***In-situ* pull-off of ZnO nanowire from carbon fiber and improvement of interlaminar toughness of hierarchical ZnO nanowire/carbon fiber hybrid composite laminates**

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ABSTRACT

Zinc oxide (ZnO) has attracted much attention for various applications because of its unique electrical, optical, magnetic and piezoelectric properties. ZnO nanowires (NWs) are often grown onto the carbon fiber (CF) surface to improve the electrical conductivity and flexibility of ZnO, and it is important to understand and further enhance the interaction between ZnO NWs and CFs. Herein, ZnO NWs were grown onto carbon fabrics through a facile hydrothermal method, and the pull-off force to detach an individual ZnO nanowire from CF was measured using a nano-manipulator inside a scanning electron microscope chamber. Also, a novel dopamine-based functionalization method was developed to improve the interfacial adhesion between ZnO NWs and CFs. It was found that introducing polydopamine (PDA) on CF could increase significantly the adhesion strength between CF and ZnO NW and their interfacial shear strength with epoxy as measured by the single fiber microbond test. The hierarchical ZnO NWs on CF fabrics were then utilized to fabricate the laminates. The highest mode I and mode II interlaminar toughness were obtained in those laminates comprising CF/PDA/ZnO NWs owing to the high chemical bonding between ZnO NWs and PDA modified CF surface and strong mechanical interlocking between ZnO NWs and epoxy.

1. Introduction

Because of the unique optical, magnetic and piezoelectric properties, zinc oxide (ZnO) nanostructures, especially ZnO nanowires (ZnO NWs) with large aspect ratios, can be used in a variety of fields such as gas sensors [1,2], solar cells [3-5], light emitting diodes [6,7], dynamic sensors [8] and energy harvesting materials [9,10]. However, the practical application of ZnO is severely limited because of its intrinsically low electrical conductivity and its wide band gap. Thus, ZnO as a photocatalyst could only be excited under UV light. Furthermore, the photo excited electron and its counterpart, namely the hole, are easily recombined, hence significantly decreasing its catalytic efficiency. Many methods including nitrogen doping and hybridization with metal-based or carbon-based nanomaterials have been developed to improve its electrical conductivity and reduce its band gap. It was found that ZnO could be coated on graphene or carbon nanotubes to enhance the photocurrent and photocatalytic efficiency [11]. However, it was difficult to recollect and recycle these ZnO-based hybrid materials. Carbon fiber, which has been widely used in aircraft structures, is a good support for ZnO because carbon fiber not only possesses excellent electrical properties but can also impart flexibility to the final hybrid material [12]. For example, ZnO nanowire-carbon fibre hybrid materials can find applications in high wearable and stretchable supercapacitors, flexible piezoelectric generators and quantum dot-sensitized solar cells [13-15]. Nonetheless, most previous studies were mainly focused on the preparation, multi-functionality and application, and few efforts were devoted to mechanical properties of this hybrid material. In fact, the mechanical behaviour, in particular, the interfacial adhesion strength between ZnO NWs and the carbon fiber, has a vital role for their energy and environment applications. Therefore, if the interfacial adhesion between ZnO NWs and carbon fibers is relatively weak, ZnO NWs may easily fall off the carbon fiber during service, which may degrade the material performance and may even cause material failure. Thus, it is highly important to study the interaction between ZnO NWs and carbon fibers and further reveal the adhesion mechanism that defines the macroscopic properties of the hybrid material and ensure the stability and durability of the hybrid structure. Sodano et al. have studied the interaction between ZnO and graphite [16,17]. They applied a ZnO nanoparticle coated AFM tip close to the surface of highly oriented pyrolytic graphite to investigate the interaction between ZnO and carbon substrate. Although their method can, to some degree, reflect the interaction between ZnO and graphite substrate, it cannot measure the real adhesion force between ZnO and carbon fibers. It is thus desirable to develop a direct and concise method to measure the adhesion force

and adhesion strength between ZnO NWs and CF. Another critical issue for CF/ZnO NWs is the intrinsically poor interfacial adhesion due to the lack of sufficient functional groups on the CF surface which bond with the ZnO. Generally, chemical oxidative techniques, such as acid or plasma treatments, are used to introduce the functional groups onto the CF surface. However, oxidation functionalization can etch the fiber substrate and thus decrease the CF strength, which is undesirable for all applications. Polydopamine (PDA), a mussel-inspired polymer, is well known for its many functional groups, like catechol, amino and imino groups, and can be formed by auto-polymerization from dopamine at a pH value of 8.5. It can adhere strongly to all kinds of material surfaces, either hydrophobic or hydrophilic, through strong covalent and non-covalent bonds and then serve as a versatile platform for secondary reactions [18-20]. Especially, PDA owns a robust chelating capability toward metal ions and can act as nucleation sites to form a metal oxide-PDA core/shell structure. These advantages have drawn great interests for applications in cell adhesion, protein immobilization, bio-mineral formation and nanoparticles stabilization [21-23]. But, studies on ZnO NWs grown on PDA modified CFs have not been previously reported.

