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ABSTRACT
Rendering the unique features of individual nanoscale constituents into macroscopic thin films remains technologically challenging; the engineering of these constituents habitually compromises their inherent properties. Efficient, environmentally benign, and biodegradable DNA and cetyltrimethyl-ammonium chloride-modified DNA (DNA-CT) thin films (TFs) implanted with titania nanoparticle-coated multiwalled carbon nanotubes (MCNT-TiO2) are prepared by a drop-casting technique. The energy dispersive X-ray spectroscopy studies of DNA and DNA-CT TFs with MCNT-TiO2 identifies various elements (C, O, N, P, Na, and Ti) via quantitative microanalysis. The X-ray photoelectron, Raman, Fourier-transform infrared (FTIR), and UV-visible absorption spectra show changes in the chemical compositions and functional groups associated with binding energies, enhancement of characteristic MCNT-TiO2 Raman bands, and intensity changes and peak shifts of the FTIR and UV-Vis-NIR absorption bands, respectively. The PL spectra indicate an energy transfer in the measured samples, and the quenching of PL indicates a decrease in the recombination efficiency. Lastly, we measure the conductivity, which increased with an increasing concentration of MCNT-TiO2 in the DNA and DNA-CT TFs due to the better connectivity of MCNT-TiO2. By using these materials, the optoelectronic properties of DNA and DNA-CT TFs implanted with MCNT-TiO2 are easily tunable, enabling several engineering and multidisciplinary science applications, such as photonics, electronics, energy harvesting, and sensors.

I. INTRODUCTION

For several decades, the physical, chemical, and biological properties of deoxyribonucleic acid (DNA) molecules have been extensively studied to better understand their intrinsic characteristics (e.g., self-assembly and molecular recognition) and extrinsic capabilities with other nanomaterials (e.g., modification and scaffolding) in various applications. DNA has a water–soluble, alternating polymer backbone and demonstrates promising characteristics, including high transparency (near UV and visible), small dumping (near infrared), low optical loss, a high dielectric constant, and excellent thermal resistance. These exceptional optoelectronic characteristics are useful for bioelectronics, photonics, and various sensor and device applications.1–6 In contrast, cationic surfactant cetyltrimethylammonium chloride-modified DNA (DNA-CT) has deprived water solubility and is less delicate to water sorption. DNA-CT is readily soluble in various organic solvents...
that can rapidly evaporate. In light-emitting diodes, DNA–CT mainly has been employed as a charge transport layer. In addition, DNA can serve as a template for aligning various nanomaterials (e.g., ions, nanoparticles, carbon-based materials, and proteins) to enhance specific functionalities. It is important to assimilate a greater number of components into macroscopic materials, thereby facilitating the creation of enhanced multifunctional characteristics.

Metal oxide semiconductor-based nanocomposites have been extensively studied owing to their electronic, energy-harvesting, and environmental applications. Among various metal oxide materials, zero-dimensional (0D) titanium dioxide (TiO$_2$) nanoparticles, known as titania, are considered to be an interesting material due to their novel optical characteristics, wide band gap semi-conductivity, nontoxic nature, biological and chemical inertness, and photocatalytic activity. Recently, there have been noticeable developments in the creation of functional nanomaterials by integrating TiO$_2$ inorganic and organic compounds. ID carbon nanotubes (CNTs) have outstanding mechanical strength; excellent electrical conduction, thermal stability, and durability; high surface area; and a unique structure. TiO$_2$ nanoparticle-coated MCNT (MCNT-TiO$_2$) nanocomposites can be used to provide promising and specific properties for environmental, physical engineering, and biological sciences applications. Due to their structural reliability, durability, and large surface area, MCNTs can be treated as efficient carriers for TiO$_2$ nanoparticles.

The development of reliable and scalable assembly techniques to construct various multifunctional devices is important in order to tailor materials for target applications. Although various functionalized nanomaterials (e.g., nanoparticles, ions, and proteins) can be embedded into DNA molecules, DNA implanted with MCNTs has rarely been reported due to the difficulties in constructing complexes with a uniformly distributed ID nanostructure. MCNTs with TiO$_2$ nanoparticles allow for additional functionalization in the composite as compared to pristine MCNTs. The optical and electrical characteristics of MCNT-TiO$_2$-implanted DNA and DNA–CT complexes, with various concentrations of MCNT-TiO$_2$ ([MCNT-TiO$_2$]), provide unique and enhanced functionality compared to pristine DNA and DNA–CT.

