



## Supercapacitor properties of nanowire poly((3,4-dihydro-2H-thieno [3,4-b][1,4]dioxepin-3-yl)methanol) free-supporting films

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### ABSTRACT

Nanowire poly (3,4-dihydro-2H-thieno [3,4-b] [1,4]dioxepin-3-yl)methanol (PProDTM) free-supporting films with conductivities around  $1.92 \text{ S cm}^{-1}$  were prepared using a template-free electro-polymerization method. The structure, morphology, mechanical properties, and thermal stability of the PProDTM films were characterized by Fourier transform infrared spectroscopy, UV–vis spectroscopy, scanning electron microscopy, dynamic mechanical analysis and thermogravimetric analysis. Moreover, the capacitance performances of PProDTM films were investigated in aqueous and organic electrolytes (acetonitrile (ACN) and dichloromethane (DCM)). In 0.1 M  $\text{H}_2\text{SO}_4$ , a symmetrical supercapacitor based on PProDTM exhibited specific capacitance of  $89.2 \text{ F g}^{-1}$  at a current density of  $1.0 \text{ A g}^{-1}$ , an energy density of  $3.1 \text{ Wh kg}^{-1}$  at power density of  $0.5 \text{ kW kg}^{-1}$  and the cycling capacitance retention was 74.8% after 5000 cycles. As the scan rate and current density increased, the specific capacitance of PProDTM films clearly decreased in DCM, but no obvious changes occurred in water and ACN. In ACN containing 0.1 M  $\text{Bu}_4\text{NBF}_4$ , a symmetrical supercapacitor based on PProDTM exhibited specific capacitance of  $99.6 \text{ F g}^{-1}$  at a current density of  $1.0 \text{ A g}^{-1}$ , an energy density of  $3.5 \text{ Wh kg}^{-1}$  at power density of  $0.5 \text{ kW kg}^{-1}$  and the cycling capacitance retention was 82.2% after 5000 cycles. These results imply that our flexible free-supporting PProDTM films are promising for future use in supercapacitors.

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## 1. Introduction

As a novel energy storage device with both high power density and energy density [1], supercapacitors are widely used in many fields, including in portable electronics [2], hybrid electric vehicles [3], and renewable energy systems [4,5]. Emerging as a “superstar” material, poly (3,4-ethylenedioxythiophene) (PEDOT) has been one

of the most promising supercapacitor electrode materials, due to its p-doping privilege, high conductivity, low initial oxidation potential, and good thermal stability [6,7]. Previous studies showed that PEDOT has high enough stability for use in practical applications [8]. Due to its low specific capacitance compared with polyaniline and polypyrrole, many works based on the molecular structural engineering of PEDOT have been reported, which can be mainly classified into the following groups:

- (1) **Preparing PEDOT with special structures:** The nano-structures of PEDOT such as nanotubes, nanoflower, and nanocorals can enhance its capacitance properties by increasing the specific surface area. For example, Liu et al. synthesized PEDOT nanotubes with a specific capacitance of  $140 \text{ F g}^{-1}$  using porous anodic alumina as a template [9]. By using bis (2-ethylhexyl) sulfosuccinate sodium as a surfactant, Hu et al. synthesized a 3D flowerlike PEDOT with a specific capacitance of  $111 \text{ F g}^{-1}$  [10]. Abdiryim et al. reported

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a coral-like PEDOT with a specific capacitance of  $174 \text{ F g}^{-1}$  by using an alcoholic aqueous solution [11].

- (2) **Modifying the molecular structure of PEDOT with functional groups:** The capacitance performance of PEDOT has also been improved using different functional groups. Güllü et al. reported PEDOT derivatives containing fused two 1,4-dioxane rings, with a specific capacitance of  $183\text{--}260 \text{ F g}^{-1}$  [12]. By attaching a quinoxaline ring to 3,4-butylendioxythiophene group, Güllü et al. synthesized a PEDOT derivative with specific capacitance of  $213.7 \text{ F g}^{-1}$  [13]. Poly (2,3-dihydrothieno [3,4-*b*] [1,4]dioxin-2-yl)methanol) was prepared on carbon fibre via a simple electrodeposition method by Ma et al., and exhibited a remarkable specific capacitance of  $280 \text{ F g}^{-1}$  [14]. Electropolymerized poly (5,5-bis(2,3-dihydrothieno [3,4-*b*] [1,4]dioxin-5-yl)-2,2-bithiophene) with  $171 \text{ F g}^{-1}$  was obtained by Mo et al. through copolymerization of PEDOT and bithiophene [15].
- (3) **Building analogues of PEDOT by replacing oxygen atoms:** Heteroatoms such as electron-withdrawing sulfur or electron-donating nitrogen, when substituted for oxygen atoms, can affect the electrochemical performance of PEDOT. Tang et al. prepared a sulfur analogue of PEDOT, poly (3,4-ethylenedithiophene), with a higher discharge specific capacity ( $425 \text{ mAh g}^{-1}$ ) than PEDOT ( $140 \text{ mAh g}^{-1}$ ), proving it as a promising cathode material for rechargeable lithium batteries [16]. A nitrogen analogue of PEDOT, poly (N-methyl-3,4-dihydrothieno [3,4-*b*] [1,4]-oxazine) with a specific capacitance of  $150\text{--}325 \text{ F g}^{-1}$ , has been reported by both the Güllü group [17] and Xu group [18].

