Simple synthesis process for ZnO sphere-decorated CNT fiber and its electrical, optical, thermal, and mechanical properties

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An easy process to produce ZnO sphere-decorated CNT (ZSDC) fibers was established. The prepared ZSDC fibers showed aggregated ZnO nanoparticles deposited homogenously as spheres on the CNT fiber surfaces and non-aggregated ZnO nanoparticles invading the inside of the fiber and occupying the gaps among the individual CNTs. The ZnO nanoparticles inside the fiber acted as cross linkers of the individual CNTs by chemical bonding, which improved the Young’s modulus and tensile strength of the ZSDC fiber by 340% and 60%, respectively, when compared with bare CNT fiber. The ZSDC fiber exhibited superior light absorption properties throughout the entire region of the visible to near-IR (NIR) spectrum (400–2100 nm) as well as higher thermal stability at 880 °C in a nitrogen environment compared to the bare CNT fiber. In addition, the composite fiber showed very high electrical conductivity (983 S cm⁻¹). This high electrical conductivity suggests that electron movement through the fiber is not hampered by the semi-conductive ZnO nanoparticles. A unique high intensity radial breathing mode (RBM) peak was observed in the Raman spectrum of the ZSDC fiber, whereas the bare CNT fiber did not show a RBM peak. This RBM peak of the ZSDC fiber indicates that there is a special arrangement of ZnO nanoparticles caused by chemical bonding that generates this RBM mode of the CNT fiber in ZSDC.

1. Introduction

Fiber-shaped materials and their devices, such as supercapacitors and photovoltaic cells, have attracted increasing attention. Many fibers have been utilized as the substrates for a range of devices. Polymer fibers have been one of the most notable innovations for the advance of flexible devices owing to their low cost, light weight and high flexibility. High conducting metal wires are generally employed instead of polymers to develop electronic devices because of the insulating behavior or truncated electrical conductivity of polymers. However, metal wires are not compatible with the current weaving technology used to produce textile formats, owing to their higher weight and lower flexibility; lower weight, higher strength and higher flexibility are required to shape the fiber in a textile.

Superior mechanical properties, superb electrical conductivity and exceptional flexibility have made CNT fibers a good candidate for fiber-shaped devices. Furthermore, both well-known spinning methods (dry and wet) can be used to spin this low density and highly conductive material into extended lengths. The main problem impeding their electronic application is that CNT fibers have comparatively low electrocatalytic behavior. As a result, fiber-shaped devices fabricated from these low electrocatalytic CNT fibers have low photoelectric conversion efficiencies (PCE) and low energy storage efficiencies. To improve the electrochemical and optical properties of CNT fibers, semi-conductive metal oxides or novel metal nanoparticles are required. To harness the significant electronic, optical and electrochemical properties of CNT fibers, the homogeneous deposition of nanoparticles on a large scale is essential. Many specialized techniques, e.g., functionalization, pretreatment, oxidation, the use of surfactant, and unusual fabrication processes are used. Moreover, graphene is used as a third phase for the large scale homogeneous deposition of nanoparticles as a second phase, even though smooth deposition is not achieved in many cases. Normally, nanoparticles deposit randomly on a CNT fiber surface. Thus the homogeneous deposition of nanoparticles on individual CNTs or CNT fiber surfaces is also a challenge. Sometimes, homogeneous deposition occurs but appropriate electrical conductivity is not achieved. Smooth deposition and high electrical conductivity are both required. Semi-conductive metal oxide deposition reduces the electrical conductivity of CNT fibers considerably. Therefore, it would be an exciting step forward if the electrical conductivity of a CNT-semiconductor composite could be preserved at a similar level to that of a bare CNT fiber. To achieve this, well-developed processes are
needed to prepare CNT-semi-conductive nanoparticles with high electrical conductivity, similar to that of the bare CNT fiber, as well as improved mechanical properties and electrochemical properties.

