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Synthesis and characterization of self-assembled ZnO nanoarrays on hybrid structural fibers

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ABSTRACT

Hybrid carbon fibers with self-assembled and well-aligned zinc oxide (ZnO) nanoarrays can lead to novel structural materials that enable promising applications in multifunctional composites with beneficial properties including enhanced interlaminar mechanical properties and potential load sensing capabilities. In this paper, atomic layer deposition (ALD) and hydrothermal methods were integrated to synthesize ZnO nanoarrays in the shape of aligned nanowires and nanorods on carbon fiber fabrics. The surface morphology of ZnO nanoarrays were controlled by adjusting the reagent concentrations and hydrothermal reaction time. As-synthesized hybrid fibers were characterized to understand their critical properties including nanostructure morphology, crystal structures, ZnO weight concentration, and contact angle between water and ZnO nanoarrays. The results demonstrated that the ZnO nanostructures and morphology can be controlled and optimized for lightweight composite applications.

1. Introduction

Advanced fiber reinforced composites have been used extensively in high-performance structural applications [1–5]. Due to weak adhesive bonding in composites, barely visible damage, such as delamination and fiber pull-out, can significantly weaken the mechanical strength of composites and even cause catastrophic structural failures [6,7]. Hybrid fibers with nanostructured surfaces using carbon nanotubes (CNT) and zinc oxide (ZnO) nanowires have been developed to enhance interfacial mechanical properties [8–11]. Due to their superior mechanical and thermal properties, well-aligned CNT nanoforests have been synthesized mainly using chemical vapor deposition (CVD) method to enhance the bonding strength and interfacial properties in fiber reinforced composite laminates [12]. However, the high CVD temperature can degrade the mechanical strength of carbon fiber fabrics in composite laminates. Due to increased surface area to volume ratio, structural fiber fabrics coated with ZnO nanowires are expected to increase the bonding between the fiber and polymer matrix in composites. The low hydrothermal temperature of ZnO nanowires allows direct growth of ZnO nanostructures on structural fibers and used for structural composite applications. In addition, as a type of piezoelectric materials, ZnO nanowires can respond to applied external loads on composites, leading to novel functional composites with load sensing functions [13].

In recent years, increasing attention has been drawn to the advancement of synthesis technology for the growth of aligned ZnO nanoarrays in the shape of nanowires [14,15], nanorods [14–17], nanorings [18], nanosprings [19], and other nanostructures [20,21] on various types of substrates using chemical vapor deposition [22], physical vapor deposition [23], and hydrothermal [24] methods. However, most aligned ZnO nanowires on continuous structural fibers have been synthesized using a two-step method: first, the dip-coating method to generate ZnO seeds on fiber surfaces, and then the hydrothermal method for nanowire growth [10,25]. Since the dip-coating method can hardly control the size and shape of ZnO seeds, low seeding quality affects the alignment and property of hybrid fibers with ZnO nanoarrays.

Atomic layer deposition (ALD) has been well accepted as a micromanufacturing technology to grow thin films [26]. Since ALD is able to meet the needs for atomic layer control and conformal deposition using sequential and self-limiting surface reactions, this approach is considered to be one of the best methods to achieve high conformality, in particular, on high aspect structures. Binary metal oxides, including Al_2O_3 [27], TiO_2 [28], ZnO [29], and metal thin films, such as Cu [30], can be deposited on various substrates. Besides conformality, low deposition temperature is another key advantage of ALD, allowing the

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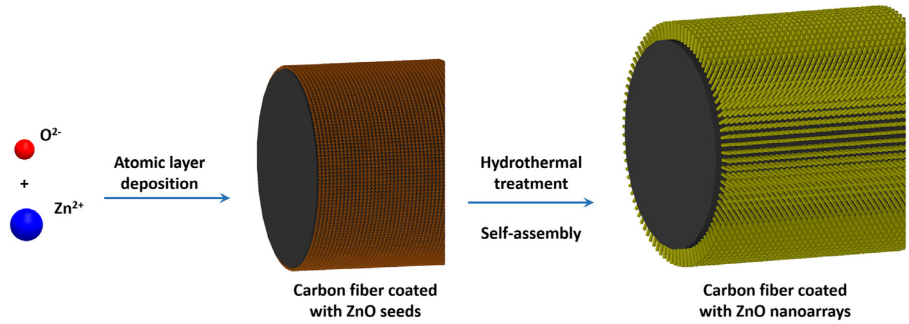

Fig. 1. Schematic of synthesis procedure of hybrid structural fibers using combined ALD and hydrothermal methods.