In this paper, we propose a novel dopamine-based functionalization method to improve the interfacial adhesion between ZnO NWs and CFs. Carbon fiber was first modified with dopamine, and then ZnO nanowires were grown onto the modified carbon fibers by a facile hydrothermal method. The force to detach an individual ZnO nanowire from CF was measured using a nano-manipulator inside a scanning electron microscope chamber. This is an *in-situ* and direct measurement method for the adhesion force between CF and ZnO NWs. In this way, the adhesion force and interfacial adhesion strength were found to increase by 200% after the CF was modified by PDA. To further evaluate the interfacial performance of the CF/ZnO NWs hybrid materials, single fiber microbond pull-out tests were conducted by embedding the hybrid fibers in epoxy, and it was found that the interfacial shear strength was greatly enhanced for the CF/PDA/ZnO NWs.

CF/ZnO composites can be used to manufacture laminates for aerospace applications since ZnO NWs on CF are similar to z-pinning [24,25] and CNTs grown on CFs [26]. Both techniques have been applied in laminates for toughening but this is often accompanied by some loss of in-plane strength which is undesirable for laminate applications. By contrast, the hierarchical CF/ZnO NWs is prepared at a low temperature without strong acid treatment, thus retaining the

CF strength [27]. Furthermore, the rigid ZnO NWs on CFs in the composite laminates are more effective for improving the toughness compared to those flexible fillers like CNTs because they collapse easily on the CFs during epoxy infusion [26]. However, ZnO NWs are stiff and can maintain their upright geometry during processing, providing strong mechanical interlocks with epoxy matrix [27]. Hence, ZnO NWs on CFs should confer both delamination toughening and through-thickness strengthening to the laminates. Here, in this study, both mode I and mode II interlaminar toughness of CF/ZnO NWs laminates were indeed found to be increased. Further increases in these toughness values were achieved for the CF/PDA/ZnO NWs hybrid laminates due to the enhanced interfacial interaction between ZnO NWs and PDA modified CF.

2. Experimental Work

2.1. Materials

Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, ACS reagent, $\geq 98\%$), sodium hydroxide (NaOH, ACS reagent, $\geq 97.0\%$, pellets), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, reagent grade, 98%), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, ACS reagent, $\geq 99.0\%$), dopamine hydrochloride, ethanol, acetone, and piperidine were purchased from Sigma-Aldrich, Australia. Plain woven PAN-based CF fabrics were obtained from Inter-Turbine Advanced Logistics Pty Ltd and the epoxy matrix used was Araldite-F (diglycidyl ether of bisphenol A, Huntsman).

2.2. Fiber modification and ZnO nanowire growth

Before the growth of ZnO NWs, woven CF fabrics were cut into square swatches ($8 \times 8 \text{ cm}^2$) and then extracted using acetone at 70°C for 48 h to remove the surface sizing and other contaminants. Subsequently, they were placed in a mixed solution containing Tris-buffer solution with a pH of 8.5 (10 mM, 200 mL) and dopamine hydrochloride (0.04 g), and polydopamine (PDA) coated CF fabrics were obtained after 6 h reaction at room temperature. Then, PDA treated CF fabrics were rinsed with distilled water and dried at 100°C for 10 min, which was coded as CF/PDA.

The growth of ZnO NWs on CF fabric consisted of two steps including ZnO seed coating and ZnO NW growth. The first was the formation of a ZnO crystal seed layer on the CF fabric surface. ZnO seed solution was first prepared by dissolving zinc acetate dehydrate (0.11 g) in

200 ml ethanol at 65 °C under vigorous stirring, and at the same time 40 ml ethanol solution containing 0.04 g NaOH was also obtained. The two as-prepared solutions were mixed and diluted to 400 ml by adding ethanol. The PDA treated CF fabrics were dipped in the resultant ZnO colloid solution and annealed at 150 °C for 15 min and dip coating was repeated twice to obtain the ZnO seed layer coated on the CF/PDA. The second step, that is, the ZnO NW growth, was completed in the ZnO growth solution obtained by mixing zinc nitrate hydrate (0.025 M) and hexamethylenetetramine (HMTA) (0.025 M) aqueous solution. ZnO growth was performed in a sealed glass bottle at 95 °C for 4 h in an oven. Finally, the ZnO NWs covered CF fabrics were obtained after rinsing with deionized water and drying at 80 °C, and were coded as CF/PDA/ZnO NWs. The ZnO NWs coated bare CF was coded as CF/ZnO NWs.

