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Effect of constructive rehybridization on transverse conductivity of aligned single-walled carbon nanotube films

Mingguang Chen [1,2,†], **Wangxiang Li** [1,3,†], **Thaís Eloá da Silveira Venzel** [1],
Guanghui Li [1,2], **Mikhail E. Itkis** [1,2,3], **Robert C. Haddon** [1,2,3], **Elena Bekyarova** [1,2,3,*]

[1] Center for Nanoscale Science and Engineering, University of California, Riverside, CA 92521, United States
[2] Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, United States
[3] Department of Chemistry, University of California, Riverside, CA 92521, United States

Alignment of densely packed single-walled carbon nanotubes (SWNTs) largely preserves the extraordinary electronic properties of individual SWNTs in the alignment direction, while in transverse direction the films are very resistive due to large energy barriers for tunneling between adjacent SWNTs. We demonstrate that chromium atoms inserted between the sidewalls of parallel SWNTs effectively coordinate to the benzene rings of the nanotubes via hexahapto bonds that preserve the nanotube-conjugated electronic structure and serve as a conduit for electron transfer. The atomically interconnected aligned SWNTs exhibit enhanced transverse conductivity, which increases by ~2100% as a result of the photoactivated organometallic functionalization with Cr. The hexahapto mode of bonding the graphitic surfaces of carbon nanotubes with transition metal atoms offers an attractive route to the reversible chemical engineering of the transport properties of aligned carbon nanotube thin films. We demonstrate that a device fabricated with aligned SWNTs can be reversibly switched between a state of high electrical conductivity (ON) by light and low electrical conductivity (OFF) by applied potential. This study provides a route to the design of novel nanomaterials for applications in electrical atomic switches, optoelectronic and spintronic devices.

Keywords: Aligned carbon nanotubes; Organometallic functionalization; Conductivity; Interconnects; Chromium

Introduction

Single-walled carbon nanotubes (SWNTs) have excellent electronic properties, which make them attractive candidates for next-generation electronics and optoelectronics [1–4]. Whereas individual SWNT devices have been demonstrated, their practical utilization in electronic circuits remains a challenge. High-quality, thin films of random SWNTs have been considered as an alternative solution, however the outstanding SWNT properties are largely diminished in macroscopically assembled thin films due to the intertube junction resistance, which significantly exceeds that of individual SWNTs [5–8]. Recent advances in the alignment of SWNTs made possible the preparation of films of densely packed parallel SWNTs [9–15], and this stimulated a growing interest in their electronic properties and utilization in electronic devices [16–20]. In fact the anisotropic electrical and thermal properties of aligned SWNTs have long been a topic of interest [21–23]. In such films, the conductivity along the alignment direction (parallel conductivity) is much higher as compared with the direction perpendicular to the SWNT axis (transverse conductivity). The large anisotropy can be explained with a simple model assuming that the film resistance is dominated by the intertube junctions: for a given

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[*] Corresponding author at: Center for Nanoscale Science and Engineering, University of California, Riverside, CA 92521, United States (E. Bekyarova).

E-mail address: Bekyarova, E. (elenab@ucr.edu)

[†] These authors have equal contribution.

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SWNT film length there are dramatically less tube–tube contacts in parallel versus perpendicular direction due to the very large aspect ratio of the SWNTs (~10^3). Thus, seamlessly interconnecting the SWNTs post-alignment would have a dramatic effect on the degree of electrical anisotropy. Bridging graphene surfaces, and in particular carbon nanotubes, has been successfully accomplished using covalent chemistry. Although this chemistry has proven to be useful for development of advanced electronic applications, including molecular switches [24,25], the covalent bond formation to the carbon atoms of the graphene lattice results in a change of the hybridization from sp^2 to sp^3 [26–30], and therefore it causes a decrease in conductivity. The ability to form a bond to the sidewalls of carbon nanotubes without significant rehybridization is critical for the electronic and optoelectronic applications of these materials. Very few chemical reactions preserve the π-conjugation of the carbon-nanotube sp^2 network examples include cycloaddition [31–33] and organometallic reactions [34,35]. The ability of the organometallic bond to form without significant rehybridization is the key to the usefulness of this new mode of bonding in electrically connecting carbon materials based on the benzenoid ring system. We have classified this type of bonding as constructive rehybridization, in which the extended π-electronic structure of graphene is complexed with a transition metal, and the degree of rehybridization at the site of complexation is insufficient to saturate the conjugated electronic band structure [36,37].

Here, we utilize aligned SWNT thin films that consist of a statistical mixture of semiconducting and metallic (2:1) SWNTs to insert chromium atoms between a pair of parallel SWNTs and interconnect them. This mode of bonding dramatically reduces the electrical resistance of the films in direction perpendicular to the SWNT axis, while it has negligible effect on the conductivity parallel to the SWNT alignment. We suggest that the chromium atoms coordinate to the benzenoid rings of adjacent SWNTs to covalently link them via hexahapto bond. The study demonstrates that this type of bonding is feasible in homogeneous, dense, aligned SWNT films. The hexahapto bond preserves the geometric and electronic structure of individual SWNTs [35] while extending the dimensionality from 1D to quasi 2D.