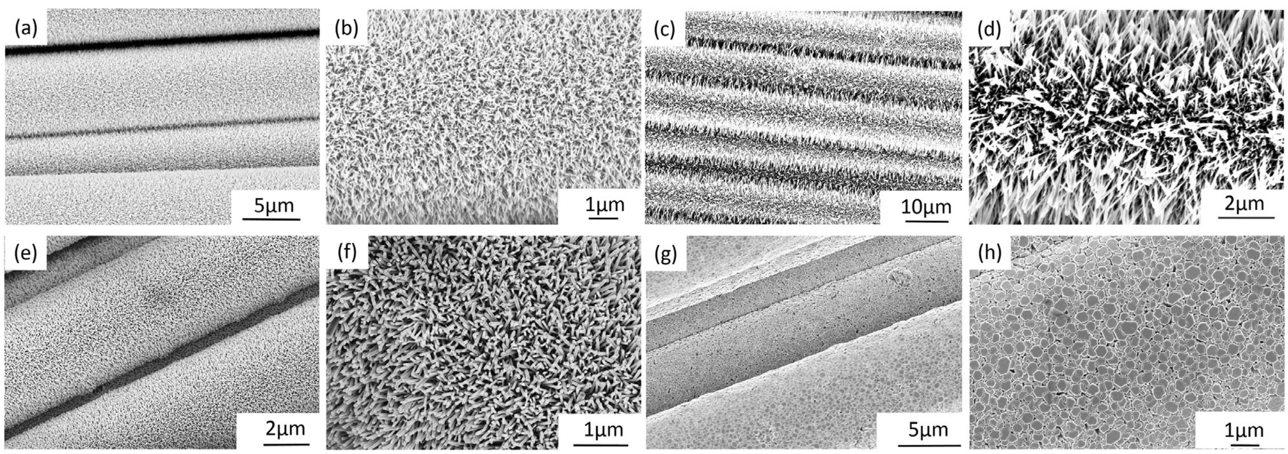

Fig. 2. FESEM images of synthesized hybrid structural fibers: (a and b) FESEM images of ZnO fine nanowires on carbon fibers; (c and d) FESEM images of ZnO fuzzy nanowires on carbon fibers; (e and f) FESEM images of ZnO fine nanorods on carbon fibers; (g and h) FESEM images of compact nanorods on carbon fibers showing the fully coverage of carbon fiber by ZnO.

Table 1
Hydrothermal parameters.

Sample name	$Zn(NO_3)_2$ (mmol/L)	HMT (mmol/L)	Growth time (h)	Nanoarray morphology
A1	25	25	5	Fine nanowires
A2	50	50	5	Fine nanowires
A3	100	100	5	Fine nanorods
A4	200	200	5	Compact nanorods
B1	25	25	17	Fine nanowires
B2	50	50	17	Fuzzy nanowires
B3	100	100	17	Fine nanorods
B4	200	200	17	Compact nanorods
C1	25	25	30	Fine nanowires
C2	50	50	30	Fuzzy nanowires
C3	100	100	30	Fine nanorods
C4	200	200	30	Compact nanorods

process of temperature sensitive materials and substrates. The employment of ALD method to grow ZnO seed layer on carbon fiber fabrics has the potential to accurately control ZnO nanoparticle size with improved uniformity. Since the mechanical properties of carbon fiber fabrics can be significantly degraded at high temperature, low deposition temperature of ALD allows to coat conformal ZnO thin films as seed layer on carbon fiber fabrics without degrading the fiber's strength. Our recent study has demonstrated the capability to grow ZnO seed layer on carbon fiber fabrics using ALD method [31,32]. This paper focuses on the impacts of the reagent concentrations and hydrothermal reaction time on ZnO nanoarray morphology.

In this paper, we report an integrated approach for the morphological control of ZnO nanowire arrays on carbon fiber fabrics, using ALD to deposit ZnO seeds and the low temperature hydrothermal method for nanowire synthesis. The unique combination of ALD and hydrothermal methods allowed to generate high ZnO seed layers on carbon fiber and to control ZnO nanoarray morphology. The nano structures of synthesized ZnO were tailored by adjusting the hydrothermal process time and reagent concentrations. Detailed properties of the fabricated hybrid fibers were characterized.

2. Experimental

2.1. Materials

Diethylzinc and deionized water were purchased from Sigma–Aldrich and used for 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. All the materials were used as received.

2.2. Synthesis procedure of hybrid fibers

In this paper, a two-step hybrid fiber synthesis procedure, combining ALD and hydrothermal methods, was developed to synthesize ZnO nanoarrays. High quality ZnO seeds were first deposited on carbon fibers via ALD, and then grown into nanoarrays in an aqueous solution using the hydrothermal method. The schematic of synthesis procedure is shown in Fig. 1.

