–22]. Therefore, in order to avoid the issues associated with the dip-coating method, in this paper the ALD method was adopted to produce uniform and high-quality ZnO seed layers on carbon fiber fabrics. Then, we focused on studying the

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Table 1. Experimental procedures used in hydrothermal syntheses of ZnO nanoforest on carbon fiber fabrics.

Sample name	$Zn(NO_3)_2$ concentration (mMol L^{-1})	HMT concentration (mMol L^{-1})	Growth temperature (°C)
A1	25	25	70
A2	50	50	70
A3	100	100	70
B1	25	25	80
B2	50	50	80
B3	100	100	80

hydrothermally synthesized, vertically aligned ZnO nanoarrays on carbon fiber fabrics. Various hydrothermal growth parameters were investigated, including reaction temperature and concentration of chemical reagents, and the properties of ZnO nanoarrays coated carbon fiber fabrics were characterized using field emission scanning electron microscope (FESEM), thermogravimetric analysis (TGA) and energy-dispersive x-ray spectroscopy (EDX). We believe that the developed carbon fiber fabrics with ZnO nanoarray coatings will lead to the development of advanced composite materials with enhanced mechanical properties and potential load sensing capabilities.

2. Experiments

2.1. Materials

Unless otherwise stated, all the following listed materials and reagents were used as received. Plain weave carbon fiber fabrics were purchased from Fibre Glast. Diethylzinc and deionized water were purchased from Sigma–Aldrich and used for the ZnO seeding via ALD. Trichloroethylene (TCE, 99%), zinc nitrate hexahydrate ($Zn(NO_3)_2$, 99%) and hexamethylenetetramine (HMT, 99%) were purchased from Sigma–Aldrich and used in the hydrothermal synthesis of ZnO nanoarrays on carbon fiber fabrics.

2.2. Synthesis of ZnO nanoarrays on carbon fiber fabrics

A two-step synthesis approach was developed to grow vertically aligned ZnO nanowires on carbon fiber fabrics. First, the ALD method was used to deposit the ZnO seed layer on carbon fiber fabrics. Then, a low temperature hydrothermal method was employed as the second step to synthesize ZnO nanoarrays in the forms of nanowires and nanorods. To obtain an optimal ALD procedure, the seed layer was first grown on a silicon substrate, and characterized using atomic force microscope (AFM), x-ray diffraction (XRD), and FESEM. The detailed synthesis procedure has been reported in our previous publication [23]. The identified nucleation procedure was employed to deposit the ZnO seeds on carbon fiber fabrics, followed by FESEM characterization of the seed morphology.

In the second step, carbon fiber fabrics were degreased by dipping them into TCE and methanol solvents, respectively, for 10 min under ultrasonic agitation, then washed under running deionized water for 10 min, and finally dried in an environmental oven. $Zn(NO_3)_2$ and HMT aqueous solutions were prepared. Each was stirred at 600 rpm for 10 min at 55 °C, then mixed together and stirred at 600 rpm for 10 min at 55 °C. The solution was stored in a water bath at 90 °C for 1 h to consume impurities. Finally, the carbon fiber fabrics were submerged into the prepared solution to hydrothermally synthesize ZnO nanoarrays. Detailed solution concentrations and hydrothermal growth temperature are listed in table 1. The morphology of ZnO nanoarrays was studied using FESEM to characterize the average diameters and length to diameter ratio of ZnO nanoarrays. The elemental composition of the carbon fibers before and after ZnO nanoarrays coating were studied by EDX, the ZnO crystal orientation on the synthesized ZnO nanoarrays were tested by XRD, and the decomposition property and weight ratio of the ZnO on carbon fibers were then characterized using TGA.

3. Results and discussions

The identification of the optimal ALD procedure to deposit a thin layer of ZnO seeds on the substrate is a critical aspect of this paper. ZnO seeds were uniformly deposited on the silicon substrate, as shown in the FESEM (figure 1(a)) and AFM (figure 1(b)) images. The same experimental procedure was adopted to deposit ZnO seed layer on carbon fiber fabrics. The FESEM image of the uniformly deposited ZnO seeds on a single carbon fiber was shown in figure 1(c). XRD tests were used to validate the crystal structures of the ZnO seeds and synthesized