2.3. Preparation of ZnO-based CF/EP composite laminates

CF/EP samples used for the interfacial shear strength (IFSS) tests were prepared by dripping epoxy resin droplets onto a carbon fiber monofilament with an embedded length of 60-80 μm , followed by curing the epoxy. The CF/EP composite laminates for double-cantilever-beams (DCB) and three-point end notched flexure (ENF) tests were made of sixteen plies of plain woven carbon fabrics and Araldite F/piperidine with a weight ratio of 20/1 by hand lay-up. Since the crack propagated along the mid-plane of the laminate in both DCB and ENF tests, ZnO NWs grown on CF and CF/PDA fabrics were only inserted into the composite laminate as the 8th and 9th plies, and a 25 μm thick polyimide film was placed in the mid-plane of the laminate as the initial crack. The composite laminates were then sealed in a vacuum bag and vacuumed for 0.75 h, followed by epoxy curing at 120 °C for 16 h under a pressure of 200 kPa. For comparison, composite laminates with no ZnO NWs were also prepared. Hereafter, we refer to these 3 types of CF/EP laminates as: Control, CF/ZnO NWs-CL and CF/PDA/ZnO NWs-CL, respectively, where CL stands for composite laminates.

2.4. Characterization

Fourier transform infrared (FTIR) spectra in the wavelength range 500 to 4000 cm^{-1} were obtained with a Bruker Vertex 80v spectrometer at room temperature. Raman scattering spectra was conducted on a Renishaw Raman Invia Reflex with an excitation wavelength of 514 nm. X-ray diffraction (XRD) patterns of the samples were recorded using a XRD Shimadzu S6000

in the 2θ range 10° to 80° . The surface morphology and elemental composition of the samples were investigated with a scanning electron microscope (Zeiss ULTRA Plus) equipped with an EDS detector. Transmission electron microscope (TEM) images were obtained using a Philips CM120 Biofilter TEM.

In the pull-off test of detaching a ZnO NW from a CF, a nano-manipulator equipped with a force measurement system (FMS) (Kleindiek Nanotechnik) was used; the tests were conducted inside the SEM chamber. The force measurement facility is mainly consisted of an atomic force microscope (AFM) tip, a force sensor and a force export system. The spring constant and length of the AFM tip are 2–4 N/m and 120 μm , respectively, and the force measurement resolution is about 1 nN. Special SEM compatible glue was used to attach the AFM tip onto a ZnO NW, which was uncured under a low imaging current and could rapidly polymerize upon exposure to an electron beam over the area contacting the ZnO NW. Subsequently, the AFM tip was gradually moved away along the direction nearly perpendicular to the CF surface by rotating the nano-manipulator until the NW was detached, during which the pulling force *versus* time curve was *in situ* recorded.

Single fiber tensile testing was conducted on a mechanical universal testing machine (Instron 5500R, USA) based on ASTM D3379-75. At least 60 specimens were tested for each fiber type, and the results were analysed with Weibull's statistics. Moreover, the interfacial shear strength (IFSS) of carbon fibre/epoxy composites was evaluated by the single fiber microbond tests performed on an interfacial strength testing instrument (Tohei Sanyon Co., Ltd, Japan) with a crosshead displacement rate of 0.06 mm/min. The IFSS values were calculated by:

$$\text{IFSS} = F_{\max} / \pi dl \quad (1)$$

where $F_{\max}$ is maximum load, d average carbon fiber diameter, and l embedded length of single filament in epoxy resin.

Double-cantilever-beams (DCB) and three-point end notched flexure (ENF) tests were used to measure mode I and mode II interlaminar fracture toughness on an Instron 5567 machine according to the ASTM D5528 [28] and ESIS protocol [29], respectively. For modes I and II delamination tests, the crack mouth opening displacement rate was set at 2 mm/min, and the

initial crack length was 50 mm and 25 mm, respectively. At least ten samples were measured for each type of the CF/EP laminates: Control, CF/ZnO NWs-CL and CF/PDA/ZnO NWs-CL.

3 RESULTS AND DISCUSSION

3.1. Morphology and characterization of the ZnO NW based CF hybrid materials

Figures 1(a), (b) and (c) show the surface topography of bare CF, CF/PDA and CF/PDA/ZnO NWs, respectively. It can be found the bare CF with a diameter of $\sim 7.5\ \mu\text{m}$ has many intrinsic grooves on its surface, Fig. 1(a), which are fully covered by a thin layer of $\sim 15\ \text{nm}$ thick PDA, inset in TEM image in Fig. 1(b), when the fiber has been treated by polydopamine. The time for dopamine polymerization should be strictly controlled to avoid PDA aggregates formed on the CF. In our work, a smooth PDA layer could be achieved after 6 h. However, many PDA granules would form on the CF surface if the polymerization time was extended to 24 h (Fig. S1(a)), which could undermine the uniformity of subsequent ZnO NW arrays grown on CFs (Fig. S1(b)).

