Sensor Materials

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Electric Current Test Paper Based on Conjugated Polymers and Aligned Carbon Nanotubes**

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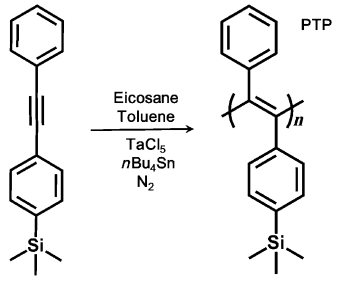
Although pH test papers cannot determine the pH value of a solution with the accuracy of a pH meter, they can be used to rapidly and easily determine narrow pH ranges in numerous applications by showing different colors. Since these color changes can be directly observed with the naked eye (Figure S1 in the Supporting Information), pH papers have been widely used in many fields. A broad spectrum of such test papers have also studied for other measurements, for example for determining the concentration levels of heavy metal ions.[1] Electric power represents one of the most widely used energy sources, and electric currents are typically measured by a current meter, which is inconvenient or even unavailable in many applications. It is critically important but remains challenging to synthesize low-cost and high-efficiency sensing materials that chromatically respond to electric currents.

Responsive polymers have attracted increasing attention as sensing materials due to the advantages of their tunable structure, light weight, low cost, and high performance.[2–4] Among them, polydiacetylene is one of the most studied candidates. Polydiacetylene shows obvious color changes in the visible-light range in response to various environmental stimuli such as changes in temperature, pH, chemical or mechanical stress, and exposure to light, magnetic, and electrical fields.[5–9] This chromatic transition is caused by the conformation change of polydiacetylene in response to these stimuli. However, the color changes are typically slow (tens of seconds to minutes) and irreversible, which has largely limited their application to sensing. To this end, a lot of attention has been paid recently to polyacetylene derivatives in which functional side groups were incorporated to tune the electronic state of the backbone with improved sensitivity and reversibility.[10] These polyacetylene materials were found to exhibit excellent sensing properties under stimuli including solvent and heat.[10,11] However, to the best of our knowledge, no responses to electric currents have been realized, though it is critically important for the optoelectronic application of polyacetylene.

Herein we report on a novel electrochromatic composite based on a polyacetylene derivative, poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] (PTP, Scheme 1), and aligned multiwalled carbon nanotubes (MWCNTs); this composite exhibits rapid changes in both color appearance and fluorescent intensity in response to currents ranging from 20 to 240 milliampere. In addition, the electrochromatic transitions were reversible for more than a thousand cycles. Although this application as an electric current indicator is our main demonstration here, the composite material can be also widely used for various other sensing applications.



Scheme 1. Synthesis of PTP.

First, the MWCNT arrays and PTP were synthesized (for more details see the Experimental Section). MWCNT sheets were then spun from MWCNT arrays,[12,13] and the sheet thickness could be typically varied from appropriately twenty nanometers to several micrometers. Figure 1 a exhibits a typical scanning electron microscopy (SEM) image of a MWCNT sheet, in which MWCNTs were highly aligned with many voids among them. The MWCNT/PTP composite film was then prepared by directly coating a PTP solution onto the MWCNT sheet (typically with a thickness of appropriately 400 nm), followed by evaporation of the solvent at room temperature (Figure S2). The composite film had a thickness

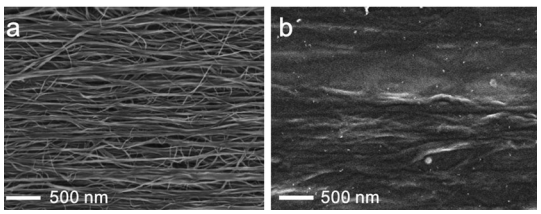


Figure 1. SEM images of a bare MWCNT sheet (a) and a MWCNT/PTP composite film (b).

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of approximately 600 nm. Figure 1b further shows an SEM image of a composite film viewed from on top. The aligned structure of MWCNTs had been well maintained, and the PTP was mainly coated on the top surface of the MWCNT sheet (Figure S3).