Carbon fiber fabrics were first degreased by dipping them into TCE and methanol, respectively, for 10 min under ultrasonic agitation, washed under running deionized water for 10 min, and finally dried in an environmental oven. The prepared carbon fiber fabrics were used for the ALD and hydrothermal synthesis of ZnO nanoarrays on carbon fiber

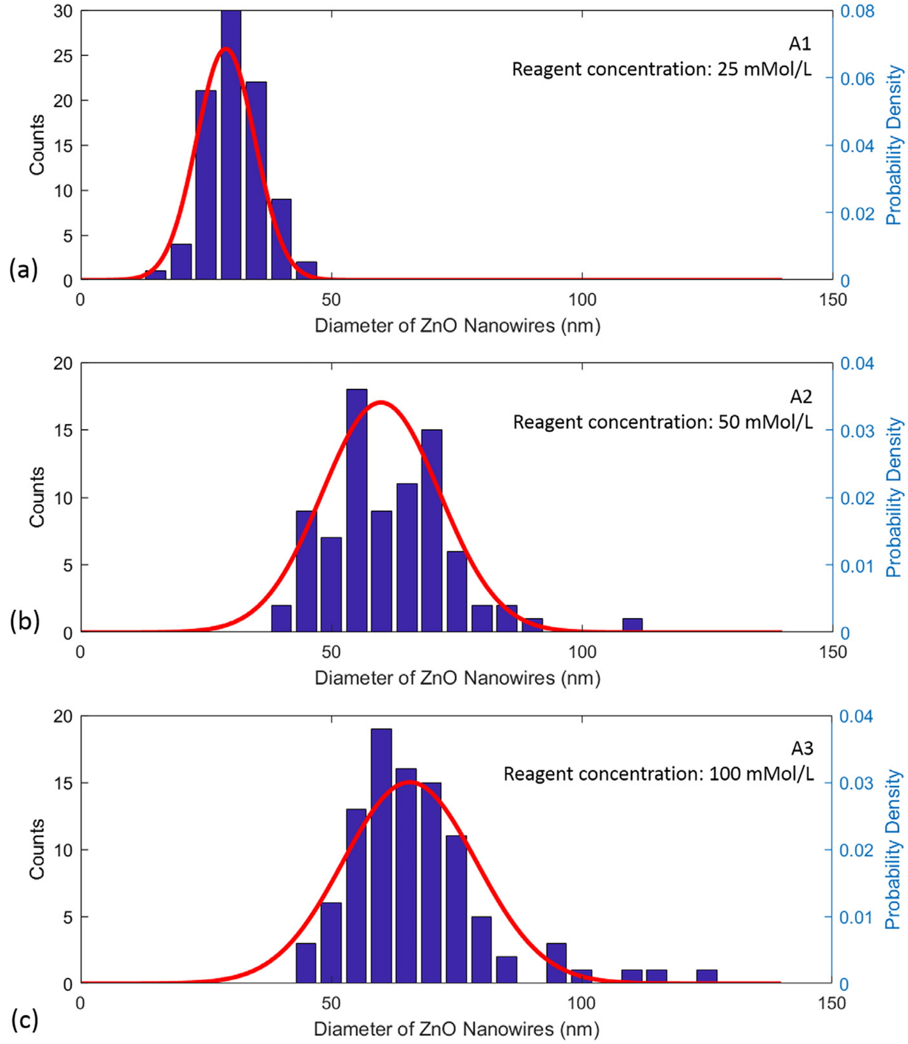

Fig. 3. Effect of reagent concentration on diameter distributions of ZnO nanoarrays grown on carbon fiber substrates. Growth time: 5 h.

fabrics.

To synthesize ZnO nanoarrays on carbon fiber fabrics, a customized thermal ALD system was used to deposit ZnO seeds on the cleaned carbon fiber fabrics. In the reaction process, a double-exchange chemical vapor reaction was adopted between DI water and DEZn precursors. The dose time was controlled via computer driven pneumatic valves, and N_2 gas was used to carry these vaporized sources to the reaction chamber. The H_2O and DEZn were alternately distributed, and a 10 s ultra-high purity N_2 purge period was carried out after each dosing process. It should be noted that this period was enough to ensure the pressure returned to its base level before the next pulse.

In the second step, $Zn(NO_3)_2$ and HMT aqueous solutions were prepared for the hydrothermal process. 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. The morphologies of synthesized nanoarrays were controlled by adjusting the hydrothermal reaction time from 5 h to 30 h and reagent concentration from 25 mmol/L to 100 mmol/L. The ZnO nanoarrays were naturally aligned due to the self-assembly nature of ZnO nanoarrays.