With the aid of the aforementioned advantages and unique characteristics, we fabricate DNA and DNA–CT TFs implanted with various [MCNT-TiO$_2$] by a drop-casting method. In addition, the MCNT-TiO$_2$-implanted DNA (named as MCNT-TiO$_2$–DNA) and MCNT-TiO$_2$-implanted DNA–CT (MCNT-TiO$_2$–DNA–CT) TFs are characterized in terms of their elemental composition (energy dispersive X-ray spectroscopy, EDS), chemical states and chemical functional groups (X-ray photoelectron spectroscopy, XPS), binding interactions and vibration/stretching modes (Raman and Fourier transform infrared (FTIR) spectroscopies), optical absorption (UV–Vis–NIR spectrophotometer), photoluminescence (PL mapper), and electrical properties (semiconductor parameter analyzer).

II. EXPERIMENTAL

A. Sample preparation

Initially, we purchased DNA produced from salmon (GEM Corporation, Shiga, Japan) and MCNT–TiO$_2$ (US Research Nanomaterials, Inc., Houston, TX, USA). The outside diameter, inner diameter, and length of MCNTs are >50 nm, 5–15 nm, and 5–20 µm, respectively, and the diameter of TiO$_2$ nanoparticles is ∼8 nm. For prepare the MCNT–TiO$_2$–DNA and MCNT-TiO$_2$–DNA–CT solutions, 0.05 g of DNA and DNA–CT fibers as well as proper amounts of MCNT–TiO$_2$ are mixed in 5 mL of de-ionized (DI) water and 5 mL of 1-butanol, respectively, followed by magnetic stirring for 48 h to attain uniform complex solutions. The final [DNA] and [DNA–CT] in MCNT–TiO$_2$–DNA and MCNT–TiO$_2$–DNA–CT solutions are 1.0 wt% with various [MCNT–TiO$_2$] (i.e., 0.05, 0.10, 0.15, 0.20, and 0.30 wt%). 20 µL of the MCNT–TiO$_2$–DNA or MCNT–TiO$_2$–DNA–CT aliquot is drop-casted onto an oxygen plasma-cleaned substrate then allowed by natural drying. Oxygen plasma-treated glass and fused silica (5 × 5 mm$^2$) are used for EDS, XPS, Raman, FTIR, and current measurements as well as absorption and PL measurements, respectively.

B. Characterization techniques

The chemical, compositions, charge transfer/functional groups, Raman modes/chemical bindings, chemical bonds/interactions, absorption, photon energy transfer phenomena, and electrical behaviours of the DNA and DNA–CT TFs implanted with MCNT–TiO$_2$ are analyzed via the EDS (ISM–7600F, JEOL USA, Inc.), XPS (ESCALAB 250Xi, Thermo Scientific, UK), confocal Raman (Alpha 300 R, Wittec, Germany), FTIR (MIR–ATR (ZnSe), Bruker Inc., USA), UV–Vis–NIR ( Cary 5G, Varian, CA, USA), PL mapper (Accent RPM2000, Nanometrics, CA, USA), and semiconductor parameter analyzer (4200–SCS, Keithley Instruments Inc., USA), respectively.

III. RESULTS AND DISCUSSION

The fabrication procedures for the DNA and DNA–CT TFs implanted with TiO$_2$–coated MCNT are shown in Figs. 1(a) and 1(b). In order to prepare the DNA solution, DNA fibers were mixed in DI water followed by magnetic stirring. DNA and CT were dissolved separately in DI water to prepare the DNA–CT. Then, CTMA was added slowly into the DNA solution while stirring. After filtering, CTMA-modified DNA fibers in a solid phase were obtained. To prepare the DNA–CT solution, DNA–CT fibers were dissolved in 1-butanol. An appropriate amount of MCNT–TiO$_2$ was mixed into the DI water (1-butanol) and then allowed by magnetic stirring to attain a consistent solution of MCNT–TiO$_2$–DNA (MCNT–TiO$_2$–DNA–CT). 20 µL of the MCNT–TiO$_2$–DNA (MCNT–TiO$_2$–DNA–CT) solution was then drop-casted on a given substrate in order to obtain a ∼2-µm-thick thin film.