For CF/PDA/ZnO NWs, Fig. 1(c) indicates that uniform ZnO nanowires with vertical alignment are well distributed on the PDA modified CF surface. The CF diameter has been increased to $\sim 11\ \mu\text{m}$ and the ZnO NW length is $1.75\ \mu\text{m}$ with an aspect ratio of 9. By contrast, the CF/ZnO NWs have a similar morphology as that of CF/PDA/ZnO NWs (Fig. S2), which indicates the thin PDA layer does not affect the growth of ZnO NWs. This is because ZnO NW growth begins with the ZnO seed layer adsorbed on CF surface or PDA modified CF surface. As long as ZnO growth is completed under the same processing conditions, nanowires with the same diameter and aspect ratio are obtained.

The formation of the CF/PDA/ZnO NW heterostructure is schematically demonstrated in Fig. 1(d). Dopamine is self-polymerized on the CF surface to form a thin layer of PDA. Specifically, dopamine is first oxidized into dopamine monomers and then polymerized into oligomers by covalent bonds. Subsequently, the oligomer molecules are aggregated into polydopamine through non-covalent bonds (van der Waals forces, H-bonds, and π -stacking) [18,19]. The PDA layer formed has many functional groups including quinone, carboxyl, catechol, amino and imino groups. There exist different kinds of interaction such as coordination and hydrogen bonding between ZnO and PDA. The main interaction, namely, the coordination between the

catechol groups and the Zn^{2+} ion, promotes the gradual formation of a ZnO seed layer, from which the ZnO NWs are nucleated and grow on the PDA modified CF. Finally, the hierarchical CF/PDA/ZnO NWs is obtained.

The XRD patterns of CF and its hybrid materials are shown in Fig. 1(e). The diffraction peak located at 26° in all the curves is assigned to the C(002) plane from the CF. For the CF/PDA, no other peaks are observed presumably due to the low molecular weight of PDA, while many characteristic diffraction peaks appear for CF/PDA/ZnO NWs. The diffraction peaks at 31.8° (100), 34.5° (002), 36.3° (101), 47.6° (102), 56.7° (110), 62.9° (103), 66.4° (200), 68.1° (112) and 69.3° (201) can be indexed to the hexagonal wurtzite ZnO, which are consistent with the values in the standard card (JCPDS 36-1451) [30]. The Raman spectra of the three types of CFs are also given in Fig. 1(f) in which all the samples exhibit two peaks at 1360 and 1590 cm^{-1} , which can be assigned to disordered carbon (D band) and sp^2 hybridized graphite carbon (G band), respectively. It can be found that the intensity ratio of D to G band ($I_{\text{D/G}}$) do not change much, indicating ZnO NWs growth exerts no influence on the graphite structure of CF. However, three new peaks at 326 , 431 and 1140 cm^{-1} are observed in the Raman spectrum of CF/PDA/ZnO NWs. The peaks near 330 and 1130 cm^{-1} are due to the multiple-phonon scattering processes of ZnO and the band located at 431 cm^{-1} is assigned to the E2 (high) mode, which is the characteristic peak of the hexagonal wurtzite phase [31]. In addition, compared with PDA modified CF, the G band showed a shift of 11 cm^{-1} in the CF/PDA/ZnO NWs, which could be attributed to the chemical interaction between ZnO and PDA modified CF [32]. Fig. 1(g) shows the FTIR spectra of the three fiber samples. For CF, only the characteristic peak of aromatic C-C stretching vibration appears at 1623 cm^{-1} . The new absorption peak at 1513 cm^{-1} , attributed to the N-H shearing vibration, can be observed on the PDA coated CF and CF/PDA/ZnO NWs. Additionally, these two surfaces have a broad peak in the range $3100\text{-}3600\text{ cm}^{-1}$, which could be ascribed to the aromatic protons, $-\text{NH}_2$, $-\text{NH}-$ and $-\text{OH}$ group stretching vibrations resulting from the PDA layer on CF. It is also worth noting that the hydroxyl groups of PDA molecules show a broad absorption band with a peak located at about 3466 cm^{-1} for CF/PDA, while it is shifted to 3480 cm^{-1} for CF/PDA/ZnO NWs. Furthermore, the band at 1656 cm^{-1} for CF/PDA attributed to the stretching vibration of aromatic rings in PDA is moved to 1648 cm^{-1} for the CF/PDA/ZnO NWs. These shifts may suggest possible interaction such as coordination between ZnO and the PDA layer on CF. Based on the data of the XRD, Raman and FTIR, both PDA modification and ZnO growth do not change the graphite structure of CF, while the

characteristic peak shifts in these spectra elucidate the interactions among CF, PDA and ZnO NWs.

Fig. 1 (a) SEM images of a pristine CF; (b) PDA treated CF (Insert: TEM image of PDA coated CF); (c) CF/PDA/ZnO NWs; and (d) mechanism of CF/PDA/ZnO NW hierarchical structure formation. (e), (f) and (g) XRD, Raman and FTIR spectra of CF, CF/PDA and CF/PDA/ZnO NW, respectively.