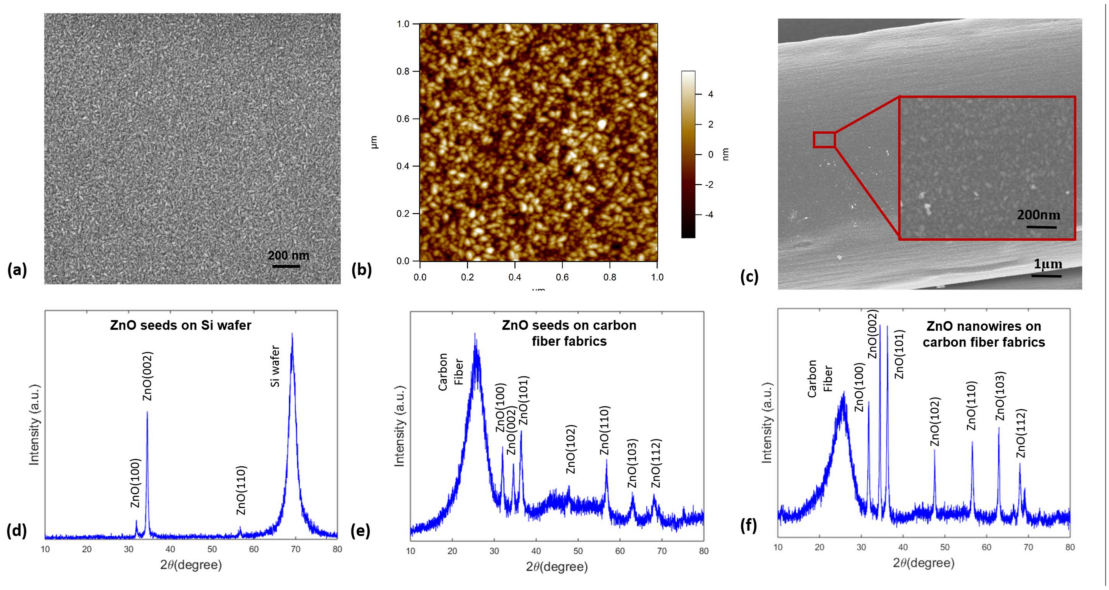

Figure 1. (a) FESEM image of ZnO seeds on a silicon substrate; (b) AFM image of ZnO seeds on a silicon substrate; (c) FESEM image of ZnO seeds on carbon fiber fabrics; (d) XRD pattern of ZnO nucleation on the silicon substrate; (e) XRD pattern of ZnO nucleation on carbon fiber fabrics; (f) XRD pattern of ZnO nanowires on carbon fiber fabrics.

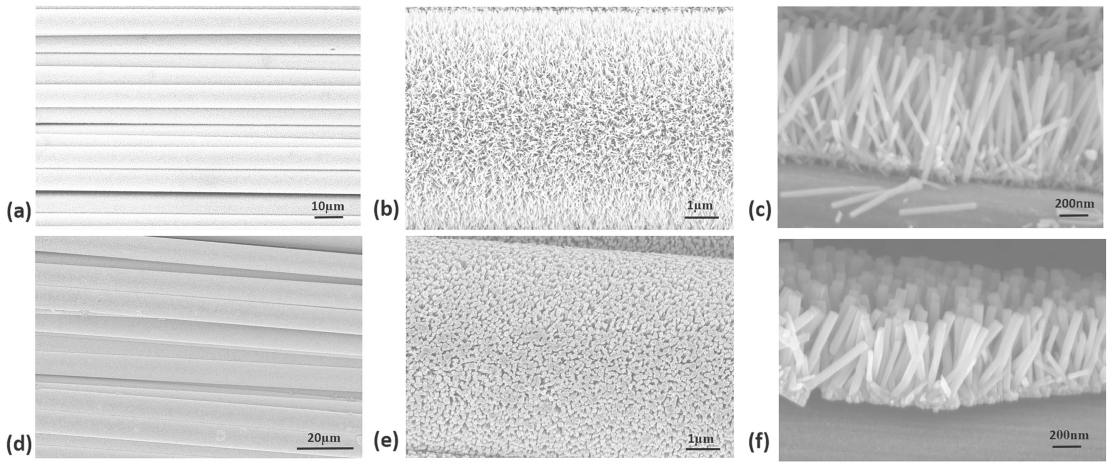

Figure 2. (a)–(c) FESEM images of sample B1 showing the vertically aligned ZnO nanowires on carbon fibers; (c)–(f) FESEM images of sample B2 showing the vertically aligned ZnO nanorods on carbon fibers.