Films of aligned semiconducting SWNTs with improved intertube junctions have potential applications as the active constituents in high-performance electronics and advanced optoelectronics. Other areas of interests are quantum computing and magnetic nanodevices as some of these graphene-transition metal compounds are magnetic [38] and the aligned SWNTs offer a platform for the assembly of ordered magnetic systems. The hexahapto bonding of atomic chromium [Cr(0)] to graphene surfaces may complement existing technologies that employ ion-selective sensors for environmental monitoring [39–43].

The reversible nature of the graphene–hexahapto complexation [44] is further explored for the reversible chemical engineering of the transport properties of aligned SWNTs and preparation of atomic switches. This was accomplished by turning on an SWNT array by a photochemical complexation with transition metal atoms, and turning it off by electric field.

Experimental section

Preparation of aligned SWNT films

Purified unsorted arc-discharge SWNTs (P2-SWNTs, Carbon Solutions, Inc.) were dispersed in water using sodium deoxycholate (1 wt%). Dispersion with a concentration of 0.4 mg/mL was prepared by ultrasonication in a bath sonicator for 10 min followed by a tip sonication (Cole-Parmer cup-horn sonicator, power level 40 W, 1/2-inch probe) for 1 h in an ice bath. The obtained dispersion was centrifuged for 1 h at 40,000 r.p.m (Beckman TL-100 ultracentrifuge with Beckman TLA-100.3 rotor) to remove large SWNT bundles. The supernatant was collected as a stock solution (concentration ~20 μg/mL). Aligned SWNT films were prepared by slow filtration using a modified literature procedure [15]. For the filtration, a portion of the stock solution was diluted with nanopure water to obtain a dispersion with SWNT concentration of 2 μg/mL (surfactant concentration 0.1%). The SWNT dispersion (2.5 mL) was filtered through a standard vacuum filtration system with a polycarbonate filter membrane (Nuclepore track-etched polycarbonate hydrophilic membrane, 200 nm pore size) without applying vacuum during the filtration. At the end of the filtration process, vacuum was applied overnight to dry the SWNT film and the membrane. The film was removed from the filtration system after the SWNT film and the membrane were completely dry.

Atomic force microscopy (AFM)

Glass substrates with transferred aligned SWNTs films were placed on the AFM stage to collect images in a tapping mode with Digital Instruments Nanoscope IIIA. For collecting AFM images of SWNT dispersions, a drop was cast on a freshly cleaved mica and dried in air.

Scanning electron microscopy (SEM)

Aligned SWNTs were transferred onto a glass substrate and imaged with a Leo XB1540 Focused Ion Beam Mill SEM using in-lens mode in the clean room of the University of California, Riverside.

UV–vis–NIR spectroscopy

Absorption spectra of films and dispersions of SWNTs were collected with a Varian Cary 5000 spectrophotometer. Spectra of aligned SWNTs were recorded on films transferred on a glass substrate.

Raman spectroscopy

Raman spectra were recorded with a Nicolet Almega XR Dispersive Raman microscope using 532 nm laser excitation at 25% laser power; laser spot size is 1 μm.

Fabrication of two-terminal devices

Two-terminal devices were fabricated to study the effect of hexahapto complexation of Cr on the resistance of aligned SWNT films. The aligned SWNT thin films were transferred on a glass substrate with pre-patterned gold contacts separated by 10 μm (channel length). The SWNT film width was in the range of 500–800 μm. For device preparation, the polycarbonate membrane with the SWNT film was placed on the substrate with the SWNT film facing the glass surface and a few drops of ethanol

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were added to improve adhesion. The polycarbonate membrane was removed by first dissolving it in *n*-methyl-2-pyrrolidone (NMP) vapors followed with an NMP bath washing for 1 h. Two device configurations were used in which the SWNT alignment direction was transverse and parallel to the channel length (respectively current flow). The devices were annealed at 300 °C for 8 h in vacuum (10^{-6} Torr) and immediately transferred into a glove box for the photochemical reaction.

Photochemical reaction

$Cr(CO)_6$ (Sigma–Aldrich 98%) was dissolved in degassed acetonitrile inside a glove box to obtain a solution with concentration of 1×10^{-3} M. Using a pipette, a drop (~0.1 mL) of the solution was cast onto the SWNT film surface, followed by irradiation with UVC light of 254 nm.

Resistance measurement

The resistance of the films was monitored in-situ with a LabVIEW-controlled Keithley 236 source measure unit connected to the device set-up inside the glove box via an electrical feedthrough.

Fabrication of electro-optical switches

Aligned SWNT film devices fabricated in the transverse configuration were annealed at 300 °C for 8 h in vacuum (10^{-6} Torr) and transferred to a glove box. In these experiments the aligned SWNT thin-film devices had a channel length of 100 μm and width in the range of 500–800 μm. The films were sealed using adhesive frames (Frame-Seal™, Bio-Rad Laboratories) and the chamber of the frame was filled with an acetonitrile solution of $Cr(CO)_6$ (0.05 mM) and ionic liquid (diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide, DEME-TFSI, IoLiTec, Inc.). The volumetric ratio of Cr reagent solution to DEME-TFSI was 85:15. A Pt wire ($d = 25$ μm, Alpha Aesar), inserted through the seal into the solution, was used to apply potential (top gate). A quartz substrate (Ted Pella; 2.54 cm × 2.54 cm × 0.1 cm) served as an UV-transparent window. The potential applied between source (S) and drain (D) was 0.05 V (Keithley 236) and the gate voltage (V_G) was 0.6 V (Keithley 2700). The data were collected with a custom LabView software.