In addition to these analogues, replacing ethylenedioxy groups with propylenedioxy groups is another interesting pathway. Compared with PEDOT, (3,4-Dihydro-2*H*-thieno [3,4-*b*] [1,4]dioxepine) (ProDOT) had a low oxidation potential and higher doping levels [19]. Poly (3,4-Dihydro-2*H*-thieno [3,4-*b*] [1,4]dioxepine) (PProDOT) has been used in electrochromic devices because of its distinct colours [20], higher coloration efficiency [21], and higher electrochromic contrast ratio [22]. The capacitance performances of PProDOT were also studied, showing excellent cycle-life stability with 84% retention of the initial capacitance after 21000 charge/discharge cycles [23]. Additionally, Sezai Sarac et al. described the capacitance behaviour of a derivative of PProDOT, poly (2,2-dimethyl-3,4-propylenedioxythiophene), which exhibited a capacitance of  $12.05 \text{ mF cm}^{-2}$  on carbon fibre [24]. Developing new derivatives of PProDOT is, therefore, a necessary and significant issue to address. Hydroxymethyl groups should have more advantages compared to methyl groups. As a strong electron donor, a hydroxymethyl group can decrease the band gap of the polymer by increasing the HOMO level [25]. The hydroxymethyl group also has good hydrophilicity and electrochemical activity, which can improve the capacitance properties of conducting polymers [14]. Lastly, the introduction of hydroxymethyl groups can produce many intermolecular hydrogen bonds C–H...O to aid the formation of nanostructures such as nanowires, nano-networks and tubular structures [26]. However, the properties of PProDOT substituted with hydroxymethyl groups are currently unknown.

It is well-known that PEDOT is difficult to be prepared into free-standing paper, and the nano-structural PEDOT film was usually prepared under the assistance of the templates or surfactants [27,28]. However, in this paper, as-synthesized ProDTM as monomer was easily electropolymerized into a free-supporting poly (3,4-Dihydro-2*H*-thieno [3,4-*b*] [1,4]dioxepin-3-yl)-methanol) (PProDTM) film using a template-free electropolymerization method. The capacitance performance of the PProDTM films was investigated in different electrolytes by cyclic voltammetry,

galvanostatic charge/discharge, and electrochemical impedance spectroscopy. The characterization of structural, morphology, and mechanical properties and thermal stability of PProDTM films were also investigated. Furthermore, capacitor devices with PProDTM were assembled and investigated by electrochemical methods.

## 2. Experimental

### 2.1. Materials

Sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%, AR) and anhydrous lithium perchlorate ( $\text{LiClO}_4$ , 98%, AR) were purchased from Aladdin Industrial Inc. Potassium chloride (KCl, 98%, AR) and chloroform-*d* (99.8%, GR) were purchased from J&K Scientific Co., Ltd. Indium tin oxide coated glass (ITO glass) was purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Acetonitrile (ACN, AR) and dichloromethane (DCM, AR) were purchased from Shanghai Vita Chemical Reagent Co., Ltd. and purified by distillation over calcium hydride before use. Tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ , 98%) and tetrabutylammonium tetrafluoroborate ( $\text{Bu}_4\text{NBF}_4$ , 98%) were purchased from Energy Chemical Reagent Co., Ltd. and dried under vacuum at  $60^\circ\text{C}$  for 24 h before use. 3,4-Dihydro-2*H*-thieno [3,4-*b*] [1,4]dioxepin-3-yl)-methanol (ProDTM) was synthesized according to our previous work [29]. The synthetic route of ProDTM was shown in Supporting information.  $^1\text{H}$  NMR (Fig. S1) (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.52 (s, 2H), 4.19 (dd, 2H,  $J = 12.2, 5.4 \text{ Hz}$ ), 3.88 (dd, 2H,  $J = 12.3, 3.4 \text{ Hz}$ ), 2.37 (s, 1H), 1.63 (s, 2H).

### 2.2. Characterization

$^1\text{H}$  NMR spectra were recorded on a Bruker AV-400NMR spectrometer at room temperature and tetramethylsilane was used as the internal standard to measure the chemical shifts. The structure and surface morphologies of PProDTM films were further investigated by Fourier transform infrared (FT-IR, Bruker Vertex 70) spectroscopy, ultraviolet–visible (UV–vis, Analytik Jena) spectroscopy and scanning electron microscopy (SEM, JEOL JSM-6700F). Thermogravimetric analysis (TGA) was performed under a nitrogen stream at a temperature range of  $0\text{--}1300 \text{ K}$  with a thermal analyser (NETZSCH TG209). Electrochemical studies were carried out on a CHI 660B potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd., China). Both electrical conductivity and Seebeck coefficient were measured by the four-point method.

### 2.3. Assembly of supercapacitor device

The PVA- $\text{H}_2\text{SO}_4$  gel electrolyte was prepared by adding 10 g PVA powder in  $\text{H}_2\text{SO}_4$  (100 mL, 0.5 M), and vigorously stirring the mixture at  $85^\circ\text{C}$  until the solution became clear, at which point the solution was kept at  $85^\circ\text{C}$  without stirring.

The supercapacitor device employs a sandwich-type configuration. A thin PVA- $\text{H}_2\text{SO}_4$  gel electrolyte layer was coated on two pieces of PProDTM-modified carbon cloth. A diaphragm dipped in  $\text{H}_2\text{SO}_4$  was put between two PProDTM-modified carbon cloths, and the device was wrapped in plastics film. All device fabrications and electrochemical measurements were performed in air.

## 3. Results and discussion

### 3.1. Electrochemical polymerization of ProDTM

Successive cyclic voltammograms (CVs) were used to study the electrochemical polymerization process of ProDTM and redox process of its polymer. As shown in Fig. 1, the oxidation onset

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