ZnO exhibits robust photo-induced hole oxidation ability and displays electron mobility that is nearly two orders of magnitude higher than that of TiO2 (ref. 46) because enhanced photo-generated electron movement can be achieved by a higher electron mobility. On the other hand, the recombination of photo-generated electrons and holes can be hindered by a higher electron mobility. As a result, these behaviors lead to an improved charge carrier life time,46 which is very important for photovoltaic and photocatalysis applications (fuel cells and degradation). ZnO is a very useful material for many applications, such as solar cells,47 photocatalysis (water splitting and degradation),48–54 photoluminescence,55 LEDs,56 and light absorbance improvement.57 In addition, it is economical and environmentally friendly.

Considering the above issues, ZnO was considered as a semi-conductive58 material for deposition on CNT fiber surfaces to prepare a ZSDC fiber composite. The prepared composite shows an excellent Young’s modulus (21 GPa), which is 4 times higher than that of the bare CNT fiber, and a very good tensile strength compared to the bare CNT fiber. The experimental results suggest that ZnO nanoparticles play significant roles in improving the mechanical properties of CNT fibers through chemical reactions with the existing functional groups of individual CNTs in a fiber. This is a new finding and the first utilization of ZnO nanoparticles to improve the mechanical properties of CNT fibers. This strong interaction by chemical bonding is also helpful in minimizing the insulating behavior of ZnO and maintaining the high electrical conductivity (983 S cm−1) of ZSDC fibers, similar to that of bare CNT fibers, and higher than that of CNT–novel metal nanoparticle composites (CNT–Pt,45,59 CNT–Ag59 and CNT–PDMS60 fiber. The new RBM peak of the ZSDC fiber gives new insight into the chemical bonding between ZnO nanoparticles and individual CNTs in ZSDC fiber composites. This paper proposes a logical vibrational optical mode of ZnO, which generates the RBM of the CNT fiber in the ZSDC fiber. No specialized costly and complex techniques for oxidation, functionalization or pretreatment are used to smooth the deposited ZnO spheres on the CNT fibers. Finally, the as-prepared ZSDC fiber composite shows dramatic improvement in the light absorption properties from the visible to the NIR region (400–2100 nm) and very good thermal stability at high temperatures.

2. Experimental work

2.1 Chemicals

ZnO nanoparticles and the aggregated spheres were prepared on a CNT fiber surface from zinc acetate dihydrate (99%, Sigma-Aldrich). Zinc acetate dihydrate was dissolved in ethanol (95%, Duksan, Korea). An electrical conductive circuit of the CNT fiber was prepared to measure the electrical conductivity by a gold wire (0.05 mm diameter, code 171105, Nilaco Corporation, Japan) and silver paste (Leit Silver, Sigma-Aldrich). Acetone (99.5%, Daejung Chemicals and Metals, Korea), ferrocene (98%, Sigma-Aldrich) and thiophene (99%, Sigma-Aldrich) were used to synthesize the CNT fiber. Densification of the CNT fiber was performed by dimethyl sulfoxide (DMSO, 99.5%, Sigma-Aldrich).

2.2 Instrumentation

A bath sonicator was used for sonication to prepare the zinc acetate solution. A Keithley four point probe (2400 Source Meter and 2000 MULTIMETER) was used to measure the electrical conductivity of the CNT fiber and the ZSDC fiber composite. The morphology of the materials was checked by field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan) and the crystallinity was checked by X-ray diffraction (XRD, thin film, MPD, PANalytical). The light absorption properties were measured using an ultraviolet/visible/near-infrared spectrophotometer (UV/VIS/NIR, Cary-5000, Agilent). Vibrational characterization was performed by Raman spectroscopy (HORIBA JOBIN YVON, Lab RAM HR, Laser 514.54). Chemical interactions were determined by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, USA). A universal testing machine (UTM 4464, INSTRON, USA) was used to measure the tensile strength and modulus of elasticity of the CNT fiber and its ZSDC fiber composite. A focused ion beam (FIB) was applied to cut the prepared composite fiber (HELIOS NANOLAB 650, FEI company, USA). Energy dispersive X-ray spectroscopy (EDX, EDAX, OXFORD, BRUKERS) was utilized for elemental analysis.