3.2. In-situ pull-off of ZnO NW from CF

As mentioned earlier, the pull-off force of ZnO NW from CF was measured by a nano-manipulator equipped with a sensitive force measurement system inside the SEM chamber. For CF covered with full ZnO NWs, it is difficult to find an attaching point to connect the AFM tip with the top end of one ZnO NW. Thus, the concentrations of the ZnO seed and growth solution were carefully controlled to obtain a relatively sparse distribution of the ZnO NW on CF. Fig. 2(a) depicts the pull-off of an individual NW from a CF substrate using an AFM tip. The ZnO-

based CF hybrid was fixed on a Cu holder, and one end of the NW was grown on the CF while the other end was adhered to the AFM tip by curing of the SEM compatible glue under the high electron beam. Upon an applied pulling force, the AFM tip together with the ZnO NW gradually moved away from the CF. After several tens of seconds, the ZnO NW was completely detached from the carbon fiber.

Fig. 2 (a) Schematic illustration of pulling off individual ZnO NW from CF by using an AFM tip; (b) F/A (i.e., pull-off force divided by contact area) *versus* time during the pull-off process. (c, d) SEM images of pull-off of a ZnO NW on CF surface.

The adhesive stress between bare CF or PDA-modified CF and ZnO NW can be determined from typical records of applied pulling force F divided by contact area A_c (i.e., F/A_c , where A_c is πR^2 and R is contact radius or half ZnO NW diameter) as a function of time, Fig. 2(b). When the tip is moved away from the CF, F/A_c exhibits a monotonously increasing trend for both cases and reaches a peak, followed by a precipitous drop to zero. The pulling force at the peak is the pull-off force (i.e., adhesion force $F_{\text{pull-off}}$) between ZnO NW and bare or PDA-modified CFs, and the adhesion strength σ is given by:

$$\sigma = F_{\text{pull-off}}/A_C \quad (2)$$

Table 1 Pull-off (adhesion) force, theoretical vdW force and adhesion strength between (a) ZnO NW and CF, and (b) ZnO and PDA-modified CF of hierarchical CFs.

Hierarchical CFs	d_{ZnO} (nm)	$F_{\text{pull-off}}$ (μN)	F_{vdw} (μN)	σ (MPa)
CF/ZnO	300	1.65 $\pm$ 0.3	1.99	23.32 $\pm$ 4.56
CF/ZnO	500	4.4 $\pm$ 0.43	5.53	22.41 $\pm$ 5.66
CF/ZnO	700	8.7 $\pm$ 0.55	10.84	22.61 $\pm$ 3.68
CF/PDA/ZnO	300	4.2 $\pm$ 0.89	-	59.41 $\pm$ 5.32
CF/PDA/ZnO	500	12.25 $\pm$ 1.25	-	62.38 $\pm$ 6.33
CF/PDA/ZnO	700	27.5 $\pm$ 1.75	-	71.45 $\pm$ 8.54

NB: d_{ZnO} : diameter of ZnO NW; $F_{\text{pull-off}}$: measured maximum pulling force ; F_{vdw} : predicted vdW force; σ : adhesion strength.

Table 1 summarizes the calculated adhesion strengths σ between bare or PDA-modified CFs and ZnO NWs with diameters (d_{ZnO}) of 300, 500 and 700 nm. For a given ZnO NW of same diameter, the pull-off force $F_{\text{pull-off}}$ between PDA-modified CF and ZnO NW is much larger than that between CF and ZnO, exhibiting an $\sim 200\%$ improvement. Similar increase for the adhesion strength σ is also observed due to the similar A_C for bare CF and PDA-modified CF. However, for given CFs or PDA/CFs, σ for ZnO NWs of different sizes are close to each other, implying the intrinsic nature of the adhesion is identical, regardless of the size of the ZnO NWs, but is dependent on whether the CF is bare or PDA coated.

It is known that the adhesion force stems from the van der Waals (vdW) attraction, electrostatic forces or chemical bonding, etc. To clarify the nature (either physical absorption or chemical bonding) of the adhesion force under the two different circumstances, the sole

contribution of vdW force is separately isolated from the total adhesion by theoretical prediction using Hamaker's approach. Since the growth orientation of ZnO nanowire with diameter of several hundred nanometers is almost perpendicular to the axial direction of the CF with diameter in several micrometers, thus it can be considered as "point" contact (as compared to line contact). According to the Hamaker approach [33], the vdW attraction force F_{vdW} between one ZnO NW and CF at equilibrium separation D_0 is given by:

