From Broadband to Electrochromic Notch Filters with Printed Monochiral Carbon Nanotubes

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Supporting Information

ABSTRACT: Dense layers of semiconducting single-walled carbon nanotubes (SWNTs) serve as electrochromic (EC) materials in the near-infrared with high optical density and high conductivity. EC cells with tunable notch filter properties instead of broadband absorption are created via highly selective dispersion of specific semiconducting SWNTs through polymer-wrapping followed by deposition of thick films by aerosol-jet printing. A simple planar geometry with spray-coated mixed SWNTs as the counter electrode renders transparent metal oxides redundant and facilitates complete bleaching within a few seconds through iongel electrolytes with high ionic conductivities. Monochiral (6,5) SWNT films as working electrodes exhibit a narrow absorption band at 997 nm (full width at half-maximum of 55 ± 73 nm) with voltage-dependent optical densities between 0.2 and 4.5 and a modulation depth of up to 43 dB. These (6,5) SWNT notch filters can retain more than 95% of maximum bleaching for several hours under open-circuit conditions. In addition, different levels of transmission can be set by applying constant low voltage (1.5 V) pulses with modulated width or by a given number of fixed short pulses.

KEYWORDS: electrochromic filter, notch, single-walled carbon nanotubes, near-infrared, pulse-width modulation

INTRODUCTION

Electrochromic (EC) materials change their transmittance or reflectance across a characteristic spectral range upon modulation of their charge state (neutral, reduced, or oxidized) via an applied voltage (typically 1–3 V). This electrochromism provides the basis for a number of practical applications such as smart windows, tunable filters, information displays, and so forth, and has received considerable attention over the last decade.2–6 EC materials range from inorganic oxides (e.g., tungsten trioxide) and Prussian blue to organic polyaniline, conjugated polymers (e.g., containing propylene dioxythiophene units), and redox-active molecules (e.g., viologens) and can cover broad wavelength ranges from the ultraviolet to the near-infrared (nIR).4,7–13 A typical EC device consists of a film of the EC material on a transparent working electrode, a counter electrode, and an electrolyte sandwiched between them. The electrolyte might be liquid or solid. Its ionic conductivity determines to a large degree the switching speed of the device. Transparent conductive oxides (e.g., indium tin oxide) are often employed as the electrode material; however, in recent years, flexible substrates and geometries for soft electronics are sought after, and thus, alternative electrode materials are being investigated (e.g., metal nanowire networks).14–17

The current range of EC materials allows for easily produced EC filters with absorption bandwidths of several hundred nanometers. Especially in the nIR—important for heat management but also telecommunication applications—the very broad absorption of polarons in conjugated polymers can be utilized.15 However, notch filters, for example, for blocking laser light, require a very narrow absorption band with very high optical density. Commercial notch filters are made of dielectric stacks that result in high transmission rejection through destructive interference and reflection in the stop band. In the nIR, they typically show a blocking region with an optical density of 4–6 and a full width at half-maximum (fwhm) of 30–70 nm. However, the dielectric stack geometry leads to highly angle-dependent absorption maximum, restrictions regarding substrates (not flexible, usually fused silica), and clearly, the optical density of these notch filters is not tunable.

Dense films of monochiral (single species) single-walled carbon nanotubes (SWNTs) would be ideal candidates for the realization of EC nIR notch filters owing to their excitonic E₁₁₁ transition in the nIR with a very high absorption cross
section, very narrow linewidth, and diameter-specific spectral position. The absorption modulation of SWNTs in electrochemical cell configurations has been demonstrated for both semiconducting and metallic nanotubes that were purified by various methods including polymer-wrapping and density-gradient centrifugation. Both electron and hole doping lead to very effective absorption bleaching. However, despite the promising properties of single SWNT species, all current examples of carbon nanotube-based EC devices exhibit very broad nIR absorption spectra and only modest modulation depth. This is partially due to the use of fairly thin (<150 nm) SWNT networks. The use of polymer iongels based on ionic liquids with high ionic conductivity and wide electrochemical con gurations has been demonstrated for the puri cation of certain SWNT species and employ them in thin- lm EC devices with notch characteristics in the nIR. Airbrushing and aerosol-jet printing are used as scalable methods for the deposition of SWNTs as the working and the counter electrode. We use a simple and practical single-layer device geometry that avoids transparent conductive oxide electrodes altogether and makes use of the high charge carrier mobility in SWNT networks. The use of polymer iongels based on ionic liquids with high ionic conductivity and wide electrochemical windows enables fast switching within a few seconds and modulation depths of up to 43 dB. Further, these SWNT notch filters can be operated in a voltage-pulsed mode to create reproducible and persistent absorption levels.