The EDS spectra of DNA TFs with MCNT–TiO$_2$ were confirming the presence of the major elements of C, N, O, Na, P, and Ti (Fig. 1(c)). By analyzing the spectra, we determined that the atomic weight% of C, N, O, Na, and P in DNA were...
43.90, 16.60, 30.94, 4.58, and 3.98%, respectively. Similarly, the atomic weight% of C, N, O, Na, P, and Ti in MCNT-TiO2-DNA were found to be 44.08, 13.0, 42.04, 3.58, 3.38, and 5.62%, respectively. As expected, after adding MCNT-TiO2 into DNA TFs, the atomic weight% of N, Na, and P were enhanced but the atomic weight% of C and O were reduced, as compared to DNA TFs. The EDS spectra provided evidence of the encapsulation of DNA molecules with MCNT-TiO2.

The chemical states, chemical functional groups, and elemental compositions of the DNA and MCNT-TiO2-DNA TFs, as well as the MCNT-TiO2 powder, were analyzed using XPS. Fig. 2(a) shows the XPS survey spectra of the DNA thin film (C, O, N, P, and Na had corresponding binding energies of 284.8, 532.1, 399.2, 132.7 eV, respectively), DNA-CT thin film (C, O, N, P, and Na had corresponding energies of 285.4, 532.2, 402.4, 132.7 eV, respectively), MCNT-TiO2 thin film (C, O, N, P, Na, and Ti had corresponding energies of 285.4, 530.9, 398.1, 131.8, 1069.9 eV, and 456.8 eV, respectively), and MCNT-TiO2 powder (C, O, N, P, Na, and Ti had corresponding energies of 285.4, 531.0, 285.2, and 459.8 eV, respectively). The XPS survey graphs showed peaks associated with C, O, N, P, Na, and Ti at their characteristic binding energies, thereby confirming the presence of MCNT-TiO2 in the DNA thin film.

Figs. 2(b)–2(g) show the comparative high–resolution, deconvolved core XPS graphs of C 1s, O 1s, Ti 2p, N 1s, P 2p, and Na 1s for respective samples. These show a shift in the binding energy, changes in the chemical composition, and variations in the peak intensity. The XPS spectra provided evidence of the encapsulation of DNA molecules with MCNT-TiO2.

The XPS spectra provided correlative analysis of the characteristic elements in the DNA and MCNT-TiO2-DNA TFs. After adding MCNT-TiO2 into the DNA thin film, the binding energies at 288 and 290.0 eV in the C 1s orbital were suppressed. In the core orbitals of O 1s, Ti 2p, N 1s, P 2p, and Na 1s, a negative shift (with a magnitude of ~1.5 eV, which occurred due to charge transfer from MCNT-TiO2 to DNA) in the binding energies as well as significant suppression of the peak intensities (at 536.2, 472.8, 405.1, 139.8, and 1075.5 eV, respectively) were observed. The variations of the binding energies of the Ti 2p core spectra were observed at 458.3 eV (2p3/2) and 464.2 eV (2p1/2) for MCNT-TiO2+DNA and 459.8 eV (2p3/2), 465.5 eV (2p1/2), and 472.8 eV (satellite) for pristine MCNT-TiO2+DNA. The chemical states of Ti 2p3/2 and Ti 2p1/2 were assigned to the spin–orbit splitting photoelectrons. The binding energies of the N 1s core spectra were found at 399 (C=NH2), 400.4 (N=O and N=C=O), and 405.1 eV (N–H) for DNA; 399.5 (C=NH2), 398.1, and 402.3 eV (N=O) for DNA-CT; and 397.4 eV (N=C, N=C, and N=O) and 542.7 eV (satellite peak) for MCNT-TiO2+DNA. The binding energies of the O 1s core spectra were observed at 531.1 (C=O, C=O, and C=O) and 530.4 eV (C–C and C–C–C) for DNA-CT; 530.4 (C–C–C and C–C–C) for MCNT-TiO2+DNA; and 533.7 eV (C–C and C–C–C) for MCNT-TiO2+DNA. The binding energies of the Na 1s core spectra were observed at 1069.9 eV (Na–O) and 1076.5 eV (Na–O) for DNA and 1069.9 (Na–O) and 1072.0 eV (Na+–P=O) for MCNT-TiO2+DNA.