Results and discussions

Aligned SWNT thin films provide an ideal platform to study the nature of the interaction between transition metal atoms and graphitic surfaces, due to the densely packed individual SWNTs and the giant anisotropy of electrical resistance in directions parallel and perpendicular to the nanotube alignment. In this work, we prepared aligned SWNT thin films and explored the effect of bridging the adjacent carbon nanotubes with Cr atoms on the film conductivity in transverse and parallel directions.

We have pursued the organometallic chemistry of carbon nanotubes in solution phase [34,45,46] and in solid-state [36,47,48] reactions and have shown that this leads to the formation of covalent bis-hexahapto-SWNT-M bonds (M = Cr, Mo, W, V, Mn). Previous studies utilized random networks of SWNT thin films, in which the transport properties were dominated by the carbon nanotube junctions, and our experiments showed that the covalent hexahaptobonds formed by chromium to the sidewalls of the SWNTs are very effective in reducing the nanotube junction resistance and increasing the film conductivity [36,48]. If achieved in aligned SWNT films, this mode of bonding would have a profound effect on the degree of electrical anisotropy, and we anticipated that hexahapto bond formation is feasible in homogeneous and sufficiently dense films of aligned SWNTs, in which the distance between adjacent SWNTs approaches the van der Walls distance of 3.15 Å [49]; a stable molecular structure in the bis(benzene) chromium complex is associated with a distance of 3.226 Å between two benzene rings [50].

Homogeneous, dense, preferentially aligned SWNT thin films were prepared by slow filtration [15] as shown in Fig. 1a–c. The SWNT dispersions, used for the film preparation, contained individual SWNTs as evidenced by the absorption spectrum that exhibits sharp and well resolved electronic absorption bands and the AFM imaging (Fig. 1d–f). The length of the SWNTs is in the range of 0.5–4 μm (Fig. 1e), and the average diameter is ~1.4 nm (Fig. 1f), in good agreement with the average diameter of arc-produced SWNTs [51,52].

The alignment of the SWNT thin films was assessed with AFM and SEM; typical images shown in Fig. 2a and b illustrate that the SWNTs are relatively well aligned and exist in small bundles (average bundle size 5–7 nm). Further, spectroscopic characterization confirmed the SWNT alignment, which resulted in polarization-dependent absorption and Raman spectra as illustrated in Fig. 2c and d. For these measurements, the SWNT films were rotated to align the electric field of the incident light parallel and perpendicular to the nanotube alignment direction.

For the absorption measurements, baseline corrections for the bare glass substrate were performed in both directions. The first two interband transitions of semiconducting nanotubes (S_{11} and S_{22}) and the first interband transition of metallic nanotubes (M_{11}) are strongly suppressed in the perpendicular direction as compared to the parallel polarization (Fig. 2c). The largest Raman intensity in the spectrum of aligned SWNT films is observed when the polarization of the laser beam was along the SWNT axes and the absorption/emission of light is highly suppressed for light polarized perpendicular to the nanotube axis, producing a very weak signal [53–55]. The intensity of the G-peak in the parallel direction ($I_{\parallel}$) is 3 times larger than that obtained in perpendicular direction ($I_{\perp}$), confirming the high degree of alignment of the SWNTs [15].

We prepared two sets of devices (Fig. 3a), in which the SWNT films were placed in two distinct orientations: (i) parallel aligned SWNT films, in which the SWNTs span the channel length for measurement of the parallel conductivity (current flows along the SWNT axis) and (ii) transverse aligned SWNT films, in which the tubes are aligned along the width of the electrodes for the transverse conductivity measurement (current flows across the individual nanotubes).

The measured transverse conductivity of aligned pristine SWNT films (thicknesses τ in the range of 0.5–1 nm) after thermal annealing varied between 1 and 30 S/cm. In the parallel direction the aligned SWNT films exhibited conductivity of ~270–1500 S/cm. Thus, the electrical anisotropy of the aligned SWNTs in our experiments varied in the range of 50 to about