■ RESULTS AND DISCUSSION

To create EC devices with semiconducting carbon nanotubes by additive deposition techniques and without any transparent oxides, we chose a lateral working electrode/counter electrode geometry on a thin glass substrate. The basic processing steps and the device structure are shown in Figure 1a. The counter electrode and contact to the optically active SWNT working electrode were based on a dense network of mixed metallic and semiconducting carbon nanotubes spray-coated through a shadow mask from an aqueous sodium cholate dispersion (see the Experimental section). The raw nanotube material (TUBALL: t-SWNT) exhibits a broad distribution of diameters and a mean length of over 5 μm. Such long nanotubes signi cantly reduce the sheet resistance (here about 100 Ω/ sq). The low price of this material (~8 $/g) makes it an ideal candidate for large-area applications. A horseshoe geometry (see Figure 1b) was chosen for the counter electrode to keep a short distance to and around the working electrode. This layout ensured a high electric field for fast ion movement and hence short response times. The counter electrode was roughly twice the area of the optically active film of the working electrode including the t-SWNT contact to avoid charging limitations for thicker layers.

Purely semiconducting SWNTs for the EC working electrode were extracted from different nanotube sources by the selective polymer-wrapping method. For the transition from EC broadbicolor to notch filters, three different SWNT dispersions with an increasing degree of selectivity were prepared. First, HipCO raw material (diameter range 0.8−1.2 nm) was dispersed in a toluene solution of the polythiophene P3DDT to obtain a dispersion with a broad range of semiconducting nanotubes because of its high spatial control to maintain a clear gap between the working and counter electrode. Using repeated printing cycles, it was possible to create films of increasing thickness from 10 to over 360 nm and the associated optical densities (ODs) with minimal volumes of SWNT ink. Spin-coating iongel electrolytes based on diferent ionic liquids (e.g., [EMIM][TFSI]) and encapsulation completed the devices (see the Experimental section). Scanning electron (Figure 1c,d) and atomic force micrographs (Supporting

Figure 1. (a) Schematic device fabrication process including airbrushing mixed t-SWNTs through a shadow mask to pattern the contacts and counter electrode, and aerosol-jet printing of (6,5) SWNTs as the optically active working electrode. (b) Illustration of the completed device. (c,d) Scanning electron micrographs of dense t-SWNT and (6,5) SWNT networks.
attributed to trion formation, that is, charged excitons. Along with the reduction of excitonic voltage is much stronger for the E11 than for the E22 transition. However, the relative drop of oscillator strength with cell thickness of nanotubes in agreement with their electrochemical distribution of nanotube diameters. Because of the many doping of the P3DDT and associated polaron absorption.

In contrast to the broad absorbance of the HiPCO/P3DDT films, the (7,5) SWNT/PFO cell was dominated by a narrow absorption band at 1041 nm (fwhm = 43 nm) with only small contributions from other nanotube species. The (6,5) SWNT/PFO-BPy sample showed a single narrowband E11 absorption at 997 nm (fwhm = 55 nm) and a weak phonon sideband at 860 nm. On the basis of the narrow fwhm of the absorbance peak, both of these films are operable as notch filters.

After application of a positive cell bias, the excitonic transitions were clearly bleached and absorption peaks corresponding to positive trions arose at 1212 nm for (7,5) and at 1166 nm for (6,5) SWNTs. In agreement with the work by Hartleb et al.,32 the well-resolved spectra of the (7,5) and (6,5) SWNT films showed a gradual change from E11 exciton and trion bands at moderate doping levels to a broad H-band in the highly doped regime. However, we found that the H-band of the (6,5) SWNTs also disappeared when the charge carrier concentration was increased even further (see Figure 2c). The required large applied potentials were facilitated by using iongels based on ionic liquids with wide electrochemical windows. In this transparent state of the notch filter, the transmittance was mainly limited by scattering at the four glass interfaces of the device. The residual wrapping polymers PFO and PFO-BPy did not show any absorption changes (bleaching or polaron absorption) because of their large band gaps (2.9 and 3.2 eV, respectively) compared to the semiconducting nanotubes.

In general, bleaching of the SWNT absorption is possible by electron and hole doping; however, despite encapsulation in dry nitrogen, not all devices showed optical modulation upon electron injection or only for significantly larger absolute cell voltages (see the Supporting Information Figure S5). This behavior was most likely due to electron-trapping by residual water55 in the relatively thick SWNT network.

To obtain high OD in the blocking state, (6,5) SWNT films with thicknesses up to 360 nm were prepared, yielding an OD of 4.5 at 997 nm. The fact that even for the thickest of these films the OD at the E11 transition could be bleached to the level of 0.2 shows that the intrinsic porosity of SWNT networks allows the electrolyte ions to penetrate the entire film. Consequently, the maximum modulation depth of these devices was well-individuated and formed dense networks after spraying or printing. A clear material contrast was observed at the boundary region between the mixed metallic/semiconducting t-SWNT film and the polymer-sorted semiconducting SWNT layer using the secondary electron in-lens detector of the scanning electron microscope (Supporting Information, Figure S3).