Due to the high alignment of MWCNTs, these composite films exhibited excellent mechanical and electronic properties, for example a tensile strength of up to 300 MPa and electrical conductivity of up to 380 $S\,cm^{-1}$ at room temperature. Since the conjugated PTP backbone was surrounded by a rigid "jacket" formed through the intra- and interchain molecular interactions of benzene and silicon moieties in the side chains,[14] the polymer main chain was shielded from the thermal attack. As a result, PTP exhibited a high thermal stability, reflected by its decomposition temperature of above 400 °C. After the incorporation of aligned MWCNTs, the decomposition temperature of the composite material was further increased to higher than 500 °C (Figure S4). Figure 2a,b further indicate that the composite films are flexible and can be bent for over one hundred cycles without breaking. The structure stability had been also verified previously by monitoring the electrical resistance of a composite film during the bending.[15] The resistances remained almost unchanged after bending for over a hundred cycles. Based on these combined properties one can expect that the composite film will have promising applications in flexible electronic and sensing devices that operate at high temperatures.

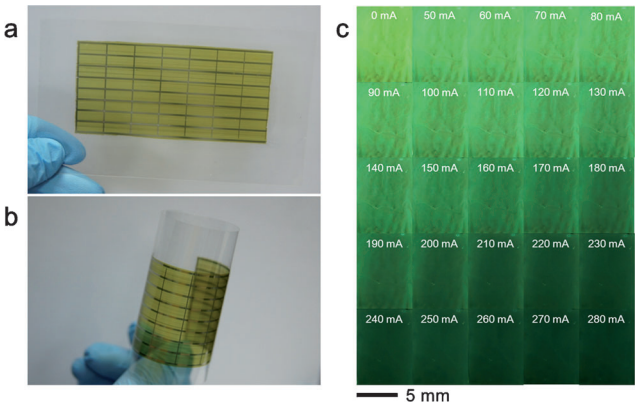

Figure 2. a, b) Photographs of flexible MWCNT/PTP composite films (56 standard units) on a poly(ethylene terephthalate) substrate. Each yellow rectangle corresponds to a standard current test paper, and the gray silver stripes are used as electrodes. c) Photographs of a standard current test paper when increasing currents from 0 to 280 mA were applied. The color of the test paper gradually changes from yellowish green to dark green.

Unexpectedly, the aligned MWCNT/PTP composite film chromatically responded to electric currents under UV light, and the color change was directly observed with the naked eye. Figure 2c shows photographs of a composite film with the applied current increasing from 50 to 280 mA. These photographs were recorded by a digital camera under illumination with UV light. A gradual color change from yellowish green to dark green was clearly observed, and the chromatic transition could be completed in one second upon passage or removal of the current. This electrochromatism of MWCNT/PTP composite film was highly reversible and could be repeated for over a thousand cycles with a current of less than 130 mA.

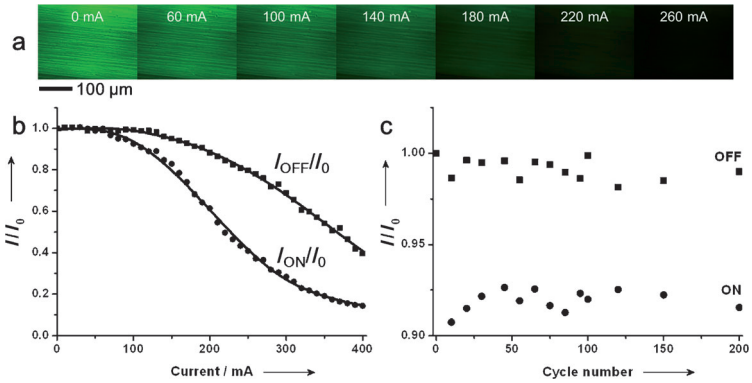

Figure 3. Fluorescent characterization of MWCNT/PTP composite films under different applied currents. a) Fluorescent micrographs. b) Dependence of the intensity ratio at the characteristic fluorescence peak on electric current upon connection ("ON") and after disconnection ("OFF") of direct currents. c) Dependence of the intensity ratio at the characteristic peak on the cycle number with an applied current of 100 mA. Here I_0 and I_{ON}/I_{OFF} correspond to the peak intensities before and after passage of the current, respectively.