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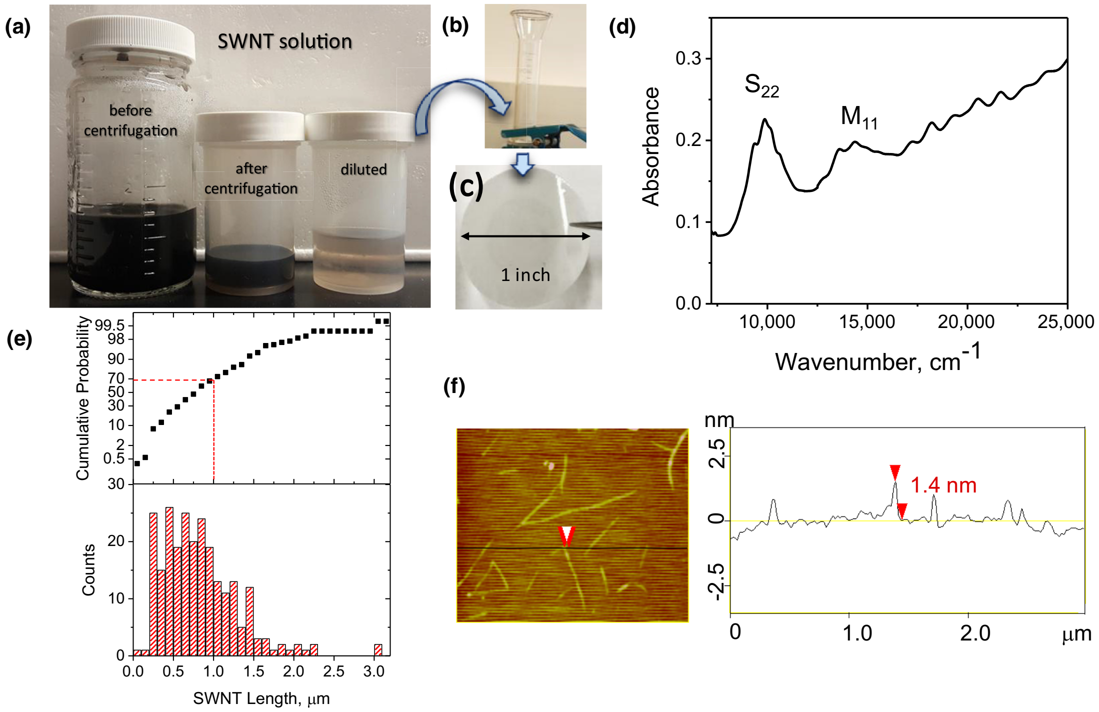

FIGURE 1

Aligned SWNT film preparation: (a) Aqueous dispersions of electric arc-discharge SWNTs used for preparation of aligned SWNT films. (b) Filtration apparatus for film preparation. (c) A photograph of aligned SWNT thin film on filtration membrane. (d) Absorption spectrum of SWNT dispersion. (e) Distribution of SWNT length estimated from AFM images. (f) AFM image and height profile of SWNTs present in the dispersions used for film preparation.

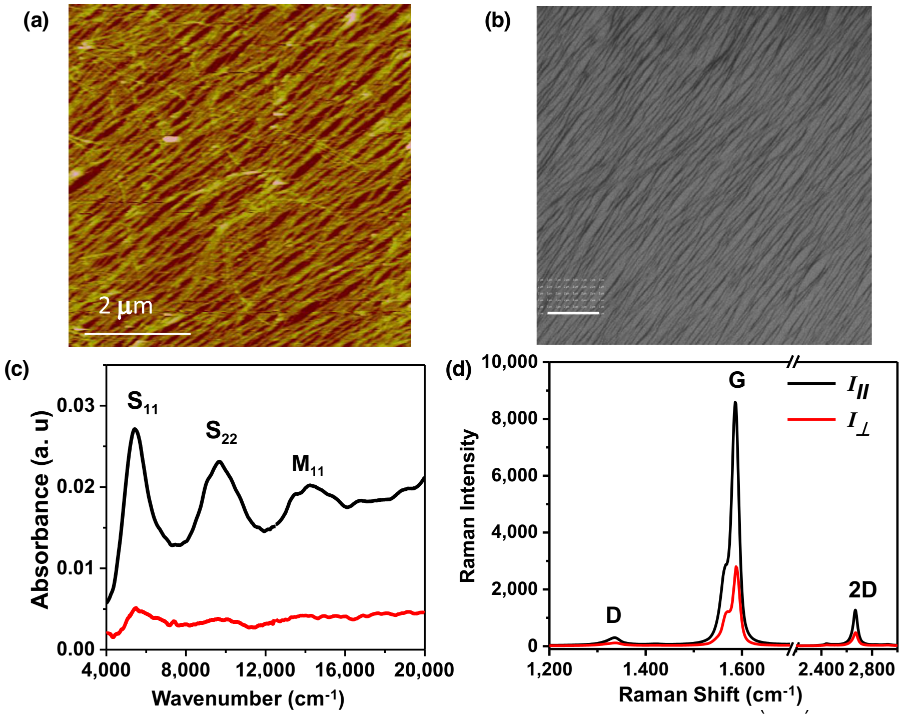

FIGURE 2

Characterization of aligned SWNT films: (a) AFM and (b) SEM images of densely packed, aligned SWNTs. (c) Absorption spectra of aligned SWNTs recorded with the incident light beam parallel (black) and perpendicular (red) to the SWNT alignment direction (d) Raman spectra of aligned SWNTs collected with the polarization direction of the incident laser beam parallel (black) and perpendicular (red) to the nanotube alignment direction.