When an external voltage is applied between the two terminals of an EC cell, electrolyte cations and anions move according to the electric field lines and migrate into the porous nanomaterial networks where they form electric double layers around the nanotubes. Concurrently, electrons or holes are injected into the semiconducting SWNTs of the working electrode, whereas the counter electrode accumulates the complementary charge carriers. This capacitive behavior of our EC devices was apparent from their cyclic voltammograms (CVs, Supporting Information, Figure S4), which also indicate the available electrochemical window. The cells were always operated within their potential limits to avoid faradaic reactions of the electrolyte. Note that we apply the electrochemical convention for the definition of electrodes and bias. Thus, a positive cell voltage corresponds to hole injection/accumulation at the working electrode, that is, the optically active SWNT film of the device.

Figure 2 shows the absorbance spectra of the working electrodes based on the three different polymer-sorted SWNT dispersions at cell voltages from charge neutral to strong hole-doping. The neutral semiconducting SWNTs dispersed with P3DDT, (b) 78 nm thick film of (7,5) SWNTs wrapped with PFO, and (c) 35 nm thick film of (6,5) SWNTs sorted with PFO-BPy.

Figure 2. Absorption spectra at different positive cell voltages and controlled hole-doping of EC cells with the [EMIM][TFSI] iongel as the electrolyte and with (a) 166 nm thick film of HiPCO SWNTs dispersed with P3DDT, (b) 78 nm thick film of (7,5) SWNTs wrapped with PFO, and (c) 35 nm thick film of (6,5) SWNTs sorted with PFO-BPy.
reached 43 dB (Supporting Information, Figure S6). Given the sharp absorption of the (6,5) SWNT notch filters at 997 nm (Supporting Information, Table S1), their characteristics were studied in more detail.

While most EC devices are designed as a sandwich structure, in which the working and counter electrode face each other with very small distances, we have employed a lateral structure. This choice has a large effect on the electric field strength and distribution in the cell and thus the time-dependence of ion migration and the optical response after a voltage step. To investigate how charging and bleaching occur in different regions of the cell, we used photoluminescence (PL) imaging of a (6,5) SWNT network. PL is very sensitive to charges, and the resulting PL quenching provides a large contrast between doped and undoped nanotubes. When stepping the cell voltage from positive (hole-doping) to negative (electron-doping) for a device with a thick film of (6,5) SWNTs, the integrated PL shows a transient maximum (see the Supporting Information, Figure S7 and Video S1) that indicates temporary charge neutrality. The spatially resolved PL of the 2.5 × 2 mm² (6,5) SWNT film shows a clear emission front moving from the edges through the film over several seconds. It indicates a redistribution of ions and hole depletion until the film is charge neutral and electron injection can occur, which again quenches emission. The speed of the emission front movement seems to be mainly limited by the ion drift in the network, as the charge carrier mobility in doped SWNT networks is very high. The shape of the emission front edge is determined by the electric field distribution for the lateral electrode structure, as modeled in Figure S8 (Supporting Information).

Aside from absorption bleaching and PL quenching, the charging of the (6,5) SWNT film can be followed by in situ resonant Raman spectroscopy, as shown in Figure S9 (Supporting Information). The characteristic changes of the G’- and 2D-mode frequencies and intensities of (6,5) SWNTs were confirmed for negative and positive cell voltages. Further insight into the properties of the electrochemical cell can be gained through electrochemical impedance spectroscopy (EIS). Figure S10 (Supporting Information) shows the impedance spectra for a (6,5) SWNT device with an [EMIM][TFSI] ionic liquid at different cell voltages. Note that this ionic liquid was chosen for its high ionic conductivity, which enables significant charging of the semiconductor at moderately high frequencies. The clear decrease in the magnitude of impedance as the cell voltage changes from negative (filling of electron traps) to positive values (hole-doping) can be interpreted as an increase in effective electrode area due to the high conductivity of the doped (6,5) SWNT film. The relatively low phase angles (<75°) even at 10⁻¹¹ Hz indicate a significant resistive contribution of the ionic gel because of the large distance between the electrodes. This resistance clearly limits the response time of the EC cell and a dependence on SWNT film thickness, and conductivity of the ionic liquid might be expected.

For practical purposes, the response time of an EC device is evaluated by switching the device from its blocking (maximum absorbance) to its transparent state (minimum absorbance) in a potential step experiment. The current decays exponentially as a function of time, indicating capacitive charging. Figure 3a shows both the electrical and optical response when the cell voltage was stepped between 0 and +2.0 V. Note that an imposed cell voltage of 0 V does not imply the absence of an applied voltage or open-circuit conditions. Integrating the current yields a total injected charge of 1.8 × 10⁻³ C for a sample with a 35 nm thick (6,5) SWNT film and an [EMIM][TFSI] ionic gel.