2.3 CNT fiber synthesis

CNT fibers were prepared using the method reported elsewhere using a liquid feedstock. Acetone, ferrocene (0.2 wt%) and thiophene (0.8 wt%) were injected into a chemical vapor deposition (CVD) furnace that had been pre-heated to 1200 °C.61 Acetone, ferrocene and thiophene were used as the carbon source, catalyst and promoter, respectively. These injected three materials are known as liquid feedstock. The carrier gas flow to the CVD furnace was kept at 1000 sccm.61 The prepared continuous CNT array was passed through water by inclining it into the water tank. Finally, it was coiled to a collector at a rate of 5 m min−1. Dimethyl sulfoxide (DMSO) was used as a densification agent and the sample was dried at 100 °C.

2.4 ZSDC fiber preparation

Zinc acetate dihydrate (2.5 g) was sonicated for 70 min in 45 mL of ethanol at room temperature to obtain a clear homogeneous solution. A steel wire frame was used to mount the CNT fiber. The mounted CNT fiber was placed into a glass Petri dish. The prepared zinc acetate solution in ethanol was transferred gently into the Petri dish using a plastic dropper. The mounted CNT fiber was kept in the zinc acetate solution for 3 to 5 min. The fiber was then removed and shaken by striking the steel frame on a table. Note that it was necessary to avoid touching the zinc acetate soaked CNT fiber during the striking process. Striking was performed to prepare droplets of zinc acetate on the CNT fiber. These struck CNT fibers were dried in a preheated furnace.
2.5 Purification of the CNT fiber

A glass slide was used to mount the CNT fiber. This was placed in a furnace for 40 min at 400 °C to oxidize any metal particles. After heating, the fiber was cooled to room temperature and dipped in concentrated HCl. The dipped CNT fiber mounted on the glass slide was boiled at 80 °C for 4 h to remove any metal impurities as metal chloride. The slide was then removed and washed several times with DI water to eliminate the metal impurities.
impurities and HCl. Finally, it was again placed in a furnace and heated at 400 °C for 40 min.

3. Results and Discussion

3.1 Characterization of the ZSDC fiber

Fig. 1a presents FESEM images of many ZSDC fibers on a silicone substrate. Step-by-step high resolution FESEM images were taken to show the real features of the ZnO nanoparticles on the CNT fiber surfaces. For example, Fig. 1b was taken from the big rectangular area in Fig. 1a. Fig. 1c was taken from the smaller rectangular area in Fig. 1a. Fig. 1d was taken from the rectangular area in Fig. 1b. Similarly, Fig. 1f shows the rectangular marked area of Fig. 1d. Fig. 1a, b and d show a smooth layer of ZnO nanoparticles on the CNT fiber surface. The high resolution FESEM image of this smooth layer (Fig. 1f) reveals non-individual ZnO nanoparticles aggregating into spheres. Therefore, spheres of ZnO nanoparticles are the building blocks of the deposited smooth layer on the surface of the CNT fiber. To obtain a clearer understanding, high resolution FESEM images (Fig. 1e, g and h) were obtained from different parts of Fig. 1c. These also exhibited the same sphere shape morphology as shown in Fig. 1f. Fig. 1g and h display sphere sizes of 150 to 300 nm on the CNT fiber surface with about 70% of the spheres measuring around 250 nm. Fig. 2 presents a schematic diagram of the total synthesis process for the ZSDC fiber. The raw CNT fibers (Fig. 2a) were covered with a zinc acetate solution (Fig. 2b). Subsequently, the fiber was struck to prepare droplets of zinc acetate on the CNT fiber surface (Fig. 2c) and heated in a preheated furnace at 165 °C for 3 min. Finally, the fibers (Fig. 2c) were again heated to 470 °C over 30 min to prepare the ZSDC fiber (Fig. 2d).