2.2. Property characterization

The investigation of the ZnO nanoarray morphology was carried out using a field emission scanning electron microscope (FESEM) at a voltage of 20 kV. The diameters of the ZnO nanowires were measured using the commercial software ImageJ on the FESEM images, and statistical analyses were employed to study the diameter distribution of the ZnO nanoarrays. The weight concentration of ZnO in hybrid fiber was tested using the thermogravimetric analysis (TGA). The element analysis of hybrid fibers was conducted using energy-dispersive X-ray (EDX) spectroscopy. Powder X-ray diffraction (XRD) measurements were carried out using sing a Rigaku Ultima IV diffractometer. Cu-K-alpha radiation (40 kV, 44 mA) was used via a Bragg-Brentano detector. The hydrophobic and hydrophilic surface properties of the synthesized hybrid fibers were characterized by measuring the contact angles of water and ZnO nanoarrays. ZnO nanoarray coated carbon fiber fabrics was attached on a glass substrate and place on a flat stage in front of a camera. Water droplet was pushed out from a syringe by a motor-driven lead screw mechanism. Experimental setup is shown in Supplementary Material. Only one water droplet was placed on top of the ZnO nanoarray during the tests. The contact angle was measured using commercial software ImageJ from the recorded pictures.

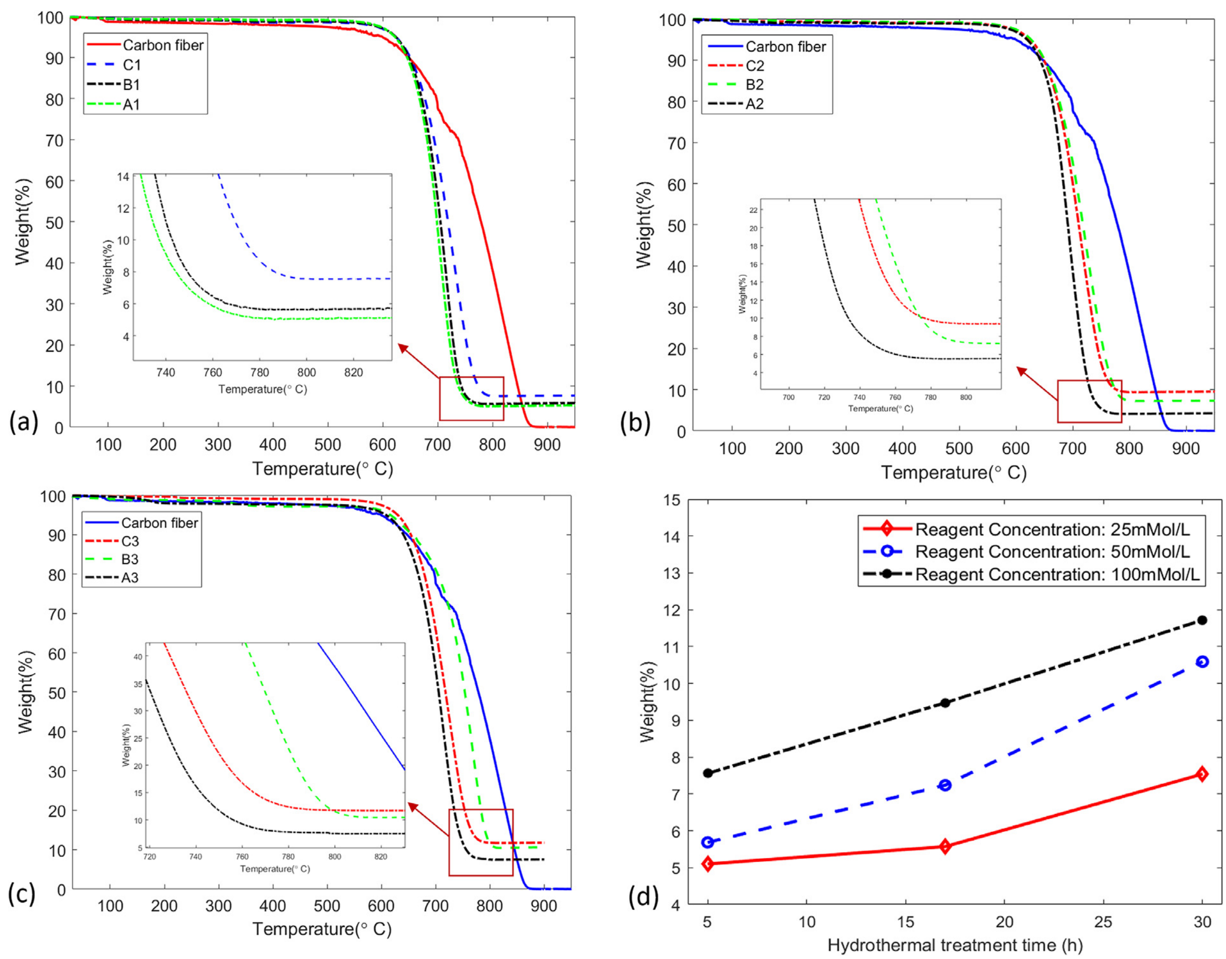

Fig. 4. TGA characterization of ZnO weight concentrations in hybrid structural fibers.