The response times for bleaching (decay of absorbance) and recovery (rise of absorbance) were extracted from the absorbance versus time plot. The response time is commonly defined as the time after which either 63% (equal to 1 − 1/e) or 90% of the absorbance change has occurred. Because the change of absorbance does not follow a perfect monoexponential decay (see the log(absorbance) versus time plot in the Supporting Information Figure S11), the response time was defined here as the time after which 63% of the absorbance change has occurred and is presented for devices with different active film thicknesses and ionic liquid iongels in Figure 3b.

The response times ranged from about 0.2 s for very thin films with an [EMIM][TFSI] ionic liquid to over 20 s for a 350 nm thick film with an [EMIM][TFSI] ionic gel. As expected, the response times increased with the active film thickness but not to a degree that would be impracticable for applications. Further, the response times for bleaching and recovery differed for each sample by up to a factor of two. Some uncertainty stems from the dependence of the response time on the cycling history of the cell. Typically, a shorter recovery time (from hole-doped to neutral) is expected because of the electrical conductivity of hole-doped SWNTs, which facilitates charge transport in the initial stages of reduction in contrast to the neutral insulating state (see the Supporting Information, Figure S7). Unexpectedly, the switching speed did not scale directly with the reported ionic conductivities of the neat ionic liquid.
with the absorbance being at its slowest, [EMIM][TFSI] (9.3 mS cm\(^{-1}\)) to medium, and [EMIM][TCB] (16.3 mS cm\(^{-1}\)) to the fastest switching. While [EMIM][TCB] shows the fastest switching speed, [EMIM][FAP] comes very close, especially for thick films. This discrepancy could be due to the impact of gelation on the ionic conductivity for the three ionic liquids.38,39 Even more importantly, ion movement and double-layer formation in a porous network of nanotubes define the switching speed in these devices rather than bulk ionic conductivity. Response times of ∼1 s are relatively fast for EC cells,40 although they are still considerably slower than the SWNT-based broadband modulators presented by Moser et al.21 using a sandwich electrode structure and pure ionic liquids.

To confirm the long-term durability of our samples, a (6,5) SWNT device with the [EMIM][FAP] iongel was switched 900 times over the course of 15 h (Supporting Information Figure S12). The EC cell did not show any degradation but instead showed improvement of both modulation depth and response time with the number of cycles at the beginning followed by very stable switching behavior. This is a well-known effect in electrolyte-controlled systems and originates from enhanced electrolyte ion diffusion into the porous network.6

The application-oriented substitution of the ionic liquid with a solid iongel electrolyte comes at the price of slower switching speeds. However, a slow ionic movement can also be used for the retention of the bleached or recovered absorption state in the absence of applied voltage. This memory effect is a highly desirable property as the voltage does not have to be applied continuously, thus reducing unwanted power dissipation. Instead, devices can be operated in an energy-efficient way with short voltage pulses. As the self-discharge under open-circuit conditions is primarily due to thermal diffusion of ions within the cell, it should depend on ionic mobility of the electrolyte. We thus compared the self-discharge behavior of (6,5) SWNT EC devices (film thickness ≈ 360 nm) with iongels based on [EMIM][FAP] and [EMIM][TCB] as representatives of low and high ionic mobility electrolytes. The devices were charged at the maximum positive cell voltage within their respective electrochemical windows and the wires were disconnected, that is, open-circuit conditions without any external electric field as a driving force. Figure 3c shows the open-circuit discharge-induced increase of absorbance at the \(\epsilon_{11}\) transition over the course of 8 h. Here, we define the fraction of the maximum absorbance change \(\Delta A\) that is retained after time \(t\) under open-circuit conditions as

\[
\frac{A(\text{neutral}) - A(\text{charged}, t)}{A(\text{neutral}) - A(\text{charged}, t = 0)} = 100\%
\]

with the absorbance being at its maximum in the neutral state (determined beforehand) and at its minimum in the charged state at \(t = 0\). As expected, the discharge of the [EMIM][TCB] sample is much faster than that of the [EMIM][FAP] sample. As a value for an acceptable discharge between refresh pulses, we chose 5% of the maximum absorbance change of the device. The [EMIM][TCB] iongel sample reached this threshold after 15 min, whereas the [EMIM][FAP] iongel sample required 6.7 h to discharge to the same level. Given that EC devices with the [EMIM][FAP] iongel switch reasonably fast (<10 s) under applied bias but retain the bleached state for a long time under open-circuit conditions, they are the best choice for stable EC notch filters.