The CNT and ZSDC fibers were placed on a silicone substrate and their XRD patterns were obtained, as shown in Fig. 3. Fig. 3b shows the peaks of the CNT fiber at 18.28° 2θ and 25.12° 2θ. The peak at 25.12° 2θ was assigned to crystalline carbon and that at 18.28° 2θ was assigned to the higher d-spaced low crystalline carbon of the CNT fiber. Owing to the oxygen-containing functional groups, the peak for the low crystalline carbon was observed at a higher d-spaced position. The other peaks in Fig. 3b, which are marked by the black stars, were attributed to the silicon substrate. These are also shown in Fig. 3a. Fig. 3c shows the carbon peaks at 15.92° 2θ and 25.12° 2θ for the ZSDC fiber. It also shows the ZnO peaks at different positions for the different planes. All the ZnO peaks of Fig. 3c are similar to the peaks in the XRD pattern of bare ZnO (Fig. 3d). These peak positions of ZnO suggest a hexagonal wurtzite ZnO structure (JCPDS no. 01-075-0576). Fig. 3c indicates 100 (31.0), 002 (33.7), 101 (35.5), 102 (46.8), 110 (55.9), 103 (62.2), and 203 (89.02) planes for ZnO in the ZSDC fiber but the other peaks for the 200 (65.7), 112 (67.3), 201 (68.4), 004 (71.9), 202 (76.32), and 104 (80.76) planes were not observed owing to the high intensity peak of the Si-substrate in the same region. The peaks at 9 to 30° 2θ in Fig. 3a–d were magnified, as shown in Fig. 3e. The CNT fiber peak at 18.28° 2θ was shifted to 15.92° 2θ in the case of the ZSDC fiber. This suggests that the ZnO nanoparticle strongly interacts with the functional group of the low crystalline carbon of the CNT fiber either by chemical bonding or by a simple interaction, such as Zn–C, Zn–O–CNT, Zn–OOC–CNT or all of these.

Raman spectroscopy (Fig. 4) of the CNT and ZSDC fibers was performed to understand the interaction of ZnO nanoparticles with the CNT fiber and their defects, through their different vibration modes. The D-bands of the CNT fiber (Fig. 4a) express the structural defects of the CNT fiber, which may be due to the presence of oxygen-containing functional groups and the lack of a conjugation system in the carbon honeycomb structure. XRD showed that the carbon honeycomb system has defects. The peaks at 96.04, 429.25 and 560.8 were assigned to the E2 (low), E2 (high) and A1-LO (longitudinal optical) phonon peaks of the ZnO nanoparticles of the ZSDC fiber composite, respectively. Fig. 4b presents the spectrum between 50 and 700 cm⁻¹. The peak at 221.4 cm⁻¹ indicates the second-order Raman spectrum arising from the zone boundary (M point) phonon 2E2(M). The position of this peak was at a slightly higher frequency position. Indeed, it is normally found in the 205 (ref. 63) to 208 (ref. 66) cm⁻¹ region but for the ZSDC fiber system (curve-c of Fig. 4a and b), this peak was observed at a higher