ZnO nanowires. Both the ZnO seeds grown on Si wafer (figure 1(d)) and carbon fibers (figure 1(e)) were tested first. When ZnO seeds were deposited on a flat Si wafer, the ZnO diffraction peaks in the XRD pattern proved the poly-crystalline nature of the thin film. Meanwhile, contrasting with the two weak (100) and (110) peaks, the dominant (002) diffraction peak indicated that the thin film was primarily grown in the *c*-axis orientation. Such optimized material quality will ensure high quality ZnO nanoarray growth in the hydrothermal growth process. When ZnO seeds were coated on carbon fiber, more diffraction peaks were detected in XRD. The (002) diffraction peak was still clear, however, the (100) and (101) diffraction peaks were also observed mainly due to the curved carbon fiber surface. The same XRD pattern was observed in ZnO nanowires compared to ZnO seeds on carbon fiber fabrics. During the hydrothermal treatment, all the ZnO diffraction peaks were enhanced, as shown in figure 1(f).

The morphology of ZnO nanoarrays on carbon fiber fabrics was studied using FESEM, as shown in figure 2. Six sets of ZnO nanoarrays were synthesized, varying the hydrothermal reaction temperature and reagents' concentrations. The hydrothermal synthesis time used was 17 h for all the experiments. It should be noted that the $Zn(NO_3)_2$ and HMT concentrations had a significant effect on ZnO morphology. As shown in figures 2(a) and (b), ZnO nanowires were obtained when 25 mMol L^{-1} of $Zn(NO_3)_2$ and HMT were used during the

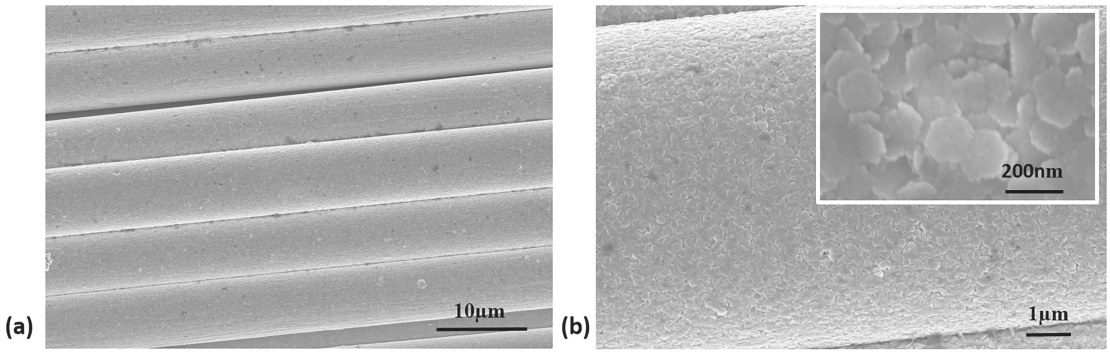

Figure 3. FESEM images of sample A3 showing a top view of the fully grown ZnO nanorods covering the entire carbon fiber.

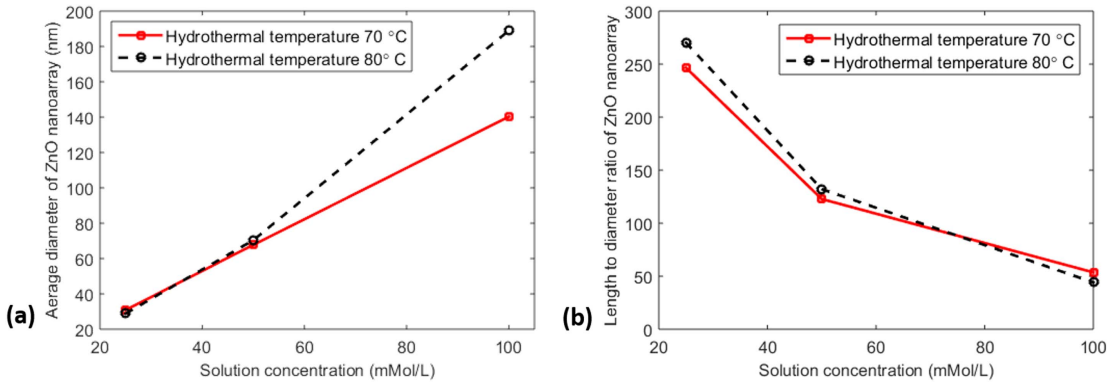

Figure 4. (a) Average diameters of ZnO nanoarrays with different concentrations of hydrothermal solutions; (b) average length to diameter ratio of ZnO nanoarrays with different concentrations of hydrothermal solutions.