So far, we emphasized EC switching between states of maximum and minimum absorbance. As demonstrated in Figure 2, the absorbance at the \(\epsilon_{11}\) transition can also be tuned by holding the cell at different intermediate voltages. However, for practical purposes, the option of tuning to different absorption levels without the need of a potentiostat is highly desirable. For creating grayscale values of display pixels, the technique of pulse width modulation is often applied.40 Instead of equilibrating the sample at a certain cell voltage, the total injected charge and thus desired doping level is achieved by varying the width of a voltage pulse with constant amplitude. For dedoping the device and absorption recovery, the polarity of the voltage source is simply inverted. A constant voltage source, such as a 1.5 V battery, would be sufficient.

Figure 4a presents the concept of a variable pulse width series applied to a (6,5) SWNT EC modulator. The bio-inspired switching behavior of the [EMIM][FAP] iongel. Voltage pulses of 1.5 V were used, and between pulses, the cell was under open-circuit conditions for a delay time, \(t_d\). Once the cell reached the desired bleaching level, it was left at open circuit for 90 s before the quasi-equilibrium value was recorded. Figure 4b shows the absorbance after different bleaching pulses and the corresponding recovering pulses of optimized width. For bleaching pulse widths of >1.5 s, the recovering pulses had to be systematically shorter than the bleaching pulses to avoid overcompensation by electron injection. The number of injected charges (holes) correlated well with the achieved absorbance values (see Figure 4c). Finally, we optimized the bleaching pulse widths (see the Supporting Information, Table S2) such that eight roughly equally spaced absorbance levels could be set in a reproducible way.
fashion. Figure 4d visualizes these levels for two consecutive pulse series.

A similar but even simpler and more convenient approach is to replace the variable pulse widths with a variable number of short pulses of constant width as schematically shown in Figure 5a. The same (6,5) SWNT notch filter as in Figure 4 could also be tuned by a number of successive 1.5 V pulses with a constant width of 0.3 s. Figure 5b shows the equilibrium absorbance at 997 nm after completion of a pulse sequence (bleaching and recovery), and the complete time trace of the absorbance is shown in Figure 5c. This method offers the same precise control of the absorbance levels as the pulse width modulation method but is achievable with much simpler electronic circuits.

■ CONCLUSIONS

We have demonstrated an additive and scalable method for the fabrication of EC nIR notch filters without any transparent oxides, based solely on SWNTs for the electrodes and the optically active material. By selection of (6,5) SWNTs via polymer-wrapping and repeated aerosol-jet printing, thick nanotube films with very high ODs (up to 4.5) in the blocking state and with narrow linewidth were created that could be bleached by electrochemical doping. The properties of the resulting EC devices were comparable to commercial dielectric notch filters in the nIR wavelength range with the additional advantage of being contrast-tunable (modulation depth of 43 dB) and independent of angle of incidence. The cells could be switched within seconds from a blocking to an almost fully transparent state while also being able to retain more than 95% of a given absorption level for several hours under open-circuit conditions. Using this retention effect, the optical density of a cell could be set to at least eight reproducible and equidistant levels of absorption by applying constant voltage (1.5 V) pulses of modulated width or a certain number of pulses of constant width. The excellent performance parameters and simple additive processing will allow these EC notch filters to be added on demand, even to nonflat substrates, to convert passive optical components into tunable optically active devices with fast response times and low operating voltages.

■ EXPERIMENTAL SECTION

Preparation of SWNT Dispersions. As described previously, (6,5) SWNTs were selectively dispersed from CoMoCAT raw material (Chasix Advanced Materials, SG65i-L83, 0.38 mg mL−1) by shear-force mixing (Silverson L2/Air, 10 230 rpm, 72 h) with poly-[9,9-dioctyfluorenyl-2,7-diyl-alt-co-(6,6')-(2,2'-bipyrindine)] (PFOP-BPy, American Dye Source, Mw = 34 kg mol−1, 0.5 mg mL−1) in toluene. Employing the same procedure with poly-[9,9-dioctyfluorenyl-2,7-diyl)] (PFO, Sigma-Aldrich, Mw ≥ 20 kg mol−1) as the wrapping polymer resulted in an enrichment of (7,5) SWNTs. A broad distribution of semiconducting SWNTs was obtained by bath sonication of HipCO raw material (Unidym, Lot# P2172) with poly-(3-dodecylthiophene-2,5-diyl) (PDSDT, Mm = 9.7 kg mol−1, 2 mg mL−1) in toluene. All dispersions were centrifuged at 60 000 g (Beckman Coulter Avanti J26XP centrifuge) for 60 min to remove unexfoliated material. The supernatant was then passed through a polytetrafluoroethylene membrane filter (Merck Millipore, JVWP, 0.1 μm pore size) to collect the SWNTs. The filter cake was subsequently washed with toluene at 80 °C (3 × 10 mL) to remove excess polymer. The final inks for aerosol-jet printing were prepared by redispersion of the filter cake in a small volume of pure toluene by bath sonication for 30 min. The dispersion was diluted with toluene and terpineol to achieve the desired SWNT concentration and a terpineol concentration of 2 vol %. Typically, a SWNT concentration of 11 mg mL−1 (corresponding to an optical density of 6.0 and 4.0 cm−1 at the E111 transition for (6,5) and (7,5) SWNTs, respectively) was chosen. For HipCO SWNTs, the concentration was adjusted to an optical density of 1.2 cm−1 at 1286 nm (see Figure S1, Supporting Information for absorption spectra of all dispersions).