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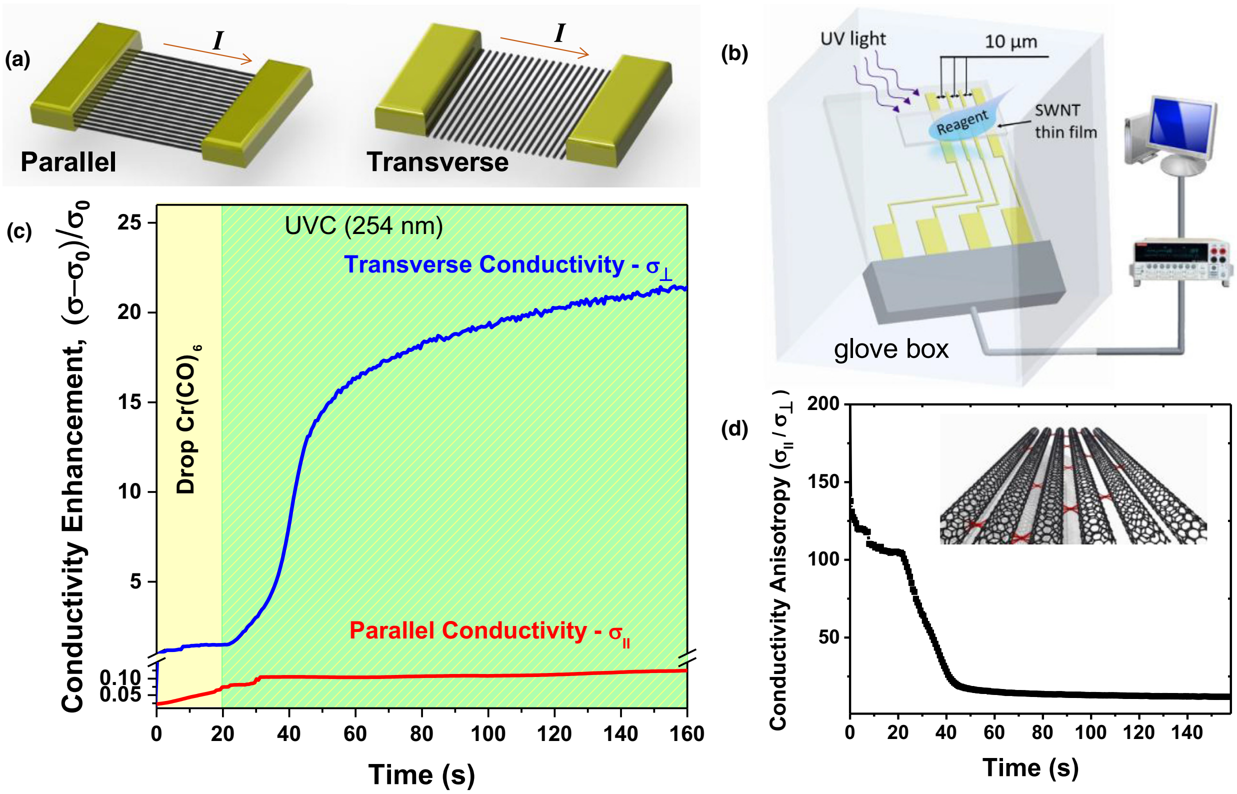

FIGURE 3

Effect of hexahapto bonds of chromium on the conductivity of aligned SWNTs. (a) Schematics of the device configurations used for measurement of transverse and parallel conductivities; the dimensions are not to scale. (b) Experimental set-up for the photochemical reaction between aligned SWNT films and $Cr(CO)_6$. (c) Enhancement of aligned SWNT thin-film conductivities (transverse and parallel) on photochemical reaction with $Cr(CO)_6$. (d) Electrical anisotropy as a function of reaction time. The inset shows a schematic of aligned SWNTs with atomic interconnects (red) (η^6-SWNT)Cr(η^6-SWNT).

270, depending on the degree of alignment. To interconnect the aligned SWNTs, we used a photochemical route that is known to generate bishexahapto bonds between the Cr atoms and the graphitic surfaces of SWNTs [46]. A drop of $Cr(CO)_6$ solution in acetonitrile was placed on the surface of the film, which was then exposed to short-wavelength light, UVC of 254 nm. The change of the film resistance was followed by in-situ measurement with the experimental setup shown schematically in Fig. 3b.

Upon irradiation of the films with UVC light of 254 nm, the resistance of the films decreased and the trend of conductivity enhancement of the aligned SWNT films in the two alignment directions is shown in Fig. 3c. The transverse conductivity, $\sigma_\perp$, of one film increased dramatically from 1 S/cm to 22 S/cm, producing a conductivity enhancement of more than 20 times (2100%), whereas nearly no enhancement was recorded for the aligned SWNT film with parallel device configuration (conductivity increase of ~10%). The dramatic increase in the transverse conductivity combined with the moderate increase in parallel conductivity leads to a reduced electrical anisotropy of the aligned SWNT thin films, which decreases from >100, in pristine films, to less than 10 after interconnecting the SWNTs with Cr atoms (Fig. 3d). The effect of interconnecting aligned SWNTs on the electrical anisotropy of the films can be further enhanced by optimization of the alignment homogeneity, tube density, and channel length.

The increase in SWNT film conductivity can be explained by the formation of covalent bishexahapto bonds between the Cr atoms and the graphitic surfaces of the nanotubes (η^6-SWNT) Cr(η^6-SWNT) as shown in Fig. 3d (inset). Because this mode of bonding preserves the electronic structure of SWNTs (constructive rehybridization), it bridges the individual SWNTs at the atomic scale, leading to improved intertube junction resistance, and it has been shown to effectively operate in random networks of SWNTs [46,48,56–59]. As discussed in our previous work [46,48,56–59], the formation of the hexahapto constructive covalent bonds between the sidewalls of a pair of individual SWNTs is both kinetically and thermodynamically favorable due to the fact that the van der Waals distance (3.15 Å) between adjacent SWNTs is close to the length of the hexahapto bond formed between Cr and the benzene ligands in bisbenzene chromium (3.226 Å). Furthermore, the formation of bishexahapto coordination will lower the energy of the system and satisfy the 18-electron rule required for a stable complex [36,46,60].