Table 2
ZnO weight concentrations of hybrid fibers.

Sample name	ZnO weight concentration	Sample name	ZnO weight concentration	Sample name	ZnO weight concentration
A1	5.10%	B1	5.68%	C1	7.56%
A2	5.57%	B2	7.24%	C2	9.45%
A3	7.54%	B3	10.59%	C3	11.72%

3. Results and discussions

In this paper, the morphology and microstructure of ZnO nanoarrays were controlled by tailoring the reagent concentrations and reaction time of the hydrothermal process, and were studied via FESEM. Four types of ZnO nanoarray morphology were obtained: fine nanowires (Fig. 2a and b), fuzzy nanowires (Fig. 2c and d), fine nanorods (Fig. 2e and f), and compact nanorods (Fig. 2g and h). Both the fine nanowires and fine nanorods showed a one-dimensional (1D) microstructure of the synthesized nanoarray, with the ZnO nanowires aligned on carbon fiber fabrics. However, the fuzzy nanowires were not well-aligned due to the lack of guidance during the hydrothermal process. The ZnO compact nanorods covered the entire carbon fiber surface when the reagent concentration was 200 mmol/L or higher during the hydrothermal process. The detailed reagent concentrations, hydrothermal growth time, and obtained morphology are listed in Table 1. The diameter distributions of the ZnO nanoarrays obtained from the corresponding FESEM images are shown in Fig. 3. The average diameters of the ZnO nanoarrays can be controlled at different reagent concentrations. When the reagent concentration increased from 25 to 100 mmol/L, the average diameters of the ZnO nanoarrays increased from 29 nm to 65 nm, correspondingly. Similar trends were obtained when the hydrothermal reaction time increased from 5 h to 30 h.

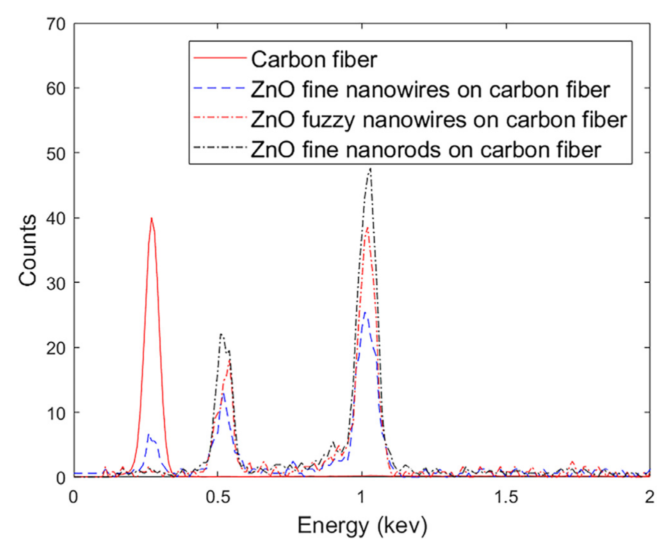

Fig. 5. EDX spectra of ZnO nanowires on carbon fibers.

Weight concentration of aligned ZnO nanowire arrays on hybrid fiber fabrics is critical for light-weight composite applications. TGA tests were conducted to burn off all carbon fiber fabrics, and ZnO weight concentrations were calculated using the residual weight of the

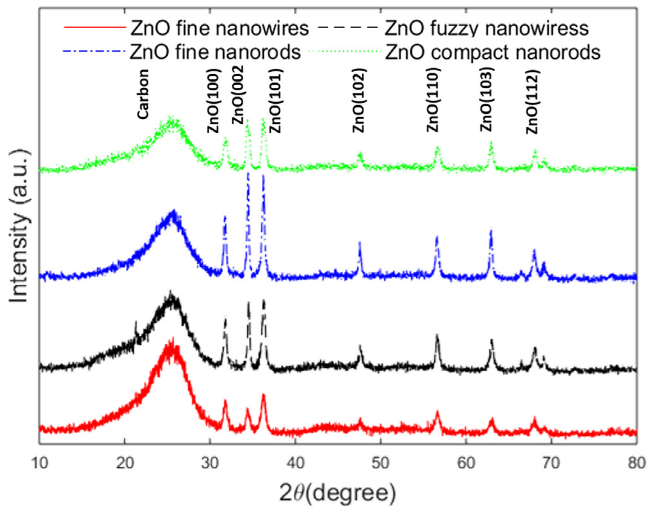

Fig. 6. XRD diffraction of ZnO nanoarrays with different morphology. .

