Vapor-phase polymerized poly(3,4-ethylenedioxythiophene) (PEDOT)/ TiO₂ composite fibers as electrode materials for supercapacitors

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Abstract

Vapor-phase polymerized poly(3,4-ethylenedioxythiophene) (PEDOT)/TiO₂ composite fibers were fabricated and applied as the supercapacitor electrode materials. TiO₂ fibers were prepared as substrates for the vapor-phase polymerization process, by electrospinning and calcination in air. The symmetric supercapacitor cells assembled with the resulting composites were studied by a series of electrical measurements including cyclic voltammetry, charge-discharge characterization and electrochemical impedance spectroscopy. To further understand the capacitive behavior, the band gap energy of the composite fibers and the specific surface area of TiO₂ fibers calcined at varied temperatures were measured. The highest specific capacitance of PEDOT on TiO₂ fibers to date, 87.9 F g⁻¹, was achieved with the composite fibers prepared by vapor-phase polymerization at 50 °C on the TiO₂ fibers calcined at 550 °C. The pseudocapacitance and the reversibility of PEDOT were improved in comparison to other PEDOT/TiO₂ binary composites.

KEYWORDS: poly(3,4-ethylenedioxythiophene), TiO₂ fibers, vapor-phase polymerization, supercapacitor

1. Introduction

Supercapacitors are attracting more attention as key devices for energy storage due to their high power density and charge/discharge efficiency. Much work has been done to explore new electrode materials for supercapacitors to get better energy storage performances. Typical electrodes studied in this field are composed of carbon particle materials for electrical double-

layer capacitors (EDLC), which accumulate the charge electrostatically at the electrode/electrolyte interface; however, the capacitance is limited by the available surface area [1]. A second group of supercapacitors is pseudocapacitors, using fast and reversible surface or near-surface redox reactions for charge storage [2]. The materials applied as the electrode for pseudocapacitors can be generally categorized into metal oxides [3-5] and conductive polymers [6-8]. Metal oxides, such as ruthenium oxides and manganese oxides, exhibit good capacitive performance, including high specific capacitance, long cycle life, fast electrochemical reversibility and high rate capability [9-10], but the cost and the toxicity constrain the development in practical applications. On the other hand, conducting polymer based capacitors may retain the capacitive features of pseudocapacitors while enhancing portability at a lower cost [11-13]. For example, polypyrrole and polyaniline have both been used to demonstrate high capacitance, though stability was somewhat limited [14, 15].

Among all the conductive polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has become one of the most attractive materials from both fundamental and practical points of view owing to its stability in the oxidized state, moderate band gap, fast doping/dedoping process, high electrical conductivity and long-term environmental stability [16-19]. Currently, PEDOT is utilized in a wide range of applications such as sensors, hole conducting materials in organic/polymer-based light-emitting diodes (OLEDs/PLEDs), transparent anodes for photovoltaic devices, non-metal electrocatalysts and electrode materials for pseudocapacitors [20-24]. Compared to the other methods of polymerization of PEDOT, the vapor phase method has shown to yield enhanced degree of crystallinity and relative high conductivity of PEDOT [25-28]. Moreover, vapor-phase polymerization method is simple and controllable as no solvent for monomer or additives other than oxidant needed during the polymerization, meaning it is

easy to clean the produced PEDOT without compromising the performance caused by the considerable amount of residual undesired chemicals. In addition, the PEDOT produced by vapor-phase polymerization method can be adapted to almost any substrate, providing flexibility in structural design and material development [29, 30].

Although conductive polymers such as PEDOT have several advantages over other materials being used as electrode for supercapacitors, they also have several challenges. The active materials tend to aggregate, which decreases the surface area for participating redox reaction, resulting in decreasing specific capacitance [31]. Also, the conversion between redox states is governed by the mass transfer of counter-ions. The difficulty in keeping pace with a fast charging/discharge process at high power demand leads to inefficient utilization of the electrode materials [32]. To improve the performance in these areas, the design of composite electrode materials with novel structure and composition are essential for future development of pseudocapacitors.