We next discuss the effect of the improved intertube junctions on the conductivity of aligned SWNT thin films in parallel and transverse directions. We first consider the transport mechanism in direction parallel to the SWNT axis. From the AFM measurements (Fig. 1e), we estimate that more than 30% of the SWNTs have a length of >1 μm and about 10% of the tubes have length between 1.5 and 3 μm. In these experiments, the channel length is 10 μm, and assuming SWNT length of 2 μm, we estimate that the formation of a conducting path between the electrodes requires about 5 nanotubes, i.e. 4 junctions. Further, our experiments involve SWNT thin films with a density of

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300 tubes/μm or higher, which is far beyond the critical density needed for percolation transport [17]. Thus, because the films are comprised of a statistical mixture of metallic and semiconducting SWNTs, there is a reasonably high probability of all-metallic SWNT conducting paths in our devices. The contact resistance between metallic SWNTs is known to be small [7,61], and interconnecting random networks of metallic SWNTs with Cr atoms leads to a moderate conductivity increase ($\ll 1$) [48]. It is also important to note that the aligned SWNTs contain small bundles (5–7 nm diameter), and these bundles are long enough to span the 10-μm-long channel of our devices, i.e. the current in parallel direction may be carried by a single bundle.

In the transverse direction, the current tunnels through more than thousands of junctions (7000 junctions assuming individual SWNTs with an average diameter of 1.4 nm; ~1400 junctions assuming SWNT bundles with an average diameter of 7 nm); thus, improvement of these junctions dramatically increases the film conductivity.

The presented analysis sheds light into the observed changes of parallel and transverse conductivity of aligned SWNT films in the present device configuration. There are very few (or no) junctions involved in the current transport along the direction of SWNT alignment, in contrast to thousands of junctions in transverse direction. The reported results are a manifestation of the constructive conductive nature of the bond formed between the Cr atoms and the graphitic SWNT surfaces. The hexahapto bridging of SWNTs is distinct from (i) the classic covalent bond, which introduces sp^3 centers in the SWNT walls and serves as a scattering center leading to conductivity decay in both directions, and (ii) ionic doping (charge transfer) [62,63], which increases the conductivity in parallel direction with little effect on the transverse conductivity.

We demonstrate that the organometallic, interconnected, aligned SWNTs can be used as optoelectronic devices with a reliable and reversible conductance switching. Because the conductivity of the aligned SWNT thin films in transverse configuration changes dramatically when adjacent nanotubes are atomically bridged with Cr, the ability to reverse the complexation offers a route to engineer a switch. The concept is based on the fact that the formation of the (η^6-SWNT)Cr(η^6-SWNT) complex is associated with the stable 18-electron electronic configuration. Adding extra electrons to the conduction band (lowest unoccupied molecular orbital, LUMO) is anticipated to destabilize the bond and electrically decouple the nanotubes. Thus, the aligned transverse SWNT channel can be reversibly switched between a high-conductivity state (ON) using UV light and a low-conductivity state (OFF) by applying a gate potential. For fabrication of a switch, an aligned SWNT thin film was placed on a glass substrate with pre-patterned gold, Au, contacts (Fig. 4a) and sealed with a solution of a Cr-precursor and ionic liquid, IL (Fig. 4b). The use of ionic liquid as a dielectric affords significantly enhanced charge modulation as compared to solid-state dielectric, due to the large double layer capacitance that occurs at the interface of the film with the IL [64–66]. Applying positive potential to the Pt-wire results in accumulation of negative ions at its surface and positive ions at the SWNT film surface, with the later acting as ultimately close-laying gate.

For these experiments, the aligned SWNTs were interconnected by exposure to UVC light (254 nm) for about 10 min, after which the light was turned off and a gate voltage of +0.6 V was applied. The film electro-optical performance was then tested by in-situ measurement of the response of the SWNT channel resistance during exposure to UV light and applying a gate potential, respectively. Fig. 4c shows that the conductivity