The XPS spectra provided correlative analysis of the characteristic elements in the DNA and MCNT-TiO2-DNA TFs. After adding MCNT-TiO2 into the DNA thin film, the binding energies at 288 and 290.0 eV in the C 1s orbital were suppressed. In the core orbitals of O 1s, Ti 2p, N 1s, P 2p, and Na 1s, a negative shift (with a magnitude of ~1.5 eV, which occurred due to charge transfer from MCNT-TiO2 to DNA) in the binding energies as well as significant suppression of the peak intensities (at 536.2, 472.8, 405.1, 139.8, and 1075.5 eV, respectively) were observed. The variations of the binding energies of the Ti 2p core spectra were observed at 458.3 eV (2p3/2) and 464.2 eV (2p1/2) for MCNT-TiO2+DNA and 459.8 eV (2p3/2), 465.5 eV (2p1/2), and 472.8 eV (satellite) for pristine MCNT-TiO2+DNA. The chemical states of Ti 2p3/2 and Ti 2p1/2 were assigned to the spin–orbit splitting photoelectrons. The binding energies of the N 1s core spectra were found at 399 (C=NH2), 400.4 (N=O and N=C=O), and 405.1 eV (N–H) for DNA; 399.5 (C=NH2), 398.1, and 402.3 eV (N=O) for DNA-CT; and 397.4 eV (N=C, N=C, and N=O) and 542.7 eV (satellite peak) for MCNT-TiO2+DNA. The binding energies of the O 1s core spectra were observed at 531.1 (C=O, C=O, and C=O) and 530.4 eV (C–C and C–C–C) for DNA-CT; 530.4 (C–C–C and C–C–C) for MCNT-TiO2+DNA; and 533.7 eV (C–C and C–C–C) for MCNT-TiO2+DNA. The binding energies of the Na 1s core spectra were observed at 1069.9 eV (Na–O) and 1076.5 eV (Na–O) for DNA and 1069.9 (Na–O) and 1072.0 eV (Na+–P=O) for MCNT-TiO2+DNA.

The XPS spectra provided correlative analysis of the characteristic elements in the DNA and MCNT-TiO2-DNA TFs. After adding MCNT-TiO2 into the DNA thin film, the binding energies at 288 and 290.0 eV in the C 1s orbital were suppressed. In the core orbitals of O 1s, Ti 2p, N 1s, P 2p, and Na 1s, a negative shift (with a magnitude of ~1.5 eV, which occurred due to charge transfer from MCNT-TiO2 to DNA) in the binding energies as well as significant suppression of the peak intensities (at 536.2, 472.8, 405.1, 139.8, and 1075.5 eV, respectively) were observed. The variations of the
FIG. 2. XPS spectra of the DNA and DNA-CT TFs implanted with MCNT-TiO$_2$. (a) XPS survey graphs of the DNA and DNA-CT TFs implanted without and with MCNT-TiO$_2$ and pristine MCNT-TiO$_2$. (b-g) Correlative analysis of the characteristic elements in DNA, DNA-CT, MCNT-TiO$_2$+DNA, and MCNT-TiO$_2$ acquired from high-resolution XPS spectra.
FIG. 3. Raman spectra analysis of the vibrational and stretching modes associated with the chemical groups present in the DNA and DNA-CT TFs implanted with MCNT-TiO$_2$. (a) Comparative Raman spectra of the DNA TFs with various [MCNT-TiO$_2$]. (b) Raman spectra of the DNA-CT TFs with MCNT-TiO$_2$.