hydrothermal treatment. ZnO nanowires with similar morphology were obtained when the hydrothermal reaction temperature was reduced to 70 °C. However, the average diameter of ZnO nanoarrays significantly increased when 50 mMol L^{-1} of $Zn(NO_3)_2$ and HMT were used during the hydrothermal treatment. As shown in figures 2(d) and (e), ZnO nanorods were synthesized on carbon fibers. Similar ZnO nanorods were obtained when the hydrothermal reaction temperature was reduced to 70 °C, though both the average diameter and length of ZnO nanorods were slightly reduced. The vertical alignment of ZnO nanoarrays were visualized from the side view, as shown in figures 1(c) and (f). Good ZnO alignment of both ZnO nanowires and nanorods were obtained from samples B1 and B2.

When $Zn(NO_3)_2$ and HMT concentrations increased to 100 mMol L^{-1}, the diameter of ZnO nanorods increased and the ZnO nanorods were grown at an increased density. As shown in figure 3, nanorods covered entire carbon fiber. Similar results were obtained from sample B3 when the hydrothermal temperature increased to 80 °C. Since this type of ZnO nanoarray coatings on carbon fibers did not significantly increase the surface area to volume ratio of carbon fibers, we did not consider those samples for interfacial strength enhancement in carbon fiber fabrics and composites.

The average diameters and the length to diameter ratio of ZnO are two critical parameters indicating potential mechanical property enhancement capabilities due to increased surface area on carbon fibers. As shown in figure 4, the averaged diameters of ZnO nanoarrays increased from 28 nm (sample A1) to 189 nm (sample B3), and the length to diameter ratio decreased from 270 (sample A1) to 44 (sample B3), when $Zn(NO_3)_2$ and HMT concentrations increased from 25 mMol L^{-1} to 100 mMol L^{-1}. The variation of ZnO diameter and length to diameter ratio proved that the solution concentration used in hydrothermal synthesis of ZnO nanoarrays on carbon fibers was the dominant effect on the ZnO morphology.

The EDX pattern (figure 5(b)) shows the elemental analysis on the ZnO nanoarrays coated carbon fiber fabrics. When carbon fibers with ZnO nanoarrays were tested using EDX, only zinc and oxygen elements were detected on the top surface, indicating the high density of ZnO nanoarrays. Although there were gaps among ZnO nanoarrays, the high length to diameter ratio of nanoarrays created full coverage of the carbon fiber surface. For comparison, when pristine carbon fibers were studied via EDX (figure 5(d)), only carbon was detected.