tested samples. As shown in Fig. 4a, carbon fibers on the hybrid fiber samples A1, B1, and C1 all started decomposing at around 600 °C. Once all the carbon fibers were burned off, the residual weight concentrations of ZnO for samples A1, B1, and C1 were 5.10%, 5.68%, and 7.56%. Since the reagent concentration used for these samples was at 25 mmol/L, the TGA results proved that longer hydrothermal synthesis time results in higher ZnO concentrations and larger ZnO nanowire and nanorod diameters. Similar TGA test results were obtained using other samples. The TGA testing results of samples A2, B2, and C2 are shown in Fig. 4b, and the TGA testing results of samples A3, B3, and C3 are shown in Fig. 4c. The TGA results reported in the supplement materials demonstrate that longer hydrothermal synthesis time results in higher ZnO concentrations and larger ZnO nanowire and nanorods diameters. In addition to the hydrothermal treatment time, reagent concentrations also impacted ZnO weight concentrations. When the reagent concentration increased from 25 mmol/L to 100 mmol/L, the maximum ZnO weight ratio reached 11.72%. The weight concentration of ZnO of all the tested samples are listed in Table 2, and summarized TGA in Fig. 4d.

Elemental analysis of the ZnO nanoarray coated carbon fiber fabrics was performed via EDX. Zinc, oxygen, and carbon were all detected on samples with ZnO fine nanowires. Only zinc and oxygen were detected on samples with fuzzy nanowires and fine nanorods due to the high ZnO density on the fibers (Fig. 5). The crystal structures of ZnO nanoarrays were studied via XRD. Fig. 6 shows that multiple diffraction peaks, including (100), (002), and (101), were recorded due to the highly cured fiber surface. Since the same XRD diffraction peaks were obtained from all the samples with different morphology, it can be concluded that the variation of reagent concentration and hydrothermal process time did not change the crystal structures of synthesized ZnO nanoarray coated carbon fiber fabrics.

The contact angles of water on the grown ZnO nanostructures have been measured from the synthesized hybrid fiber fabrics with four different types of ZnO morphologies. As shown in Fig. 7, the contact angles of water on ZnO fine nanowires, fuzzy nanowires, fine nanorods, and compact nanorods were 155.7°, 144.9°, 139.0°, and 77.8°, respectively. Compared to ZnO morphology in Fig. 2 and the average ZnO diameters shown in Fig. 3, it is obvious that the nanostructures of fine ZnO nanowires with good alignment and small average diameter could provide air/solid binary collaboration effect on the fabric surface, which increased the water repellence property of the fabrics. However, the hydrophobic properties were weakened when the average diameter

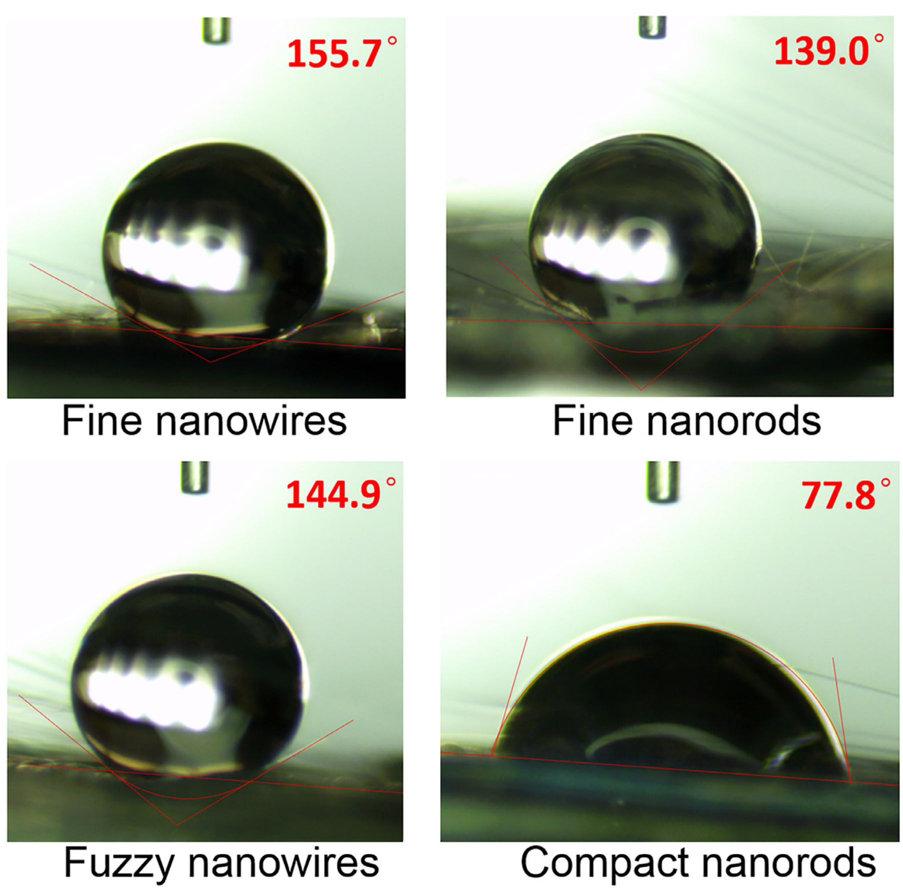

Fig. 7. Contact angles of four types of synthesized hybrid structural fiber fabrics.