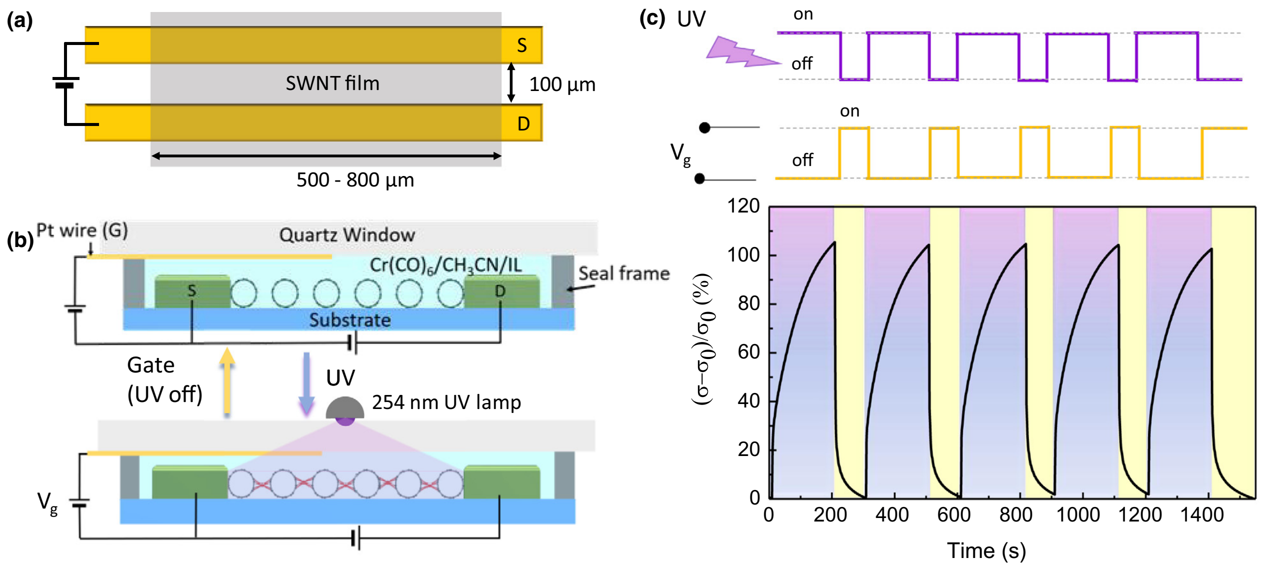

FIGURE 4

Electro-optical switch based on hexahapto-bridged aligned SWNT thin films. (a) Device geometry showing the aligned SWNT film on gold contacts before encapsulation. (b) Schematics illustrating the experimental set-up and the device details: the transverse aligned SWNT film is encapsulated with a solution of Cr reagent and ionic liquid, and a Pt-wire is used to apply potential (top gate). The aligned SWNT film is switched on by irradiation with UV light and turned off by applying gate voltage. (c) Change of device conductivity upon UV irradiation and gating.

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of the device is reversibly modulated by irradiation with UV light and gate potential. The conductivity increases by ~100% under UV light and decreases to its initial value when applying gate potential of +0.6 V (Fig. 4c). As discussed above, the increase in conductivity upon UV light irradiation is due to interconnecting the aligned SWNTs with Cr atoms (facilitated electron transport in transverse direction), whereas the decrease in conductivity during applying gate potential is assigned to reversing the hexahapto bonds. The positive gate potential shifts the Fermi level of the SWNTs increasing the electron population and destabilizing the overlap of the SWNT π-orbitals with the metal d-orbitals. It is important to note that UV irradiation of the SWNT thin-film devices fabricated only with IL (without the addition of the Cr-reagent) resulted in negligible change of resistance (Supporting Information).

The developed opto-electronic devices are distinctly different from previously reported approaches, in which the optical modulation of carbon nanotubes relies on control (selection) of the carbon nanotube band structure [67] or functionalization with photoactive molecules – chromophores and photosensitive polymers [68–70]. This novel approach opens opportunities for design of advanced atomic and molecular optoelectronic switches based on carbon nanotubes.

Conclusion

In summary, we demonstrated that bis-hexahapto-metal bonds can effectively bridge the surfaces of aligned single-walled carbon nanotube (SWNT) thin films. The formed atomic scale interconnects exert a dramatic effect on the transverse transport properties of SWNT thin films leading to a conductivity increase by a factor of ~20, while preserving the conductivity in parallel direction. The dramatically different effect of the organometallic chemistry on the electrical conductivity of aligned SWNT films confirms the covalent nature (constructive rehybridization) of the bonds formed between the Cr atoms and SWNT surfaces. This type of bond provides a means to engineer a reliable and stable opto-electronic switch, and we demonstrate a transverse-aligned SWNT device, which can be turned on by UV light and off by gate potential. This approach to optically modulate the electronic properties would advance the application of SWNTs in electronics, optoelectronics and sensors.

Furthermore, the aligned graphitic surfaces covalently functionalized with transition metals offer a platform for the assembly of ordered magnetic systems [38], which are of potential interest for quantum computing and magnetic nanodevices [71].

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mattod.2018.08.019.

