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A Fully Self-Doped Electrochromic Conjugated Polymer Device Towards Neuromorphic Applications

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Abstract: Conjugated electrochemical memristors are a promising alternative towards bioelectronic circuitry. A self-doped PEDOT is synthesized, fabricated as a three-terminal device, and studied for electrochromic, memristive, and neuromorphic capabilities.

1. Introduction

Over the past decade, organic electrochemical transistors (OECTs) have been explored as biosensors [1], printed circuits [2], and neuromorphic devices [3]. The redox potential of OECTs offer a large range in nonvolatile linear conductance states at low gate switching voltages. In the case of the conjugated polymer, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), the p-type PEDOT allows mobile holes to hop from one chain to another where, in the stabilize form, these holes are compensated by PSS anions. Neuromorphic devices based on electrochemical materials, such as PEDOT:PSS, have been shown to emulate essential artificial neuronal and synaptic plasticities for learning and memory behaviors [3-6]. Device architecture resembling that of a concentration battery tunes the device through a multitude of conductance states via electrochemical (de)doping achieved by means of voltage pulsing to the gate electrode (cf. Figure 1a). Through tuning the conductance (redox state) of the PEDOT:PSS film, a visual electrochromic behavior can be observed via the films and can be shown as absorbance characteristics (cf. Figure 1b).

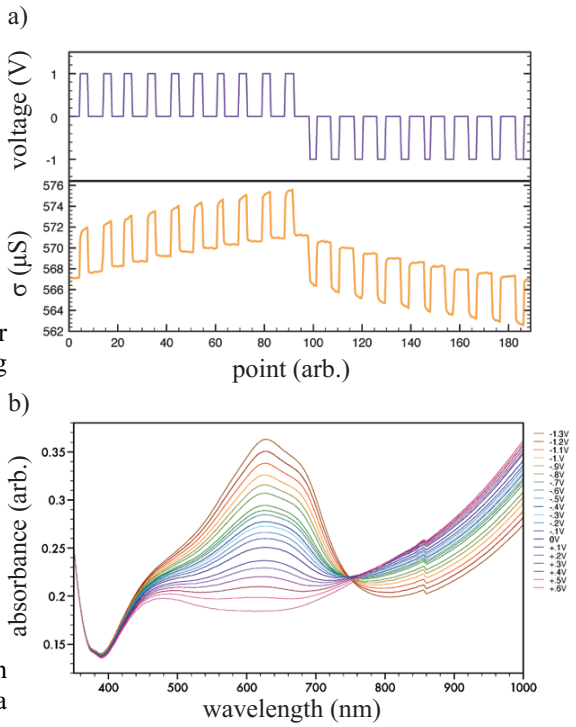

Figure 1: (a) Voltage-driven analog conductivity tuning of conjugated polymeric electrochemical memristor (cPECM) device showing 10 distant potentiated and depressed states. The gate electrode is probed with 500 ms ±1.0 V_G while monitoring the drain current (I_{DS}) with a channel voltage of -0.1 V_{DS}. (b) Electrochromic trends of a S-PEDOT film from -1.3 V (reduced) to +0.6 V (oxidized).

Major limitations of PEDOT:PSS devices are due to their inherent nature of the material to oxidize, which will impede on state retention and cycle stability for long-term memory applications [7]. Herein, a conjugated polymeric electrochemical memristor (cPECM) with a partially reduced, self-doped PEDOT (S-PEDOT) (cf. Figure 2a) is synthesized and fabricated into a flexible, all solid-state device with a polymeric gel electrolyte separation layer (Bu_4NPF_6 electrolyte embedded in a PEG-based gel) between the two electrodes. This polymeric gel layer prevents recombination reactions from occurring, thus further increasing the state retention of the device by decoupling changing the state of the device from the energy barrier of the electrolyte.

2. Experimental

2.1 Materials

Flexible indium tin oxide (ITO)-coated PET sheets were purchased and etched so that the top slide has a single ITO-electrode and the bottom slide, through previously reported photolithography techniques [8], has a bifurcated electrode with a 100 μm channel separation. The S-PEDOT polymer was roll-to-roll (R2R) gravure printed in a 5 mg/mL concentration in 2:1 methanol:water at a 20 mm/min rate and then annealed at 120 °C for 10 min. The bifurcated S-PEDOT coated electrode is vapor doped with polyethyleneimine (PEI) at 250 °C for 8 min in order to enhance protonic

transfer at the gel/S-PEDOT:PEI interface. Preparation of hydrogel-stabilized films embedded with electrolytes are described elsewhere [9]. In brief, two slides are sandwiched between a 125 μm parafilm spacer with a 12 x 20 mm cavity cut out. This cavity is injected with a photo-polymerizable polymeric-electrolyte that crosslinks after exposure to a UV-light source (ELC-500 Light Exposure System) and was UV-exposed for 6 min on each side. Figure 2b depicts a model of the final device architecture.

2.2 Electrical & Optical Characterization

Electrical characterization of fabricated three-terminal devices was performed using a HP4145A Semiconductor Analyzer to apply the voltage pulse train to the gate electrode with a Goodsky DC5V GS-SH-205T GQ relay in series in order to float the gate during measurements. A Keithley 2400 Sourcemeter is used to monitor the change in conductivity across the drain/source channel. The circuit diagram can be seen in Figure 2c. The HP4145A Semiconductor Analyzer is interpreted with custom HTBasic code and the Keithley 2400 Sourcemeter used LabView. The voltage pulsing signal was run through a 1MΩ resistor tied to the gate electrode to ensure no unintentional discharge of the device. Optical characterization was performed using a Perkin Elmer Lambda 900 UV-Vis coupled with a CH Instrument Model 660B Electrochemical Workstation to apply the voltage potentials.

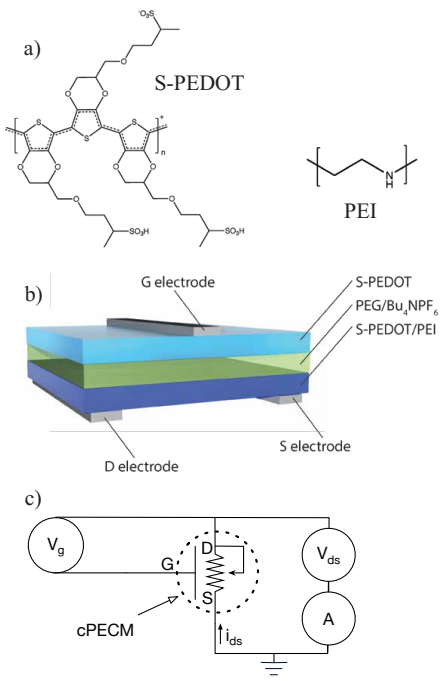

Figure 2: (a) Chemical structure of self-doped poly(3,4-ethylenedioxythiophene) (S-PEDOT) and polyethyleneimine (PEI). (b) Three-terminal device architecture consisting of electrochemical S-PEDOT layers separated by a polymeric electrolyte gel. (c) Circuit diagram for the cPECM device.

Acknowledgements

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3. References

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