Dispersions of mixed metallic and semiconducting SWNTs (t-SWNTs) for contacts and counter electrodes were prepared from TUBALL raw material (OCsiAl, Lot# 109-16092015, 2 mg mL−1) by bath (2 h) and tip sonication (tapered tip, 15 min, 20% amplitude, 1 s on/off) in an aqueous solution of sodium cholate (Sigma-Aldrich, 6 mg mL−1). The resulting dispersion was centrifuged at 2970 g (Beckman Coulter Avanti J26XP centrifuge) for 90 min. The supernatant was collected, diluted 15-fold with an aqueous solution of sodium cholate (2 mg mL−1), and purified by a second centrifugation at 2970 g for 90 min. Immediately prior to spraying, the dispersion was diluted with deionized (DI) water to an optical density of 0.5 cm−1 at 660 nm.

Device Fabrication. The t-SWNT counter electrode and contact to the working electrode (both typically 60 nm thick) were airbrushed through a shadow mask (see below) onto patterned gold contacts on glass substrates (Schott AF 32 eco, 300 μm). After deposition, the films were soaked in DI water overnight to remove the surfactant. Subsequently, the 2.5 × 2.0 mm2 active film of polymer-sorted SWNTs was aerosol-jet-printed (see below) with a 0.4 × 0.2 mm2 overlap area with the t-SWNT contact. Rinsing the sample with tetrahydrofuran removed residual terpineol. A solution of an ionic liquid—either 1-ethyl-3-methylimidazolium triflate/fluorophosphate ([EMIM][FAP], Merck), 1-ethyl-3-methylimidazolium bis(trifluorosulfonyl)amide ([EMIM][TFSI], Merck), or 1-ethyl-3-methylimidazolium tetracyanoborate ([EMIM][TCB], Merck)—and the polymer poly(vinylidene fluoride-co-hexafluoro-propylene) (Sigma-Aldrich, Mw = 400 kg mol−1) in acetone (4:1:14 by mass) was spin-coated (2000 rpm, 30 s) onto the samples, and excess iongel was removed with
acetone. After annealing at 80 °C in dry nitrogen atmosphere overnight, the devices were encapsulated by placing a cover glass slide (Schott AF 32 eco, 300 μm) on top and sealing it with UV-curing epoxy (DELO KATIOBOND LP655) by low dose exposure at 400 nm (DELOLUX 20). Aerosol-Jet Printing. Polymer-sorted SWNT inks were printed with an Aerosol Jet 200 printer (Optomec Inc.), as described previously.42 The movable sample stage was at 100 °C to enable fast evaporation of toluene. A 200 μm inner diameter nozzle was used at a sheath gas flow of 30 scm and a carrier gas flow of 25 scm. Repeated printing cycles of grids were used to adjust the film thickness between 10 and 360 nm.

Characterization. Absorption spectra were recorded with a Cary 6000i absorption spectrometer (Varian Inc.) in a double beam mode. High-resolution images of SWNT networks were obtained with a Bruker Dimension Icon atomic force microscope and a JEOL JSM-7610F field-emission scanning electron microscope. Film thicknesses were determined with a Bruker DektakXT stylus profilometer. Two-electrode electrochemical measurements under potentiostatic control were performed with a ModuLab XM MTS impedance analyzer (Solastron Analytical).