![Fig. 2](image-url) Schematic diagram of ZSDC fiber synthesis: (a) CNT fiber, (b) CNT fiber covered with zinc acetate, (c) zinc acetate droplets on the CNT fiber surfaces, and (d) ZSDC fiber, in which zinc acetate droplets are converted to ZnO nanospheres on the CNT fiber surfaces.
frequency owing to the 2-E$_2$(M) peak for bare ZnO occurring at higher frequency. The peak at 322.2 (ref. 66) was assigned to multiple phonon scattering and the A1-LO phonon. Here, the 560.08 peak was also observed at a different position instead of its normal position (574 (ref. 64), 576 (ref. 63) and 579 (ref. 67 and 68)). The shift of this peak to a lower frequency (560.8) also revealed the strong interaction between the carbon of the CNT and the ZnO nanoparticles. The position of the 560.8 (A1-LO) peak was close to the theoretical value, 548.$^a$ The 181.6 peak accounted for the RBM of CNTs in the ZSDC fiber although it was not observed in the raw CNTs (curve-b of Fig. 4a and b). The prepared CNT was multi-walled$^a$ and, generally, the RBM peak is not observed for multi-walled CNTs. Interestingly, the RBM mode was due to the participation of ZnO nanoparticles with CNTs in the ZSDC fiber which suggests that there might be chemical bonding between ZnO nanoparticles and the CNT. The vibrational mode of the chemically-bonded ZnO nanoparticles in ZSDC fibers could be oriented to the direction of radial polarization by the incident 514 nm laser. Eventually, the radial polarization of CNTs in ZSDC was increased due to the same polarization direction vibration of the ZnO nanoparticles. This polarization of the RBM mode was very effective through the convenient chemical bonding between the carbon and zinc. In this case, the Zn–O system was attached to the CNT fiber, as shown in Fig. 4c, and the Zn–O system vibrates in the radial direction in the presence of the 514 nm laser (white arrow direction), as shown in Fig. 4d. Finally, this radial direction vibration mode enhances the radial breathing (RBM) mode of the CNTs (Fig. 4d). Consequently, the RBM peak of the ZSDC fiber is detected by a 514 nm laser. On the other hand, the RBM mode was not detected for the bare CNT fiber (Fig. 4e) by the 514 nm laser (Fig. 4f). The 514 nm laser is not sufficient to reveal the RBM mode of the CNTs.$^9$ A 785 nm laser was better than the 514 and 633 nm lasers for the detection of the RBM mode of CNTs.$^{70}$ Generally, in the case of multi-walled CNTs, the RBM mode is not detected by the 514 nm laser. On the other hand, in this case, the convenient vibration mode (Fig. 4d) of Zn–O bonding to the CNT fiber is significantly helpful in increasing the RBM mode. To clearly show the shifts in the other peaks (D, G, and 2D), the regions 1275–1640 and 2550–2850 cm$^{-1}$ are shown separately in Fig. 4g and h, respectively. Curve-c (Fig. 4g and h) of the ZSDC fiber displays the D band, G band and 2D band, which are shifted 3.3, 6.6 and 13.2 cm$^{-1}$, respectively, to a higher frequency position. The peak shifts indicate a strong interaction between ZnO and the CNT fiber, which causes vibrational peak shifts to shorter wavelengths. The incidence of 1D, G, 2D, E$_2$ (high), and A1-LO phonon mode peak shifts, and a new high intensity RBM peak in the ZSDC fiber strongly suggest chemical bonding between the CNT and ZnO nanoparticles. This chemical bonding interface plays important roles in the formation of the RBM peak and the shift in the other peaks in the Raman spectra.