References

[1] P.L. McEuen, Phys. World 13 (2000) 31–36.
[2] P. Avouris, Acc. Chem. Res. 35 (2002) 1026–1034.
[3] R.H. Baughman et al., Science 297 (2002) 787–792.
[4] C.M. Lieber, MRS Bull.. 28 (2003) 486–491.
[5] M.S. Fuhrer et al., Science 288 (2000) 494–497.
[6] E. Bekyarova et al., J. Am. Chem. Soc. 127 (2005) 5990–5995.
[7] M.A. Topinka et al., Nano Lett. 9 (2009) 1866–1871.
[8] L. Hu et al., Chem. Rev. 110 (2010) 5790–5844.
[9] G.H. Yu et al., Nat. Nanotechnol. 2 (2007) 372–377.
[10] X. Li et al., J. Am. Chem. Soc. 129 (2007) 4890–4891.
[11] M. Kinoshita et al., Opt. Express 18 (2010) 25738–25745.
[12] Q. Cao et al., Nat. Nanotechnol. 8 (2013) 180–186.
[13] M. Engel et al., ACS Nano 6 (2012) 7303–7310.
[14] S. Park et al., Adv. Mater. 27 (2015) 2656–2662.
[15] X.W. He et al., Nat. Nanotechnol. 11 (2016) 633–638.
[16] S.J. Kang et al., Nat. Nanotechol. 2 (2007) 230–236.
[17] M. Engel et al., ACS Nano 2 (2008) 2445–2452.
[18] E. Cubukcu et al., PNAS 106 (2009) 2495–2499.
[19] X. Xie et al., ACS Nano 6 (2012) 7981–7988.
[20] G.J. Brady et al., Sci. Adv. 2 (2016) e1601240.
[21] W.A. De Heer et al., Science 268 (5212) (1995) 845–847.
[22] J. Hone et al., Appl. Phys. Lett. 77 (2000) 666–668.
[23] J.E. Fischer et al., J. Appl. Phys. 93 (2003) 2157–2163.
[24] C.C. Jia et al., Science 352 (2016) 1443–1445.
[25] X.F. Guo et al., Science 311 (2006) 356–359.
[26] S. Niyogi et al., Acc. Chem. Res. 35 (2002) 1105–1113.
[27] J.L. Bahr, J.M. Tour, J. Mater. Chem. 12 (2002) 1952–1958.
[28] A. Hirsch, Angew. Chem. Int. Ed. 41 (2002) 1853–1859.
[29] D. Tasis et al., Chem. Rev. 106 (2006) 1105–1136.
[30] S. Sarkar et al., Mater. Today 15 (2012) 276–285.
[31] N. Tagmatarchis, M. Prato, J. Mater. Chem. 14 (2004) 437–439.
[32] Y.S. Lee, N. Marzari, Phys. Rev. Lett. 97 (2006) 116801.
[33] A. Setaro et al., Nat. Commun. 8 (2017) 14281.
[34] S. Sarkar et al., Chem. Sci. 2 (2011) 1326–1333.
[35] E. Bekyarova et al., Synth. Met. 210 (2015) 80–84.
[36] F. Wang et al., Appl. Phys. Lett. 100 (2012) 223111.
[37] E. Bekyarova et al., Acc. Chem. Res. 46 (2013) 65–76.
[38] S.M. Avdoshenko et al., ACS Nano 5 (2011) 9939–9949.
[39] V.K. Gupta et al., Water Res.. 45 (2011) 2207–2212.
[40] H. Khani et al., J. Hazard. Mater. 183 (2010) 402–409.
[41] V.K. Gupta et al., Comb. Chem. High Throughput Screen. 14 (2011) 284–302.
[42] V.K. Gupta et al., Sens. Actuators B 113 (2006) 182–186.
[43] V.K. Gupta et al., Talanta 144 (2015) 80–89.
[44] S. Sarkar et al., Adv. Mater. 25 (2013) 1131–1136.
[45] I. Kalinina et al., Macromol. Chem. Phys. 213 (2012) 1001–1019.
[46] A. Pekker et al., Mater. Horiz. 2 (2015) 81–85.
[47] F. Wang et al., J. Phys. Org. Chem. 25 (2012) 607–610.
[48] X. Tian et al., Nano Lett. 14 (2014) 3930–3937.
[49] A. Thess et al., Science 273 (1996) 483–487.
[50] A. Haaland, Acta Chem. Scand. 19 (1965) 41–46.
[51] F. Wang et al., Nano Lett. 10 (2010) 937–942.
[52] H.P. Liu et al., Nat. Commun. 2 (2011) 309.
[53] H. Ajiki, T. Ando, Phys. B 201 (1994) 349–352.
[54] H.H. Gommans et al., J. Appl. Phys. 88 (5) (2000) 2509–2514.
[55] A. Jorio et al., New J. Phys. 5 (2003) 139.
[56] S. Sarkar et al., Chem. Mater. 26 (2014) 184–195.
[57] M.L. Moser et al., Dalton Trans. 43 (2014) 7379–7382.
[58] M.L. Moser et al., ACS Appl. Mater. Interfaces 7 (2015) 28013–28018.
[59] I. Kalinina et al., Mater. Lett. 142 (2015) 312–316.
[60] M. Chen et al., Chem. Mater. 28 (2016) 2260–2266.
[61] P.N. Nirmalraj et al., Nano Lett. 9 (2009) 3890–3895.
[62] R.S. Lee et al., Nature 388 (1997) 255–257.
[63] A.M. Rao et al., Nature 388 (1997) 257–259.
[64] Z. Wu et al., Science 305 (2004) 1273–1276.
[65] S.Z. Bisri et al., Adv. Mater. 29 (2017) 1607054.
[66] H. Shimotani et al., Adv. Funct. Mater. 24 (2014) 3305–3311.
[67] P. Avouris et al., Nat. Photonics 2 (2008) 341–350.
[68] X.F. Guo et al., J. Am. Chem. Soc. 127 (2005) 15045–15047.
[69] D.W. Steuerman et al., J. Phys. Chem. B 106 (2002) 3124–3130.
[70] X.Y. Zhang et al., Nat. Commun. 7 (2016) 11118.
[71] S. Samouhos, G. McKinley, J. Fluids Eng. 129 (2007) 429–437.

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