increased and ZnO morphology converted to fuzzy nanowires and nanorods. When ZnO completely covered the entire carbon fiber and showed morphology of compact nanorods, the contact angle reduced to 77.8°, demonstrating the hydrophilic surface property of the hybrid fabrics.

4. Conclusions

ZnO nanoarrays with controllable morphology were synthesized and characterized in this paper. A two-step approach combining ALD and hydrothermal methods was developed to synthesize ZnO nanoarrays. Characterization methods, including FESEM, TGA, EDX, and XRD, were employed to study the morphology and crystal structures of ZnO. Four types of ZnO surface morphology were grown on carbon fiber fabrics: fine nanowires, fuzzy nanowire, fine nanorods, and compact nanorods. Experimental results demonstrated that the same ZnO crystal structure was obtained regardless of the reagent concentrations and hydrothermal process time. The contact angles of the synthesized hybrid fibers were controlled by the average ZnO diameter and morphology. The developed hybrid fibers can be used to develop lightweight structural composites with enhanced interfacial properties.

Conflict of interest

There is no conflict of interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.surfin.2018.10.006.

References

[1] H. Akil, M. Omar, A. Mazuki, S. Safiee, Z.M. Ishak, A.A. Bakar, Kenaf fiber reinforced composites: a review, Mater. Des. 32 (8–9) (2011) 4107–4121.
[2] C.E. Bakis, L.C. Bank, V. Brown, E. Cosenza, J. Davalos, J. Lesko, A. Machida, S. Rizkalla, T. Triantafillou, Fiber-reinforced polymer composites for construction—state-of-the-art review, J. Compos. Constr. 6 (2) (2002) 73–87.
[3] S. Chand, Review carbon fibers for composites, J. Mater. Sci. 35 (6) (2000) 1303–1313.
[4] Y. Yuan, Y. Sun, S. Yan, J. Zhao, S. Liu, M. Zhang, X. Zheng, L. Jia, Multiply fully recyclable carbon fibre reinforced heat-resistant covalent thermosetting advanced composites, Nat. Commun. 8 (2017) 14657.
[5] L. Carabba, M. Santandrea, C. Carloni, S. Manzi, M.C. Bignozzi, Steel fiber reinforced geopolymer matrix (S-FRGM) composites applied to reinforced concrete structures for strengthening applications: a preliminary study, Compos. Part B: Eng 128 (2017) 83–90.
[6] E.J. Barbero, Introduction to Composite Materials Design, CRC Press, 2017.
[7] B. Agarwal, L. Broutman, Analysis and Performance of Fiber Composites, second ed., John Wiley & Sons, 1990.
[8] E.T. Thostenson, Z. Ren, T.-W. Chou, Advances in the science and technology of carbon nanotubes and their composites: a review, Compos. Sci. Technol. 61 (13) (2001) 1899–1912.
[9] X. Zhang, Z. Liu, Recent advances in microwave initiated synthesis of nanocarbon materials, Nanoscale 4 (3) (2012) 707–714.
[10] Y. Lin, G. Ehlert, H.A. Sodano, Increased interface strength in carbon fiber composites through a ZnO nanowire interphase, Adv. Funct. Mater. 19 (16) (2009) 2654–2660.
[11] G.J. Ehlert, Y. Lin, U. Galan, H.A. Sodano, Interaction of ZnO nanowires with carbon fibers for hierarchical composites with high interfacial strength, J.. Solid Mech. Mater. Eng. 4 (11) (2010) 1687–1698.
[12] D. Bello, B.L. Wardle, J. Zhang, N. Yamamoto, C. Santeufemio, M. Hallock, M.A. Virji, Characterization of exposures to nanoscale particles and fibers during solid core drilling of hybrid carbon nanotube advanced composites, Int. J. Occup. Environ. Health 16 (4) (2010) 434–450.
[13] L. Groo, D.J. Inman, H.A. Sodano, In situ damage detection for fiber-reinforced composites using integrated zinc oxide nanowires, Adv. Funct. Mater. (2018) 1802846.