REFERENCES

1. Mortimer, R. J.; Rosseinsky, D. R.; Monk, P. M. S. Electrochromic Materials and Devices; Wiley-VCH: Weinheim, 2015.
2. Baetens, R.; Jelle, B. P.; Gustavsen, A. Properties, Requirements and Possibilities of Smart Windows for Dynamic Daylight and Solar Energy Control in Buildings: A State-of-the-Art Review. Sol. Energy Mater. Sol. Cells 2010, 94, 87–105.
3. Cannavale, A.; Cossari, P.; Eperon, G. E.; Colella, S.; Fiorito, F.; Gigli, G.; Snaith, H. J.; Listorti, A. Forthcoming Perspectives of Photoelectrochromics: Devices: A Critical Review. Energy Environ. Sci. 2016, 9, 2682–2719.
4. Neo, W. T.; Ye, Q.; Chua, S.-J.; Xu, J. Conjugated Polymer-Based Electrochromics: Materials, Device Fabrication and Application Prospects. J. Mater. Chem. C 2016, 4, 7364–7376.
5. Rennme, J.; Shen, D. E.; Mustonen, T.; Fruehauf, N. High Performance and Long-Term Stability in Ambiently Fabricated Segmented Solid-State Polymer Electrochromic Displays. ACS Appl. Mater. Interfaces 2015, 7, 12001–12008.
6. Jensen, J.; Hösel, M.; Dyer, A. L.; Krebs, F. C. Development and Manufacture of Polymer-Based Electrochromic Devices. Adv. Funct. Mater. 2015, 25, 2073–2090.
7. Jelle, B. P.; Hagen, G. Performance of an Electrochromic Window Based on Polyaniiline, Prussian Blue and Tungsten Oxide. Sol. Energy Mater. Sol. Cells 1999, 58, 277–286.
8. Beaugé, P. M.; Reynolds, J. R. Color Control in π-Conjugated Organic Polymers for Use in Electrochromic Devices. Chem. Rev. 2010, 110, 269–320.
9. Moon, H. C.; Kim, C.-H.; Lodge, T. P.; Frisbie, C. D. Multicolored, Low-Power, Flexible Electrochromic Devices Based on Ion Gels. ACS Appl. Mater. Interfaces 2016, 8, 6252–6260.
10. Granqvist, C. G. Oxide Electrochromics: An Introduction to Devices and Materials. Sol. Energy Mater. Sol. Cells 2012, 99, 1–13.
11. Amb, C. M.; Dyer, A. L.; Reynolds, J. R. Navigating the Color Palette of Solution-Processable Electrochromic Polymers. Chem. Mater. 2011, 23, 397–415.
12. Kim, K.-W.; Oh, H.; Bae, J. H.; Kim, H.; Moon, H. C.; Kim, S. H. Electrostatic-Force-Assisted Dispensing Printing of Electrochromic Gels for Low-Voltage Displays. ACS Appl. Mater. Interfaces 2017, 9, 18994–19000.
13. Gélinas, B.; Das, D.; Rochefort, D. Air-Stable, Self-Bleaching Electrochromic Device Based on Viologen- and Ferrocene-Containing Trilimide Redox Ionic Liquids. ACS Appl. Mater. Interfaces 2017, 9, 28726–28736.
14. Eh, A. L.; Tan, A. W. M.; Cheng, X.; Magdassi, S.; Lee, P. S. Recent Advances in Flexible Electrochromic Devices: Prerequisites, Challenges, and Prospects. Energy Technol. 2017, 6, 33–45.
15. Cai, G.; Wang, J.; Lee, P. S. Next-Generation Multifunctional Electrochromic Devices. Acc. Chem. Res. 2016, 49, 1469–1476.
16. Oh, H.; Seo, D. G.; Yun, T. Y.; Kim, C. Y.; Moon, H. C. Voltage-Tunable Multicolor, Sub-1.5 V, Flexible Electrochromic Devices Based on Ion Gels. ACS Appl. Mater. Interfaces 2017, 9, 7658–7665.
17. Kang, W.; Lin, M.-F.; Chen, J.; Lee, P. S. Highly Transparent Conducting Nanopaper for Solid State Foldable Electrochromic Devices. Small 2016, 12, 6370–6377.
18. Streit, J. K.; Bachilo, S. M.; Ghosh, S.; Lin, C.-W.; Weisman, R. B. Directly Measured Optical Absorption Cross Sections for Structure-Selected Single-Walled Carbon Nanotubes. Nano Lett. 2014, 14, 1530–1536.
19. Schöppler, F.; Mann, C.; Hain, T. C.; Neubauer, F. M.; Privitera, G.; Bonaccorso, F.; Chu, D.; Ferrari, A. C.; Hertel, T. Molar Extinction Coefficient of Single-Wall Carbon Nanotubes. J. Phys. Chem. C 2011, 115, 14682–14686.
20. Weisman, R. B.; Bachilo, S. M. Dependence of Optical Transition Energies on Structure for Single-Walled Carbon Nanotubes

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The authors declare no competing financial interest.

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ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b060643.

Absorption spectra of SWNT dispersions, AFM images of dense networks of polymer-sorted and mixed SWNTs, SEM images of the overlap region between polymer-sorted and mixed SWNT film, CVs of EC devices and reference sample, absorption spectra of devices in their electron-doped states, influence of active film thickness on optical and electrochemical properties, optical density and fwhm versus active film thickness, time-dependent PL quenching, electric field distribution for given electrode geometry, EIS data for a (6,5) SWNT device at different cell voltages, Raman analysis of (6,5) SWNTs at different cell voltages, definition of response time, cycling durability, and optimized pulse widths employed in the variable pulse width series (PDF). Spatial changes of PL of a (6,5) SWNT film while changing from hole-doped to electron-doped and back (AVI)
in Aqueous Suspension: An Empirical Kataura Plot. *Nano Lett.* 2003, 3, 1235–1238.