FIG. 4. FTIR spectra analysis of the specific functional groups and chemical bond interactions associated with the frequency in the DNA and DNA-CT TFs implanted with MCNT-TiO$_2$. (a) Relative FTIR spectra of the DNA TFs with various [MCNT-TiO$_2$]. (b) FTIR spectra of the DNA-CT TFs with MCNT-TiO$_2$.

peak area, intensity, and full-width at half maximum could be caused by the distributions of chemical groups in each chemical state and the different elemental compositions in the TFs.

Raman spectroscopy was used to examine the interactions of the functional groups (i.e., MCNT-TiO$_2$ in the DNA and DNA-CT TFs). Figs. 3(a) and 3(b) show the Raman spectra of DNA and DNA-CT TFs implanted with various [MCNT-TiO$_2$]. The Raman spectrum of DNA TFs exhibited characteristic Raman bands centered at around 477, 678, 732, 786, 890, 1012, 1095, 1248, 1306, 1336, 1375, 1420, 1486, 1576, 1666, 2160, and 2960 cm$^{-1}$, which revealed the distinct vibrational and stretching modes of DNA. After surfactant modification of DNA with CTMA, the Raman spectrum of the DNA-CT thin film showed additional Raman bands at 2854 and 2890 cm$^{-1}$ (due to CH$_2$ modes) and 2937 cm$^{-1}$ (due to CH$_3$ modes).

Interestingly, MCNT-TiO$_2$+DNA and MCNT-TiO$_2$+DNA-CT exhibited intense typical Raman bands of MCNT-TiO$_2$ at 363, 485, 609, 1334, 1570, and 2694 cm$^{-1}$, which were not observed in the DNA and DNA-CT TFs. The characteristic bands at 1334, 1570, and 2694 cm$^{-1}$ were assigned to the D-band (attributed to disordered carbon atoms) and G- and G’-bands (originating from MCNT). In addition, TiO$_2$ nanoparticles were well represented by the characteristic Raman bands at 363, 485, and 609 cm$^{-1}$. As the [MCNT-TiO$_2$] in DNA and DNA-CT TFs increased, the characteristic Raman bands of MCNT (i.e., 1334, 1570, and 2694 cm$^{-1}$) increased proportionally. Consequently, the characteristic Raman bands of DNA molecules were drastically decreased as the [MCNT-TiO$_2$] in the DNA and DNA-CT TFs increased due to the physical interactions between them. The ratios between the D-band and G-band in MCNT-TiO$_2$+DNA and MCNT-TiO$_2$+DNA-CT showed slight deviations due to the different solvent environments, which can influence the amount of oxidation.

FTIR was carried out to evaluate the chemical bonds, molecular structure, and interactions between DNA (DNA-CT) and MCNT-TiO$_2$. Fig. 4 shows the FTIR-attenuated reflection spectra of DNA and DNA-CT TFs implanted with various [MCNT-TiO$_2$]. The FTIR spectra of pristine DNA exhibited several characteristic absorption bands, i.e.,
vibration modes of sugar and phosphate backbone groups (600 – 1250 cm\(^{-1}\)), stretching and vibration modes of nucleobases (1300 – 1800 cm\(^{-1}\)), and water OH stretching modes (3000 – 3600 cm\(^{-1}\)).\(^{36}\) The peaks located at ~780, 835, and 938 cm\(^{-1}\) can be assigned to sugar phosphate vibration, deoxyribose-phosphate, and adenine-thymine base pairs, respectively. The absorption of C–C/C–O of deoxyribose skeletal motion, P–O stretching vibration, and C–O deoxyribose can be found at 963, 1014, and 1050 cm\(^{-1}\), respectively. The peaks at 1082 and 1220 cm\(^{-1}\) were caused by the symmetric and anti-symmetric stretching vibrations of the phosphate groups, respectively. The absorption of the cytosine in-plane vibration, adenine C7=N stretching, thymine C2=O stretching, and guanine C=O stretching were observed at 1488, 1420, and 1373 cm\(^{-1}\), respectively. The peaks at 1082 and 1220 cm\(^{-1}\) were caused by the symmetric and anti-symmetric stretching vibrations of the phosphate groups, respectively. The peaks at 1082 and 1220 cm\(^{-1}\) were caused by the symmetric and anti-symmetric stretching vibrations of the phosphate groups, respectively.