The MWCNT/PTP composite film showed a strong fluorescence under irradiation with UV light. Upon application of a current above 60 mA, it exhibited rapid fluorescence quenching which could be traced qualitatively by fluorescent microscopy and quantitatively by fluorescent spectroscopy (Figure 3). Figure 3a shows fluorescent micrographs of a MWCNT/PTP composite film when passed with increasing direct currents, and higher currents induced more fluorescence quenching. Figure 3b further shows the dependence of fluorescent intensity on electric current when current was passed and then disconnected. It was found that, when the current was higher than 60 mA, fluorescence quenching began. The quenching degree (reflected by the intensity change at the characteristic peak in Figure S5) increased with the increasing current in the measured range up to 400 mA. The fluorescent intensity could be fully recovered after the disconnection of the current below a critical point of 130 mA. The reversible fluorescent change was also complete within one second. Specifically, the intensity of the characteristic peak reached the minimum in less than one second when current was passed through the composite film, and the peak was recovered in less than one second after disconnection of the current. The rapid fluorescent response to the electric current could also be directly observed by fluorescence microscopy. The composite film became darker upon passage of the current and recovered to the original brightness after disconnection. The reversible current-induced fluorescent quenching could be highly repeatable. Figure 3c shows the reversible fluorescent change for over 200 cycles at a current of 100 mA. When the applied current was equal to or higher

than 130 mA, changes in both color and fluorescent intensity became irreversible.

For the aligned MWCNT/PTP composite films, the current range for reversible changes in color appearance and fluorescent intensity was further tuned by varying the MWCNT content. For instance, the current ranges were controlled at 20–50, 30–90, 50–130, 80–180, and 110–240 mA for the MWCNT contents of 7, 13, 25, 44, and 61 wt%, respectively (Figure S6). In addition, a single composite film could be produced with different MWCNT contents. When MWCNT contents of 7, 25, and 61 wt% were used in a composite film, the current range spanned from approximately 20 to 240 mA. The efficient minimum MWCNT content was approximately 7% while the maximum MWCNT content could be higher than 61%.

Both the color change and the fluorescent quenching may be explained by the molecular perturbation and exciton deconfinement within the PTP backbone. As shown in Figure 4, the peaks at 375 nm and 430 nm are attributed to

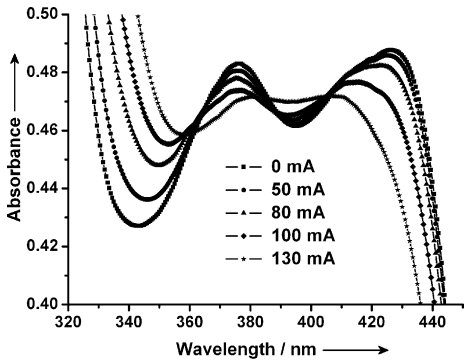

Figure 4. UV/Vis spectra of an aligned MWCNT/PTP composite film being passed with increasing electric currents.

the π–π* transition of localized electrons in PTP when the phenyl rings in the side chains are coplanar with and perpendicular to the backbone, respectively.[16] When electric currents were passed through the composite film, the two peaks were both shifted and the intensities decreased as the PTP backbone was perturbed in the two modes. The electrochromatic transition was observed as a result.

Two factors may contribute to the conformation change of PTP upon passage of electric currents. Firstly, MWCNTs were found to interact with the benzene rings of the polymer side chains by π–π interactions.[17] These interactions would be further strengthened under electric fields produced by aligned MWCNTs when electric currents are passed through them.[7c] As shown in Raman spectra (Figure S7), the characteristic peaks at 2645 and 1557 cm^{-1} for MWCNT and PTP, respectively, were shifted to 2652 and 1552 cm^{-1} after the formation of the composite film. Accordingly, they were further shifted to 2656 and 1554 cm^{-1} when a current of 100 mA was applied to the composite film. The increased interactions induced the reorganization of side chains when the electric current was higher than a critical value.[7a] Secondly, the MWCNTs functioned as collection of nanoheaters.[18] PTP was found to exhibit both color and fluorescent changes upon heating. Figure S8 shows a pure PTP film that displayed fluorescent quenching under increasing temperatures. Therefore, the electric energy was transferred from the aligned MWCNTs to the PTP by their interactions and by simple heating. The transferred energy could be enhanced by increasing the electric current and transfer efficiency. Here the transfer efficiency depends on the MWCNT density; in other words, higher density increases both MWCNT/PTP interactions and the heating efficiencies of MWCNTs with a higher transfer efficiency, which will be verified later.