To understand surface interface interactions, chemical bonding or any other interaction properties of the ZSDC fiber, XPS was performed from 0 to 1361 eV. Fig. 5a shows the 2p$_{3/2}$ (1021.8 eV) and 2p$_{1/2}$ (1044.8) peaks of bare ZnO, which are recognized as Zn in its oxidation state in ZnO. The ZSDC fiber shows the 2p$_{3/2}$ and 2p$_{1/2}$ peaks at the positions of 1022.9 eV and 1045.9 eV, respectively. Bare ZnO shows 2p$_{3/2}$ and 2p$_{1/2}$ peaks at slightly lower binding energy than that of the ZnO peaks of the ZSDC fiber. The changing binding energy of the 2p$_{3/2}$ and 2p$_{1/2}$ peaks of the ZSDC fiber also suggests an effective interaction between Zn and C. The bare CNT fiber did not show any peaks.
in this area. Fig. 5b shows the O1s peak of the ZSDC fiber and its de-convoluted curve. This peak decomposed into components located at 530.79, 531.22, 532.08, 532.5, and 533.07 eV. The summation of the de-convoluted curves was also well fitted to the original O1s curve. The 530.79 eV low energy peak was assigned to O$^{2-}$ from the wurtzite structure of the ZnO lattice. The peaks at 531.22 and 532.08 eV were attributed to O$^{2-}$ in the oxygen deficient region within the ZnO matrix. The 532.5 eV high energy peak was created from the functional group of C=O, which is bonded chemically to Zn at the low crystalline carbon site of the CNT. The remaining highest energy peak (533.07 eV) was generated from the C-O functional group. Normally, one peak occurs in the oxygen vacancy site but in this case two peaks were observed at 531.22 and 532.08 eV. Here, the high electronegativity of C compared to Zn plays a significant role in generating these two peaks. Possibly, there are two oxygen deficient environments in ZnO. One is C–Zn–C giving rise to the 531.22 eV peak, in which Zn is directly chemically bonded with carbon, and the other is –O–Zn–C giving rise to the 532.08 eV peak, where the more electronegative oxygen and
carbon are both chemically bonded to zinc. From this deconvoluted curve, it can be seen that the positions of the 532.55 and 533.07 eV peaks are at a slightly higher binding energy than the other peaks. This could be caused by the yet more electronegative oxygen environment\textsuperscript{34,73} in $\text{--O}^{-}\text{Zn--O--C}$, in which C is attached indirectly to Zn through the oxygen of C--O and C=O functional groups. Fig. 5c presents the core level C1s XP spectrum of the ZSDC fiber. Peaks were observed at 284.46, 285.64, 286.3, 287.9, 288.88, and 290.68 eV, which were assigned\textsuperscript{34} to the $\text{C}==\text{C}$ bond of sp$^2$ carbon, the C--C bond of sp$^3$ amorphous carbon, and C--O--C, C==O, and (C==O)O, bonding, respectively. The $\pi-\pi^*$ transition of the $\pi$ electron of the sp$^2$ C==C system in the CNT of the ZSDC fiber was also observed at 290.68 eV. The peak at 283.46 eV was assigned to the chemical bond between Zn and C, as observed with Zn--C\textsuperscript{54,75} which was anticipated above by the O1s core level peaks. All of the low intensity de-convoluted peaks are clearly shown in the inset of Fig. 5c. The de-convoluted peaks of the C1s core level spectrum strongly support the existence of chemical bonding between Zn and C in the ZSDC fiber.

Focused ion beam (FIB) techniques were used to cut the prepared ZSDC composite fiber, and a cross section (Fig. 6a) was examined by SEM to determine if the ZnO nanoparticles are present inside the fiber. EDX mapping of the rectangular marked area of Fig. 6a was performed, as shown in Fig. 6b. The mapping indicated Zn, O, C, and Si are present homogeneously on the inner side of the fiber. The corresponding color coding of...
Zn, O and C (inset image, Fig. 6b) of the mapping image revealed atomic percentages of 30% C, 28% O, 27% Si, and 14% Zn. Here, the Si peak was assigned to the silicon substrate. Therefore, the mapping image suggests that ZnO nanoparticles are present on the inner side of the fiber.

3.2 Optical, thermal, mechanical and electrical properties

ZSDC fibers were placed as a thin film on a transparent quartz glass substrate. Both sides of the fibers were attached to the substrate with adhesive scotch tape. In the same manner, a bare CNT fiber film was also prepared on a quartz glass substrate. Subsequently, the light absorption properties (Fig. 7a) of the ZSDC and CNT fibers were measured by UV/VIS/NIR spectroscopy. The CNT fiber (Fig. 7a) showed lower light absorption, whereas ZSDC exhibited excellent light absorption throughout the entire region (300–2100 nm) of the visible to near-IR spectrum. The super light absorption properties of the ZSDC fiber were achieved through the factors discussed previously, e.g., oxygen vacancy defects that generally lead to a d–d transition of Zn,32 functionalization directly with carbon or through the functional group of CNT,34 and doping effects in the oxygen vacancy sites of ZnO nanoparticles.35 Additionally, because the deposited ZnO nanoparticles are spherical, there is a change in the multiple light scattering effects36,37 between the ZnO nanoparticles. These multiple light scattering effects are helpful in improving the light absorption properties of the ZSDC fiber. Therefore, the combined effects improved the light absorption properties.