$$F_{vdW} = -(Ad_{ZnO}^2)/24D_0^3 \quad (3)$$

where A is Hamaker's constant and d_{ZnO} ZnO NW diameter (detailed derivation given in Supporting Information). Equilibrium separation $D_0 \approx 4.0 \text{ \AA}$, which is slightly larger than one diameter of carbon atom ($3.851 \text{ \AA}$) [34], will be used in evaluating the contribution of vdW attraction to the interfacial force at equilibrium. Calculations from recent density functional theory (DFT) also support this assumption albeit it is based on another but similar system (i.e., ZnO-BN system) [35]. The theoretical van der Waals force between a 300 nm ZnO NW and CF was calculated to be $9.8 \text{ \mu N}$ based on Hamaker's constant of $A_{ZnO-CF} = 1.673 \times 10^{-19} \text{ J}$, which is much larger than $1.65 \text{ \mu N}$ recorded. This may be during the hydrothermal growth of ZnO on CF, small organic molecules, such as water and/or ethanol, are trapped between them, greatly affecting the interfacial strength. Similar phenomenon has already been observed and reported for other material systems [36, 37]. Since both water and ethanol have almost identical Hamaker constants and water molecules are more likely to remain during the pull-off tests in vacuum, the Hamaker constant of water [$A = 4.0 \times 10^{-20} \text{ J}$] is used. Thus, the re-calculated vdW attractions compare well to those measured pull-off forces between ZnO NW and bare CF (Table 1). This indicates that vdW forces dominate the adhesion force and there is little or no chemical bonding between ZnO and bare CF, which is consistent with the inert (i.e., de-sized) surface of the CF substrate. In contrast, apart from vdW attraction, chemical bonding between PDA film and ZnO seed layer is believed to have contributed to the enhancement of adhesion force between ZnO NW and PDA-modified CFs. It is worth noting that the contribution of electrostatic force or that of the dopamine film vdW attraction to the total adhesion between PDA-modified CF and ZnO NW is almost negligible. This is because the PDA film is relatively thin compared to CF and Hamaker's constants of organic small molecules are typically around $4 \sim 5 \times 10^{-20} \text{ J}$ [38] are one order less than $2.8 \times 10^{-19} \text{ J}$ of CFs. In addition, there are no special treatments to introduce

opposite charges on the individual surfaces of ZnO NWs and CFs for electrostatic assembly [17].

It is well known that the functional groups, such as -NH_2 and -OH , in PDA can covalently or non-covalently interact with various kinds of surfaces. In particular, the catechol groups in PDA can act as good ligands and form metal-ligand complex due to the coordination bonding between catechols in PDA and the transition metal ions (e.g., Fe^{3+} , Zn^{2+}) [39]. Conversely, the interaction between ZnO and the functional groups on CF/PDA was controlled by the ZnO crystal structure. The ZnO synthesized in our study is an ionic material possessing a wurtzite structure, in which the electrostatic interactions between zinc and oxygen ions are dominant for interatomic bonding. It is known that there exist high energy and unstable polar surfaces in the wurtzite structure, which tend to lower the surface energy by either/both molecular adsorption or/and chemical interaction depending on the facet and the surrounding. Apart from the polar surfaces, the wurtzite structure is also terminated by the non-polar (1010) plane, which is tilted with oxygen atoms outside the surface, indicating the potential formation of hydrogen bonding with surrounding molecules [40-42]. Here, in our work, the strong inter-molecular interactions between PDA and ZnO NW may stem from both polar and non-polar surfaces interacting with the surrounding molecules. It is also believed that during the seeding process, owing to the coordination reaction between the catechol group and Zn^{2+} ion, the ZnO seed layer was tightly bound to the PDA modified CF substrate, which provided a good base for subsequent formation of ZnO nanowires.

3.3 Interfacial properties of ZnO NW based CF hybrid materials

The interfacial properties can also be further evaluated through single fiber microbond tests by embedding CF, CF/PDA, CF/ZnO and CF/PDA/ZnO fibers of length l and diameter d in epoxy, Fig. 3(a). A single fiber with several cured epoxy droplets was placed between two metal blades of the interfacial strength testing instrument. At the start, one epoxy droplet was pushed by two metal blades until the CF was fully debonded at a peak force F_{max} and subsequently pulled out from the epoxy matrix. The test can be repeated on other droplets on the same fiber. Fig. 3(b) shows the interfacial shear strengths (IFSS) for the four types of CF/EP composites. Average IFSS of bare CF/EP is 58.15 MPa and increases to 85.56 MPa after ZnO growth. This improvement could be attributed to the mechanical interlock caused by the penetration of stiff

ZnO NWs into the epoxy yielding an increased bonding area. However, the interaction between ZnO NW and CF, mainly van der Waals forces, is relatively weak. Previous results showed that failure during the microbond experiments generally occurred at the ZnO NWs/fiber interface [43, 44]. In our tests, no ZnO NWs were found on the debonded surface of the pulled out CF, Fig. 3(c), suggesting that all ZnO NWs were sheared off from the CF and embedded within the epoxy droplet so that failure occurred at the CF/ZnO interface, which limited further increase of the IFSS (see EDS results for the area within the yellow rectangle).