When the current was lower than the first critical value, the increased interaction between MWCNT and PTP and the produced heat from MWCNTs were not high enough to change the PTP backbone, so no color changes were observed. When the current density was equal to or higher than the first critical point, a conformation change in PTP backbone occurred, and both color change and fluorescent quenching were detected. The extent of the color change was determined by the degree of backbone distortion, and a gradual transition was produced. When the current density was lower than the second critical value, the backbone conformation could be fully reverted, so reversible color change and fluorescent quenching were realized. With the further increase of the current to higher than the second critical value, the backbone conformation could not be recovered, so the electrochromatic transition became irreversible. Due to the high thermal stability of the PTP and the introduction of MWCNTs, the critical current can be easily tuned to achieve a high level by varying the structure and content of aligned MWCNTs. These MWCNT/PTP composite films can be extensively developed as electric current indicators similar to the pH test paper.

The preparation of the composite film could be easily scaled up based on a solution process to produce high-quality standard samples (Figure S9). Specifically, MWCNT sheets were uniformly attached to a flexible substrate along the same direction and a PTP solution was applied to produce the composite film. A designed mask with many rectangles of the same length and width and separated by the same distance was placed on the composite film. The length of the rectangle was parallel to the direction of MWCNT alignment. A conductive layer (e.g., silver) was finally deposited onto the masked composite film. Figure 2a and Figure S10 in the Supporting Information show 56 standard samples on a poly(ethylene terephthalate) substrate with each sample corresponding to a rectangle. These standard samples shared the same MWCNT content and structure, and the mechanical, electrical, thermal, and sensing properties of these samples were also uniform. Therefore, the electrochromatic films are promising for practical sensing applications.

In many fields, the sensing indicators are expected to be used in a fiber format in integrated or portable electronic devices.[19,20] To this end, the MWCNT/PTP composite materials were also made in fiber form with diameters ranging from several to tens of micrometers. In Figure 5a–d the structures of bare MWCNT and MWCNT/PTP composite fibers are compared. Similar to the composite film, MWCNTs are highly aligned in the composite fiber which has a tensile strength of about 500 MPa and electrical conductivity of

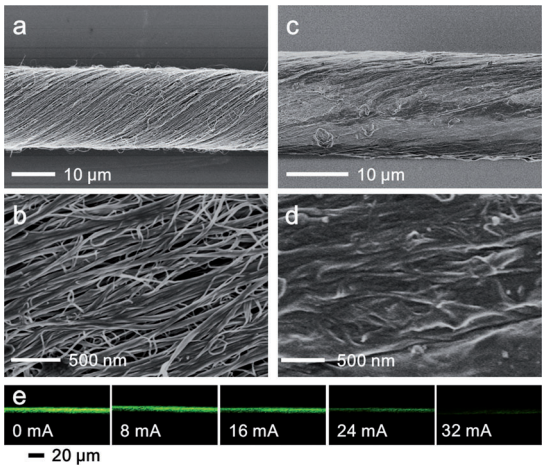

Figure 5. a) SEM image of a bare MWCNT fiber. b) SEM image of an aligned MWCNT/PTP composite fiber. c) Higher magnification of (a). d) Higher magnification of (b). e) Fluorescent micrographs of an aligned MWCNT/PTP composite fiber upon application of increasing direct currents.

about 370 $S\,cm^{-1}$. In addition, the composite fibers (MWCNT content: 25 wt%) also showed a rapid and reversible fluorescent quenching when currents were applied but with much lower values (Figure 5e). This phenomenon may be explained by the fact that, compared with the composite film which had an average MWCNT number density of $10^{10}\,cm^{-2}$, the composite fiber showed a higher average density of $10^{11}\,cm^{-2}$. As previously discussed, stronger interactions and more efficient energy transfer between MWCNT and PTP were produced. Similarly, the composite fiber also rapidly, reversibly, and gradually changed in color from yellowish green to dark green with increasing electric current.