The thermal stability of the ZSDC fiber was examined. The thermogravimetric analysis (TGA) curves of the ZSDC fiber, CNT fiber and bare ZnO were taken at 880 °C in a nitrogen environment, and are shown in Fig. 7b. The ZnO curve showed no thermal degradation but the bare CNT fiber curve showed degradation at 100 °C, which increased continuously up to 540 °C and then dramatically up to 880 °C. The curve of the ZSDC fiber showed no thermal degradation up to 400 °C. Only 2% degradation occurred from 400 to 540 °C. Sharp degradation was observed between 540 °C and 880 °C but this differed from that of the bare CNT fiber; for the ZSDC fiber, only 22.5% degradation was observed at 880 °C; on the other hand, 74.53% degradation occurred for bare CNT fiber at 880 °C. These results indicate that ZnO nanoparticles and their aggregated layer of spheres in the ZSDC fiber act as a shielding layer against thermal breakdown.

ZnO is a semiconductor with a very low electrical conductivity, $7.2 \times 10^{-7}$ S cm$^{-1}$ (Fig. 7e). Therefore, it normally decreases the electrical conductivity if it is used in any matrix to prepare composite materials. Maintaining a high electrical conductivity of the ZnO composite is therefore a challenge. The electrical conductivity of the prepared ZSDC fiber was checked in comparison with the bare CNT fiber. To measure the electrical conductivity, an electrical circuit was prepared from ZSDC fibers and CNT fibers on the glass slide. The circuit scheme is shown in Fig. 7c. A ZSDC fiber (Fig. 7c) was placed on the glass slide. Gold wires were attached to the ZSDC fiber by silver paste. They were then placed under the microscope to connect the four points (1, 2, 3, 4) to the source meter (2400) and MULTIMETER (2000) of the four point probe. Fig. 7d shows the practical electrical conductivity sample for the ZSDC fiber. A current was
applied through points 4 and 3, and the corresponding output voltage \(V\) between points 1 and 2 was measured. The measured voltage \(V\) was then converted to the equivalent resistance \(R\) and the calculated resistance was converted to the resistivity \(\rho\). Subsequently, the electrical conductivity \(\sigma\) was calculated from the resistivity. All the calculations were performed using the following formula:

\[
\begin{align*}
R &= \frac{V}{I} \\
\rho &= \frac{A}{l}R \\
A &= \pi r^2 \\
\sigma &= \frac{1}{\rho}
\end{align*}
\]

Here, \(R\) = resistance, \(V\) = output voltage, \(I\) = applied current, \(\rho\) = resistivity, \(A\) = cross sectional area of fiber, \(l\) = length of fiber between the points 1 and 2 (Fig. 7c and d), \(r\) = radius of the fiber, and \(\sigma\) = electrical conductivity.

The mean electrical conductivity of the bare CNT fiber (1085 S cm\(^{-1}\)), ZSDC fiber (983 S cm\(^{-1}\)) and purified CNT (P. CNT) fiber (1152 S cm\(^{-1}\)) were calculated. The very high electrical conductivity of the ZSDC composite fiber (983 S cm\(^{-1}\)) showed that the semiconductor ZnO does not act as an insulator in the ZSDC fiber. The direct and indirect chemical bonding between Zn and C in the ZSDC fiber might act as a conductive path between the CNTs through the chemical bonds (C–Zn–C, Zn–C, O–Zn–C, Zn–O–C or C–Zn–Zn). The electrical conductivity of the ZSDC fiber was higher than those of the CNT–Pt, CNT–Ag and CNT–PDMS composite.\(^{45,59,60}\) The electrical conductivity of the P. CNT fiber (1152 S cm\(^{-1}\)) was improved slightly compared to that of the bare CNT fiber (1085 S cm\(^{-1}\)). This suggests that the highly conducting P. CNT fiber could also be used to prepare ZSDC fiber for a greater improvement of electrical conductivity.