[14] L. Vayssieres, Growth of arrayed nanorods and nanowires of ZnO from aqueous solutions, Adv. Mater. 15 (5) (2003) 464–466.
[15] H. Yu, J. Liu, X. Fan, W. Yan, L. Han, J. Han, X. Zhang, T. Hong, Z. Liu, Bionic micro-nano-bump-structures with a good self-cleaning property: the growth of ZnO nanoarrays modified by polystyrene spheres, Mater. Chem. Phys. 170 (2016) 52–61.
[16] Z. Liu, J. Ya, E. Lei, Effects of substrates and seed layers on solution growing ZnO nanorods, J. Solid State Electrochem. 14 (6) (2010) 957–963.
[17] Z. Liu, E. Lei, J. Ya, Y. Xin, Growth of ZnO nanorods by aqueous solution method with electrodeposited ZnO seed layers, Appl. Surf. Sci. 255 (12) (2009) 6415–6420.
[18] W.L. Hughes, Z.L. Wang, Controlled synthesis and manipulation of ZnO nanorings and nanobows, Appl. Phys. Lett. 86 (4) (2005) 043106.
[19] P.X. Gao, Z.L. Wang, High-yield synthesis of single-crystal nanosprings of ZnO, Small 1 (10) (2005) 945–949.
[20] X. Wang, C.J. Summers, Z.L. Wang, Large-scale hexagonal-patterned growth of aligned ZnO nanorods for nano-optoelectronics and nanosensor arrays, Nano Lett. 4 (3) (2004) 423–426.
[21] J. Zhang, Z. Liu, J. Liu, E. Lei, Z. Liu, Effects of seed layers on controlling of the morphology of ZnO nanostructures and superhydrophobicity of ZnO nanostructure/stearic acid composite films, Mater. Chem. Phys. 183 (2016) 306–314.
[22] D. Barreca, D. Bekermann, E. Comini, A. Devi, R.A. Fischer, A. Gasparotto, C. Maccato, G. Sberveglieri, E. Tondello, 1D ZnO nano-assemblies by plasma-CVD as chemical sensors for flammable and toxic gases, Sens. Actuators B 149 (1) (2010) 1–7.
[23] L. Wang, X. Zhang, S. Zhao, G. Zhou, Y. Zhou, J. Qi, Synthesis of well-aligned ZnO nanowires by simple physical vapor deposition on c-oriented ZnO thin films without catalysts or additives, Appl. Phys. Lett. 86 (2) (2005) 024108.
[24] J.-S. Na, B. Gong, G. Scarel, G.N. Parsons, Surface polarity shielding and hierarchical ZnO nano-architectures produced using sequential hydrothermal crystal synthesis and thin film atomic layer deposition, ACS Nano 3 (10) (2009) 3191–3199.
[25] U. Galan, Y. Lin, G.J. Ehlert, H.A. Sodano, Effect of ZnO nanowire morphology on the interfacial strength of nanowire coated carbon fibers, Compos. Sci. Technol. 71 (7) (2011) 946–954.
[26] S.M. George, Atomic layer deposition: an overview, Chem. Rev. 110 (1) (2009) 111–131.
[27] J. Park, J. Huang, J. Yun, F. Liu, Z. Ouyang, H. Sun, C. Yan, K. Sun, K. Kim, J. Seidel, The role of hydrogen from ALD-Al_2O_3 in kesterite Cu_2ZnSnS_4 solar cells: grain surface passivation, Adv. Energy Mater. (2018) 1701940.
[28] R. Singh, R. Bapat, L. Qin, H. Feng, V. Polshettiwar, Atomic layer deposited (ALD) TiO_2 on fibrous nano-silica (KCC-1) for photocatalysis: nanoparticle formation and size quantization effect, ACS Catal. 6 (5) (2016) 2770–2784.
[29] M. Jędrzejewska-Szczerska, P. Wierzba, A.A. Chaaya, M. Bechelany, P. Miele, R. Viter, A. Mazikowski, K. Karpienko, M. Wróbel, ALD thin ZnO layer as an active medium in a fiber-optic Fabry–Perot interferometer, Sens. Actuators A 221 (2015) 88–94.
[30] H.-C. Yoon, J.-H. Shin, H.-S. Park, S.-J. Suh, The properties of Cu thin films on Ru depending on the ALD temperature, J. Nanosci. Nanotechnol. 15 (2) (2015) 1601–1604.
[31] J. Wang, B. Weng, P. Larson, Y. Liu, Synthesis of ZnO nanoarrays on carbon fibers using combined atomic layer deposition and hydrothermal methods, Mater. Res. Express 5 (6) (2018) 065029.
[32] B. Weng, J. Wang, P. Larson, Y. Liu, Growth process optimization of ZnO thin film using atomic layer deposition, Mater. Res. Express 3 (12) (2016) 126402.