Note that the electrochromatic transition of MWCNT/PTP composite materials had been detected with the assistance of UV light. To observe the color change directly with the naked eye, another conjugated polymer (Figure S11) with absorptions in the visible-light range was used to replace PTP. As expected, the resulting aligned MWCNT/polymer composite film exhibited electrochromatic transitions from blue to red and to yellow with increasing current (Figure S12).

In summary, aligned MWCNT/conjugated polymer composite materials showed rapid changes in both fluorescent intensity and color appearance in response to applied electric current. The electrochromatic transitions were reversible for over a thousand cycles, which enables various sensing applications. Although as an application demonstration, these composite materials were mainly investigated here as a new family of electric current indicators, they are also promising for applications in many other fields from microdevices to spacecraft. In addition, this work provides a general and effective strategy to solve the remaining problems in developing sensing materials with new promising sensitivities.

Experimental Section

To synthesize PTP, trimethyl[4-(phenylethynyl)phenyl]silane (0.75 g), toluene (1.19 mL), and eicoeane (0.50 mL) were first mixed in a Schlenk tube to form a uniform solution (2.4 mL); $TaCl_5$ (35.8 mg, 0.10 mmol), nBu_4Sn (65.6 μL, 69.4 mg, 0.20 mmol), and toluene (3.0 mL) were mixed in another Schlenk tube as a catalyst solution. After the catalyst solution had been heated for 15 min at 80°C, 2.0 mL of the monomer solution was added to start the polymerization under a nitrogen atmosphere. The polymerization was carried out for 24 h also at 80°C and quenched by addition of a mixture of toluene and methanol (1 mL, volume ratio 4:1). The resulting mixture was finally diluted with 300 mL of toluene and poured into methanol to form a PTP precipitate under stirring. The polymer product was separated by filtration and dried, and it was characterized by gel permeation chromatography and NMR, FTIR, and UV/Vis spectroscopy.[21] It showed an average molecular weight of 5.46×10^6 and polydispersity index of 1.43. ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 7.5$–6 (br s, 9, Ph), −0.5–0.1 ppm (br s, 9, $SiMe_3$); FTIR (KBr): $\tilde{\nu}$ =2990 (s), 1700 (w), 1565 (w), 1535 (w), 1430 (w),1250 (s), 1110 (m), 850 (s), 800 (s), 760 (m), 680 (s), 640 (w), 550 (s) cm^{-1}. UV/Vis (toluene): 434 nm (max), 375 nm. MWCNT sheets and fibers were prepared from MWCNT arrays by a dry spinning process.[10] Here MWCNT arrays were synthesized by chemical vapor deposition as described in the Supporting Information. For the fabrication of MWCNT/PTP composite films, MWCNT sheets were first stabilized on glass or polymer substrates, and a PTP solution in toluene (concentrations from 0.05 to 0.1 wt%) was cast onto the MWCNT sheets, followed by the evaporation of the solvent at room temperature. For the fabrication of aligned MWCNT/PTP composite fibers, as-spun MWCNT fibers were passed through the PTP solution. In the case of another conjugated polymer, the solution of monomer, i.e., CH_3-$(CH_2)_{11}CCCC(CH_2)_8COOH$ in tetrahydrofuran (concentration of 1%), was coated onto MWCNT sheets, followed by topochemical polymerization under UV light at room temperature.

The structures of MWCNTs and MWCNT/PTP composites were characterized by scanning electron microscopy (SEM, Hitachi FE-SEM S-4800, operated at 1 kV). The weight-average and number-average molecular weights were determined by GPC (HP1100 instruments, PLgel Mixed-B, 300 mm in length as the column and HPLC-grade tetrahydrofuran as the eluent at 40°C) based on a calibration by standard polystyrenes. UV/Vis, FTIR, ^1H NMR, and fluorescent measurements were made on the following instruments: Shimadzu UV-3150, Shimadzu IR Prestige-21, Bruker DMX 500, and Shimadzu-RF5301PC (with an excitation wavelength of 400 nm). Optical microscopy (Olympus BX51) was used to monitor the color change. The thermogravimetric analysis (Shimadzu DTG-60H) was conducted in air. Mechanical measurements were performed on a Hengyi tabletop Universal Testing Instrument. The fiber samples were mounted on paper tabs with a gauge length of 5 mm, and their sizes were determined by SEM. Electrical conductivities were obtained by a two-probe method.

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