Fig. 3 (a) Single fiber microbond pull out test. (b) Effect of functionalization and ZnO NWs on tensile strength of fibers and interfacial shear strength of composite laminates. (c) and (d) Debonded surface of CF/ZnO NWs and CF/PDA/ZnO NWs, respectively, during the microbond pull-out test.

From the discussion in Section 3.2, PDA modification is an effective way to improve the interaction between ZnO NWs and CF. As shown in Fig. 3(b), the IFSS increases by ~20% after the CF is modified by PDA compared to bare CF since many functional groups on the CF/PDA surface promote wetting of epoxy on CF and thus the interaction between epoxy and CF. **The PDA layer can still be observed on the debonded surface (see red rectangles in Fig. S3).** Hence, interfacial failure occurred at the PDA-epoxy interface. The IFSS is significantly increased to

95.32 MPa for CF/PDA/ZnO/EP (i.e., ~23 and ~10% better than CF/PDA/EP (73.0 MPa) and CF/ZnO/EP (85.56 MPa), respectively) arising from the much improved interaction between ZnO and CF due to the formation of chemical bonding between the PDA layer and ZnO NWs. Since the chemical bonding between PDA modified CFs and ZnO NWs is stronger than the van der Waals interactions between the de-sized CFs and ZnO NWs with epoxy, CF/PDA/ZnO/EP therefore has the highest IFSS. Fig. 3(d) shows the surface morphology of CF/PDA/ZnO NWs debonded from epoxy, and some epoxy fragments and ZnO NWs can be found on the debonded fiber area (see red and yellow rectangles and EDS results). Even though most ZnO NWs were sheared off from the CF (and this explains why the improvement in IFSS is not much more than CF/ZnO and CF/PDA), introduction of the PDA layer increases the interfacial interaction and thus the shearing force and the IFSS.

Fig. 3(b) also shows the effects of PDA modification and ZnO growth on the tensile strength of CFs. It is clear that such treatments do not produce any strength degradation as the processing was completed in a mild environment and no use of any strong oxidizing agent. This is very different to some similar whiskerization methods, such as *in situ* growth of CNTs onto CFs, which can severely reduce fibre tensile strength caused by the CF exposure to the catalyst and chemical vapour deposition environment [44]. In our study, the bare CF, CF/PDA, CF/ZnO and CF/PDA/ZnO fibers have practically the same average tensile strength of 3.43-3.44 GPa. The Weibull moduli for all the fibers are 5.02, 4.54, 4.85 and 4.24, respectively.

3.4 Interlaminar fracture toughness of CF/EP composite laminates with CF/ZnO and CF/PDA/ZnO hierarchical fibers

Rigid ZnO NWs in composite laminates are more effective for improving fracture toughness than the flexible fillers like carbon nanotubes since they collapse easily on the fiber during the epoxy infusion process [26]. By contrast, ZnO NWs are stiff and can maintain their shape and property, and therefore can interlock strongly with epoxy in the composite laminates [27]. Here, the interlaminar fracture toughness of the composite laminates was studied and the DCB results are shown in Fig. 4(a). G_{IC} for the Control is 0.49 kJ/m² and this is enhanced by 43% and 63% for CF/ZnO NWs-CL and CF/PDA/ZnO NWs-CL, respectively. G_{IIIC} for the three types of laminates are also given in Fig. 4(b), which are 1.40, 1.61 and 1.71 kJ/m² for the Control,

CF/ZnO NWs-CL and CF/PDA/ZnO NWs-CL, respectively, exhibiting 15% and 22% increases relative to the Control.

Fig. 4(a) G_{IC} and (b) G_{IIC} of three types of CF/EP composite laminates.

To examine the toughening mechanisms in mode I, SEM images of fracture surfaces of all three CF/EP laminates are shown in Fig. 5. Clearly debonded carbon fibers can be found in the Control laminate, which indicates poor adhesion of un-sized CFs on epoxy (Fig. 5(a, b)). However, the fracture surfaces with CF/ZnO NWs show both fiber/epoxy interface adhesive failure (see blue rectangle in Fig. 5(c)) and matrix cohesive failure (see yellow rectangle in Fig. 5(c)). In this case, good wetting and mechanical interlocking make the ZnO NWs/epoxy interface stronger than the CF/ZnO NWs interface, as evidenced in Fig. 5(d). During the DCB test, some ZnO NWs with epoxy are fully debonded from the CF surface (see red rectangle in Fig. 5(d)). Hence, consistent with the single fiber microbond pull-out tests, failure largely occurs at the CF/ZnO NWs interface. The enhanced toughness mainly comes from the large matrix deformation induced by the ZnO NWs (see Fig. 5(d)). While most ZnO NWs are peeled off during crack growth, they also dissipate energy contributing to the increased interlaminar toughness.