UV-Vis-NIR spectroscopy was carried out to examine the optical characteristics of a series of DNA and DNA-CT TFs implanted with MCNT-TiO\(_2\). Measurements were taken in the wavelength range from 190 to 3200 nm under ambient conditions. Fig. 5 shows the absorption spectra of DNA and DNA-CT TFs implanted with various [MCNT-TiO\(_2\)]. The characteristic absorption peaks of DNA and DNA-CT TFs without MCNT-TiO\(_2\) at wavelengths of 210 and 260 nm were produced by the phosphate backbone and nitrogenous bases, respectively.\(^{37,38}\) Although apparent splitting of the DNA absorption peaks at 210 and 260 nm was observed at relatively low [MCNT-TiO\(_2\)], a merged broad absorption peak in the UV region was noticed at high [MCNT-TiO\(_2\)] due to the interactions between DNA (DNA-CT) molecules and MCNT-TiO\(_2\). In addition, the characteristic absorption peak intensities of DNA were reduced at [MCNT-TiO\(_2\)] increased. Due to the presence of MCNT-TiO\(_2\), two absorption peaks at wavelengths of 925 and 2330 nm were found; these were caused by various functional group interactions between MCNT and TiO\(_2\) nanoparticles.\(^{39,40}\) Lastly, a broad absorption peak centered at ~2970 nm may be caused by water OH molecules present in all samples.

Absorption peak intensities of the MCNT-TiO\(_2\)+DNA and MCNT-TiO\(_2\)+DNA-CT TFs with [MCNT-TiO\(_2\)] at a fixed wavelength of 925 nm are shown in Fig. 5(c). The absorptions of MCNT-TiO\(_2\) in DNA and DNA-CT TFs monotonically increased with increasing [MCNT-TiO\(_2\)] in the Vis-NIR region; this might be associated with the absorption of MCNT. The enhanced absorption in the Vis-NIR region signifies the enrichment of the optical properties and interaction between DNA (DNA-CT) and MCNT-TiO\(_2\). The absorption band edges were gradually shifted to higher wavelengths (i.e., a red shift) due to the semiconductivity of TiO\(_2\) nanoparticles along with MCNTs. Consequently, the optical band gaps of the TFs were proportionally decreased with increasing [MCNT-TiO\(_2\)]. The efficient interaction between DNA (DNA-CT) and MCNT-TiO\(_2\) lead to the increased absorption. The absorption results of DNA and DNA-CT TFs implanted with MCNT-TiO\(_2\) may lead to

**FIG. 5.** UV-Vis-NIR absorption characteristics of the DNA and DNA-CT TFs implanted with MCNT-TiO\(_2\). (a, b) Absorption graphs of the DNA and DNA-CT TFs with various [MCNT-TiO\(_2\)]. (c) The variation of absorption peak intensities of the MCNT-TiO\(_2\)+DNA and MCNT-TiO\(_2\)+DNA-CT TFs with [MCNT-TiO\(_2\)] at a fixed wavelength of 925 nm.
advantages in various optical and sensor applications (e.g., photodetectors, UV radiation sensors, and IR detectors) because the overall absorption can cover the full spectral range from the UV, visible, and telecommunication window to far-IR regions.

The PL spectra were taken to investigate energy transfer and charge carrier trapping as well as to better understand the exchange of electron-hole pairs in the samples. The PL characteristics of the DNA TFs implanted with MCNT-TiO$_2$ at a fixed excitation wavelength of 266 nm are depicted in Fig. 6. The PL spectra of the MCNT-TiO$_2$+DNA TFs revealed a broad emission in the blue region. The PL spectra also showed a blue shift and PL quenching with increasing [MCNT-TiO$_2$]. In contrast, a remarkable decrease in the electron-hole recombination was anticipated since no characteristic peaks of MCNT-TiO$_2$ were observed in the PL spectra. The peak center, peak height (inset), and energetic emission area as a function of [MCNT-TiO$_2$] in the DNA TFs, obtained using Lorentz fitting, are displayed in Fig. 6(b). The emission peak center was gradually blue-shifted (by about 20 nm at higher concentrations) as [MCNT-TiO$_2$] increased. Similarly, the emission area and peak height decreased with increasing [MCNT-TiO$_2$] in the DNA TFs.