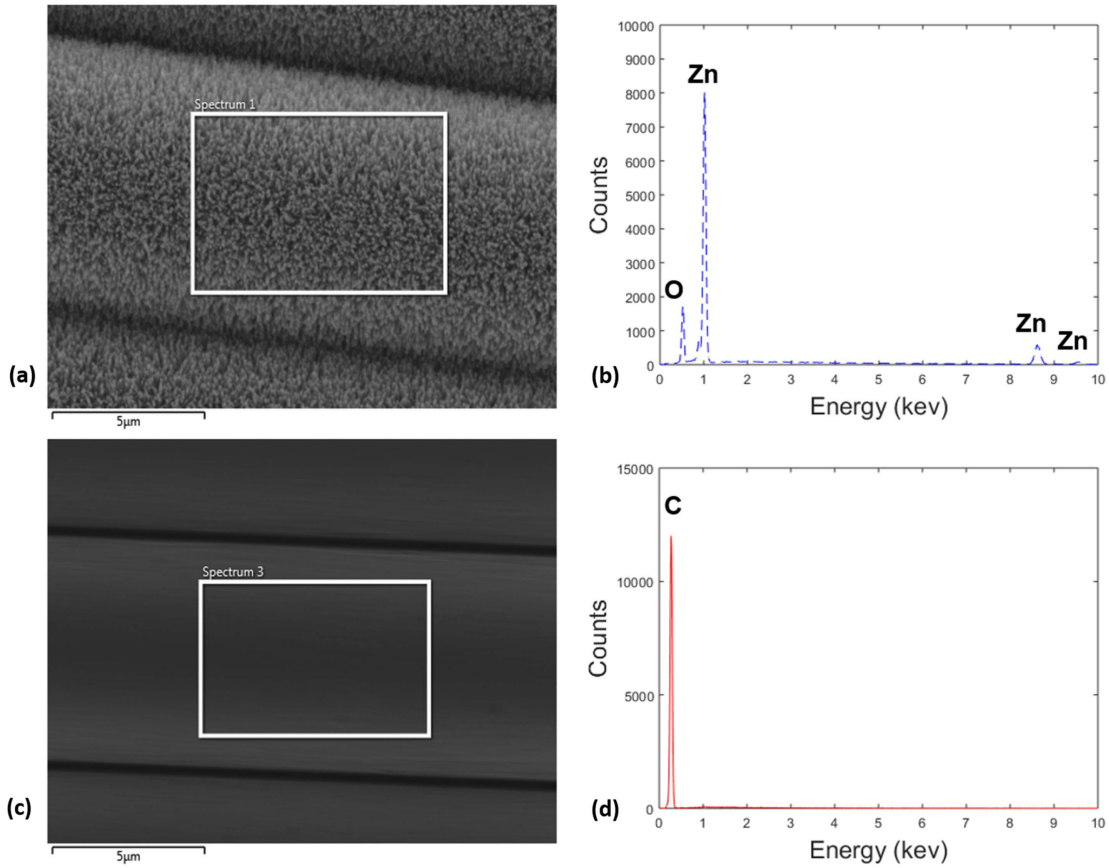

Figure 5. (a) FESEM image on carbon fiber with ZnO nanowires; (b) EDX graph measured from the highlighted area in (a); (c) FESEM image on bare carbon fiber; (d) EDX graph measured from the highlighted area in (c).

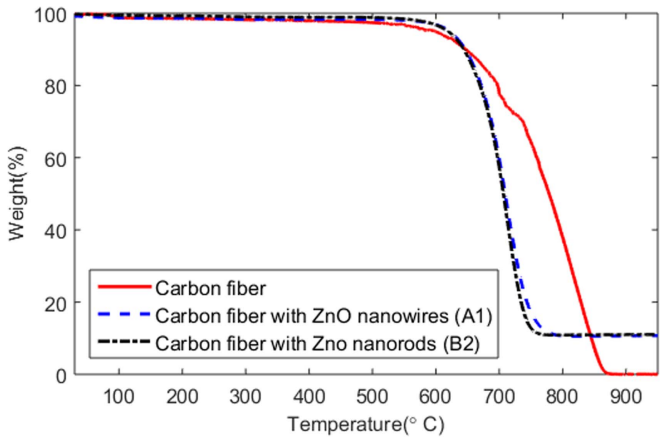

Figure 6. TGA graphs of carbon fiber, and carbon fiber coated with ZnO nanoarrays.

The weight ratios of ZnO nanoarrays on carbon fibers were investigated using TGA tests and are shown in figure 6. All the experiments were conducted by increasing the temperature by 5 °C min^{-1}. The weight of all samples began decreasing around 600 °C. ZnO modified carbon fibers reached full decomposition at 780 °C, and bare carbon fibers were fully decomposed at about 876 °C. Of the carbon fibers coated with ZnO nanoarrays, there was about 11 wt% left after the TGA tests. Since only carbon was burned off during all the TGA tests, the residual weight was considered to be only ZnO, indicating about an 11 wt% weight increase after ZnO nanoarrays synthesis on carbon fibers. In addition, the decomposition speed of bare carbon fibers was slower than the modified carbon fibers with ZnO nanowires. This is because the increased surface area to volume ratio

on the modified carbon fibers increased heat transfer efficiency. Therefore, ZnO modified carbon fibers were burned off faster than their unmodified counterparts.

4. Conclusions

This paper presents a two-step approach of vertically aligned ZnO nanoarrays synthesis on carbon fiber fabrics using the combined ALD and hydrothermal methods. The optimal ALD parameters and ZnO seeding procedure were identified using silicon substrates and adopted to grow the ZnO seeds on carbon fiber fabrics. The hydrothermal method was used to synthesize ZnO nanoarrays. By adjusting the hydrothermal solution concentration and temperature, the average diameters of ZnO nanowires and nanorods can be controlled between 28 nm and 189 nm, and the length to diameter ratio of nanowires and nanorods can be controlled between 270 and 44. All ZnO modified carbon fibers were characterized using FESEM, EDX, and TGA. Due to the dramatic increase of surface area on the modified carbon fiber fabrics, these materials can be used to develop novel structural composites with enhanced mechanical properties. Load sensing capabilities can also be obtained due to the piezoelectric properties of the ZnO nanoarray.

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ORCID iDs

Yingtao Liu https://orcid.org/0000-0002-6232-9704

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