The tensile strength and Young’s modulus of the ZSDC and bare CNT fiber were measured and the stress–strain curves are displayed in Fig. 8a. The ZSDC fiber exhibited a tensile strength of 116.89 MPa, whereas the CNT fiber exhibited a tensile strength of 72.7 MPa. The Young’s moduli were calculated to be 21 GPa and 4.8 GPa for the ZSDC and bare CNT fibers, respectively (Table 1). The ZSDC fiber showed an enhancement of the Young’s modulus from 4.8 to 21.3 GPa and the stress value from 72.70 to 116.89 MPa. Consequently, the Young’s modulus and tensile strength (stress) were improved by approximately 340% and 60%, respectively. The chemical bonding that is predicted by XRD, Raman spectroscopy and XPS between the Zn of ZnO and the C of CNT in the ZSDC fiber may improve the mechanical properties of the ZSDC fiber. This is the first report of ZnO nanoparticles increasing the mechanical properties of CNT fibers. As the mechanical properties of the ZSDC fiber were

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**Fig. 8** (a) Stress vs. strain curve of the ZSDC and CNT fiber. (b–f) Schematics to explain the mechanical properties of the fibers: (b) ZSDC fiber, (c) chemical bond formation between the different lengths of the individual CNTs inside the ZSDC fiber, (d) type of chemical bonding between the individual CNTs in the ZSDC fiber, (e) different lengths of individual CNTs in the bare CNT fiber after applied force, and (f) bare CNT fiber.
improved, something must be occurring inside the fiber. Considering Raman, XPS and XRD analysis, a possible mechanism (Fig. 8b–d) for the improvement of the mechanical properties of the ZSDC fiber is proposed. Fig. 8b and c show the ZSDC fiber and the inside of the fiber, respectively. The CNTs have different lengths but all are chemically bonded to ZnO nanoparticles, as shown in Fig. 8c and d. In this case, if a tensile force is applied to break the fiber, as in Fig. 8c, it will require a larger breaking load. On the other hand, the bare CNT fiber (Fig. 8f) will require a lower force due to the absence of chemical bonds between the different lengths of the individual CNTs (Fig. 8e). Therefore, the prepared ZSDC fiber is mechanically more robust than the bare CNT fiber.

4. Conclusions

Homogeneous ZnO nanoparticle-aggregated spheres were deposited on a CNT fiber surface without using any specialized techniques such as chemical functionalization, costly instrumentation, oxidation, or catalysis. The experimental results suggested that ZnO nanoparticles were also deposited inside of the fiber. The measured mechanical properties of the ZSDC fiber indicated approximately 340% and 60% improvements in the Young’s modulus and tensile strength, respectively, when compared with the bare CNT fiber. This is the first time that ZnO nanoparticles have been utilized to improve the mechanical properties of CNT fibers. A mechanism to support the improvement in mechanical properties was proposed based on XRD, Raman and XPS analyses. The proposed mechanism could also explain the conductive path of the electrons that preserved the very high electrical conductivity (983 S cm\(^{-1}\)) of the ZSDC fiber by disabling the semiconductor effect of the ZnO nanoparticles. This highly conductive and mechanically robust ZSDC fiber exhibited super light absorption properties from 300–2100 nm and almost non-degradable behavior up to 540 °C in a nitrogen environment. Therefore, the prepared ZSDC fiber is a candidate for flexible, textile-shaped light harvesting materials for the generation of electricity or the production of fuel by utilizing solar light, and it could be sustainable in a very high temperature environment. As the proposed fabrication process is simple, it could be a model process for the synthesis of ZnO nanoparticle nanospheres on a CNT fiber surface. Furthermore, the new finding of RBM peak generation and its explanation by a ZnO vibrational mode is expected to promote further CNT and CNT fiber research.

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