The PL spectra were heavily influenced by surface defects, oxygen vacancies, self-trapped excitons, and energy transfer in the measured samples. For MCNT-TiO$_2$+DNA, the PL intensity change might be caused by changes in the shallow defect states in TiO$_2$ and the recombination of excited electrons and holes. The quenching of the PL intensity indicated a decrease in the recombination efficiency. Due to the presence of MCNTs, which act as electron acceptors and transporters, the recombination of electrons and holes decreased with increasing [MCNT-TiO$_2$], which further prevented the recombination of electrons and holes. In addition, MCNT-TiO$_2$ in DNA TFs might be able to transfer the photoelectrons generated by MCNT-TiO$_2$ under the given excitation.
wavelength; this might be useful in physical devices and sensor applications.

Finally, we studied the electrical characteristics to investigate the electrical transport phenomena of the DNA and DNA-CT TFs implanted with MCNT-TiO$_2$; this was done with a semiconductor parameter analyzer (Fig. 7). The MCNT-TiO$_2$-DNA and MCNT-TiO$_2$-DNA-CT TFs showed semiconducting behavior, which originated from the semiconducting TiO$_2$ nanoparticles in the TFs. Although current enhancements in both MCNT-TiO$_2$-DNA (~10 times) and MCNT-TiO$_2$-DNA-CT (~100 times) TFs were noticed with increasing [MCNT-TiO$_2$], drastic increases in the currents were observed in MCNT-TiO$_2$-DNA-CT TFs as compared to the MCNT-TiO$_2$-DNA TFs. During sample preparation, MCNT-TiO$_2$ mixed with DNA-CT better in 1-butanol (lower viscosity) than with DNA in DI water (higher viscosity), which led to better connectivity of MCNT-TiO$_2$ (especially at higher [MCNT-TiO$_2$]) in the TFs. Consequently, more electrons were transported through MCNT-TiO$_2$ in the DNA-CT TFs than in the DNA TFs. The resistances of the MCNT-TiO$_2$-DNA and MCNT-TiO$_2$-DNA-CT TFs with [MCNT-TiO$_2$] at a fixed voltage of 5 V, as obtained from current-voltage curves, are shown in Fig. 7(c). As expected, the resistances monotonically decreased with increasing [MCNT-TiO$_2$] by factors of ~767 MΩ for (DNA) and ~5 GΩ for (DNA-CT) per unit wt%.

IV. CONCLUSIONS

In summary, we developed a new method to construct MCNT-TiO$_2$-implanted DNA and DNA-CT TFs by a drop-casting method. Furthermore, we studied the elemental composition, chemical states, functional groups, bonding interactions, modes of vibration and stretching, absorption photoluminescence, and electrical properties of these materials. From the EDS spectra, the atomic weight% of C and O were observed to increase, while the atomic weight% of N, Na, and P decreased after the addition of MCNT-TiO$_2$ in DNA TFs. As expected, the XPS spectra showed peaks associated with C, O, N, P, Na, and Ti at their characteristic binding energies, which confirmed the presence of MCNT-TiO$_2$ in the DNA TFs. Raman spectra, which revealed the distinct vibrational and stretching modes of the samples, were used to identify the interactions of the functional groups (i.e., MCNT-TiO$_2$ in DNA and DNA-CT TFs). Intensity changes and peak shifts of the FTIR absorbance, UV absorption, and PL emission as a function of [MCNT-TiO$_2$] suggested the strong interaction between DNA (DNA-CT) and MCNT-TiO$_2$ via electrostatic and non-covalent bonding interactions. Interestingly, the DNA and DNA-CT TFs with MCNT-TiO$_2$ showed semiconducting behavior due to the presence of semiconducting TiO$_2$ nanoparticles in the TFs. Our results suggest that high tunability of the physical and chemical characteristics can be achieved by simple control of the functionalized [MCNT-TiO$_2$] in both DNA and DNA-CT TFs. Due to their unique features, macroscopic DNA and DNA-CT TFs implanted with MCNT-TiO$_2$ may lead to new research areas in nanomaterials science and engineering.

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