(21) Moser, M. L.; Li, G.; Chen, M.; Bekyarova, E.; Itkis, M. E.; Haddon, R. C. Fast Electrochromic Device Based on Single-Walled Carbon Nanotube Thin Films. *Nano Lett.* 2016, 16, 5386–5393.

(22) Kavan, L.; Dunsch, L. Spectroelectrochemistry of Carbon Nanostructures. *ChemPhysChem* 2007, 8, 974–998.

(23) Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. Transparent, Conductive Carbon Nanotube Films. *Science* 2004, 305, 1273–1276.

(24) Hartleb, H.; Spath, F.; Hertel, T. Evidence for Strong Electronic Correlations in the Spectra of Gate-Doped Single-Wall Carbon Nanotubes. *ACS Nano* 2015, 9, 10461–10470.

(25) Yanagi, K.; Moriya, R.; Yomogida, Y.; Takenobu, T.; Naitoh, Y.; Ishida, T.; Kataura, H.; Matsuda, K.; Maniwa, Y. Electrochromic Carbon Electrodes: Controllable Visible Color Changes in Metallic Single-Wall Carbon Nanotubes. *Adv. Mater.* 2011, 23, 2811–2814.

(26) Wang, F.; Itkis, M. E.; Bekyarova, E.; Haddon, R. C. Charge-Compensated, Semiconducting Single-Walled Carbon Nanotube Thin Film as an Electrically Configurable Optical Medium. *Nat. Photonics* 2013, 7, 459–465.

(27) Shimotani, H.; Tsuda, S.; Yuan, H.; Yomogida, Y.; Moriya, R.; Takenobu, T.; Yanagi, K.; Iwasa, Y. Continuous Band-Filling Control and One-Dimensional Transport in Metallic and Semiconducting Carbon Nanotube Tangled Films. *Adv. Funct. Mater.* 2014, 24, 3305–3311.

(28) Eckstein, K. H.; Hartleb, H.; Achnich, M. M.; Schöppler, F.; Hertel, T. Localized Charges Control Exciton Energetics and Energy Dissipation in Doped Carbon Nanotubes. *ACS Nano* 2017, 11, 10401–10408.

(29) Yu, L.; Shearer, C.; Shapter, J. Recent Development of Carbon Nanotube Transparent Conductive Films. *Chem. Rev.* 2016, 116, 13413–13453.

(30) Nish, A.; Hwang, J.-Y.; Doig, J.; Nicholas, R. J. Highly Selective Dispersion of Single-Walled Carbon Nanotubes Using Aromatic Polymers. *Nat. Nanotechnol.* 2007, 2, 640–646.

(31) Jakubka, F.; Grimm, S. B.; Zakharko, Y.; Gannott, F.; Zaumseil, J. Trion Electroluminescence from Semiconducting Carbon Nanotubes. *ACS Nano* 2014, 8, 8477–8486.

(32) Matsunaga, R.; Matsuda, K.; Kanemitsu, Y. Observation of Charged Excitons in Hole-Doped Carbon Nanotubes Using Photoluminescence and Absorption Spectroscopy. *Phys. Rev. Lett.* 2011, 106, 037404.

(33) Tanaka, Y.; Hirana, Y.; Niidome, Y.; Kato, K.; Saito, S.; Nakashima, N. Experimentally Determined Redox Potentials of Individual (n,m) Single-Walled Carbon Nanotubes. *Angew. Chem., Int. Ed.* 2009, 48, 7655–7659.

(34) Park, J. S.; Hirana, Y.; Mouri, S.; Miyauchi, Y.; Nakashima, N.; Matsuda, K. Observation of Negative and Positive Trions in the Electrochemically Carrier-Doped Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* 2012, 134, 14461–14466.

(35) Aguirre, C. M.; Levesque, P. L.; Paillet, M.; Lapointe, F.; St-Antoine, B. C.; Desjardins, P.; Martel, R. The Role of the Oxygen/Water Redox Couple in Suppressing Electron Conduction in Field-Effect Transistors. *Adv. Mater.* 2009, 21, 3087–3091.

(36) Grimm, S. B.; Schießl, S. P.; Zakharko, Y.; Rother, M.; Brohmann, M.; Zaumseil, J. Doping-Dependent G-Mode Shifts of Small Diameter Semiconducting Single-Walled Carbon Nanotubes. *Carbon* 2017, 118, 261–267.

(37) Thiemann, S.; Sachnov, S.; Poebsa, S.; Wasserscheid, P.; Zaumseil, J. Ionic Liquids for Electrolyte-Gating of ZnO Field-Effect Transistors. *J. Phys. Chem. C* 2012, 116, 13536–13544.

(38) Cho, J. H.; Lee, J.; He, Y.; Kim, B. S.; Lodge, T. P.; Frisbie, C. D. High-Capacitance Ion Gel Gate Dielectrics with Faster Polarization Response Times for Organic Thin Film Transistors. *Adv. Mater.* 2008, 20, 686–690.