Different to the Control and CF/ZnO laminates, the fracture surface for the CF/PDA/ZnO NWs-CL is mostly covered by epoxy (see Fig. 5(e)), indicating that the failure is mainly dominated by cohesive failure of the matrix. It can be found that some ZnO NWs are still tightly attached on the CF surface (see red rectangle in Fig. 5(f)). Besides, some NWs are also peeled off the CFs, but the difference with the CF/ZnO NWs-CL case is that all the NW roots remain on CF surface (see green circle in Fig. 5(f) and EDS result). This morphology indicates that the ZnO NWs are not directly peeled off from the CF during crack propagation like in the CF/ZnO

NWs-CL case; there is stronger interaction between the PDA coated carbon fibers and ZnO NWs in CF/PDA/ZnO NWs-CL. For CF/ZnO NWs-CL, the crack can easily go along the interface between ZnO and CF, corresponding to the adhesive failure observed. However, good interfacial bonding between PDA modified CFs and ZnO NWs causes cohesive rather than adhesive failure during crack propagation in CF/PDA/ZnO NWs-CL. ZnO NWs strongly bonded on CF can serve as pin-like materials, toughening by a crack-wake bridging mechanism that involves them spanning across the matrix crack and thereby increase the mode I interlaminar fracture toughness. Also, high matrix deformation can be found between CF bundles. All these mechanisms contribute to the highest G_{IC} of 0.80 kJ/m^2 compared with that of the Control and CF/ZnO NWs-CL.

Fig. 5 SEM images of mode I fracture surfaces of composite laminates for (a,b) Control; (c,d) CF/ZnO NWs-CL; and (e,f) CF/PDA/ZnO NWs-CL.

The toughening mechanisms for mode II fracture are also analysed and Fig. 6 shows shear fracture surfaces. The Control laminates possess clean fiber surfaces indicating predominant adhesive failure has occurred (see Fig. 6(a)). Characteristic matrix hackles between CFs are noticeable (see Fig. 6(b)). For CF/ZnO NWs-CL, denser hackles arising from larger matrix shear deformation are clearly visible due to the presence of the ZnO NWs (see yellow and red rectangles in Fig. 6(c)). Between CFs, failure of ZnO NWs toughened epoxy matrix with obviously pulled out nanowires (see green rectangle in Fig. 6(d)) is displayed providing another source of toughness. However, the failure is still largely “adhesive” since most ZnO NWs are sheared off during crack growth, and thus the increase in G_{IIc} is moderate. In CF/PDA/ZnO NWs-CL, a combined “adhesive” and “cohesive” mode of failure (see blue rectangle in Fig. 6(e)) and matrix shear hackles (see yellow rectangle in Fig. 6(e)) are observed. Within the region bordered by the blue rectangle in Fig. 6(f), these features are prominently illustrated. Areas marked “1” are epoxy shear matrix hackles, “2” is layer of PDA/ZnO-NWs, “3” is adhesively debonded CF from PDA/ZnO-NWs layer, and “4” is cohesively failed matrix with pulled out ZnO-NWs (see inset next to the left corner of blue rectangle in Fig. 6(f)).

Fig. 6. SEM images of mode II fracture surfaces of composite laminates for (a, b) Control; (c, d) CF/ZnO NWs-CL; and (e, f) CF/PDA/ZnO NWs-CL.

4. Conclusion

A dopamine functionalization method was developed to produce a PDA layer on the CF surface. ZnO nanowires were then grown on the PDA modified CF through a hydrothermal method to obtain a hierarchical ZnO nanowire/carbon fiber hybrid. This hybrid had a thin PDA layer with a thickness of 15 nm and vertically aligned ZnO NWs with a length of 1.75 μm and

an aspect ratio of 9. *In situ* pull-off experiments of a single ZnO NW from the CF demonstrated that the PDA functionalization on the fiber surface was critical for the strong chemical adhesion of the ZnO nanowires with the CF substrate caused by the coordination reaction between the catechol groups and Zn^{2+} ion, which yielded a 200% increase in pull-off force and adhesion strength compared to bare CF/ZnO NWs. The interfacial shear strength was also increased by 64% after the growth of ZnO NWs on the PDA modified CF. It was noteworthy that PDA modification and ZnO NWs growth did not degrade the CF strength. Furthermore, both mode I and mode II interlaminar toughness were increased for CF/ZnO NWs-CL and CF/PDA/ZnO NWs-CL. In particular, for the latter laminates, the improvements were 63% for mode I and 22% for mode II due to the strong chemical bonding between PDA modified CF and ZnO NWs as well as the mechanical interlocking between ZnO NWs and epoxy.

Supporting Information

The Supporting Information contains SEM images of CF after dopamine treatment and CF/ZnO NWs; Hamaker prediction of van der Waals force; Debonded surface of CF and CF/PDA during the microbond pull-out test.

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