Significant work has been done in this field, for example, Laforgue fabricated PEDOT composite fibers by electrospinning oxidant fibers using polyvinylpyrrolidone as the substrate followed by the exposure to 3,4-ethylenedioxythiophene (EDOT) vapor. The supercapacitor assembled with these PEDOT fibers as the electrode materials showed a cell capacitance of 20 F g^{-1} with 1-ethyl-3-methylimidazolium tetrafluoroborate and poly(vinylidene fluoride-co-hexafluoropropylene) as electrolyte [33]. In another instance Tang et al fabricated a flexible hybrid electrode consisting of a ternary composite graphite/PEDOT/ MnO_2 , which exhibits a high area capacitance of 316.6 mF cm^{-2} at 10 mV s^{-1} [34].

In this study, the electrospun and calcined TiO₂ fibers were used as the substrate for vapor-phase polymerized (VPP) PEDOT to fabricate VPP PEDOT/TiO₂ composite fibers. TiO₂ is commonly used as an electrode material in electrochemical devices due to its electrochemical stability and relatively stable physical/chemical properties, as well as its great accessibility and moderate cost [35, 36]. TiO₂ when electrospun into sub-micron fiber structures provided a large surface area for VPP PEDOT, while maintaining the good capacitive behavior of the electrode materials. The effects of calcination temperature and polymerization temperature on the capacitive performance of VPP PEDOT/TiO₂ composite fibers were studied with cyclic voltammetry (CV), charge-discharge (CD) characterization and electrochemical impedance spectroscopy. Band gap energy and specific surface area of the calcined TiO₂ fibers were investigated to further understand the electrochemical behavior.

2. Experimental methods

2.1. Materials

Polymethylmethacrylate (PMMA) ($M_w = 350,000 \text{ g mol}^{-1}$), chloroform, titanium isopropoxide (TTIP), anhydrous *N,N*-dimethylformamide (DMF), 3,4-ethylenedioxythiophene (EDOT), iron(III) *p*-toluenesulfonate hexahydrate ($\text{Fe(PTS)}_3 \cdot 6(\text{H}_2\text{O})$), 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄) and propylene carbonate (PC) were purchased from Sigma-Aldrich and used as received. Pyridine was purchased from Fisher Scientific. Ethanol was obtained from Koptec. All chemicals were used without further purification.

2.2. Preparation of VPP PEDOT/TiO₂ composite sub-micron fibers

Figure 1

The typical procedures to fabricate VPP PEDOT/TiO₂ composite sub-micron fibers are shown in Figure 1. TiO₂ fibers were obtained through electrospinning and calcination following a previously described method [37]. To prepare the polymeric sol-gel used for electrospinning, 320 mg PMMA was dissolved in 2 mL chloroform and then 640 mg TTIP was added dropwise. After 30 minutes continuous stirring, 2 mL of DMF was added to the system to increase the dielectric constant of the resulting sol-gel. The sol-gel was ready for electrospinning after another 2 hours of stirring and partial hydrolysis as presented previously [38]. The electrospinning was set up as illustrated in Figure 1. The syringe containing sol-gel was fixed 4° tilted beneath the horizontal position to allow gravity to keep the flow rate of sol-gel approximately 0.5 mL min⁻¹. The continuous and smooth polymer fibers were pulled out by 25 kV voltage provided by the external power supply and collected with the Al foil collector which was 18 cm away from the tip of the syringe. The collected polymer fibers were placed under ambient conditions to achieve full hydrolysis and further condensation to amorphous TiO₂ [37]. The calcination treatment was carried out in air at 450, 550 or 700 °C for 4 hours to control the TiO₂ polymorph composition.

The calcined TiO₂ fibers were then used as the substrate for VPP PEDOT. Fe(PTS)₃·6(H₂O) was dissolved in ethanol to make 0.05 M oxidant solution under sufficient stirring. Pyridine was added to the oxidant solution as a basic inhibitor to suppress an acid-initiated polymerization reaction [8]. A sample of 100 mg calcined TiO₂ fibers were soaked and sonicated in 1.5 mL oxidant solution for 1 hour to allow thorough absorption. The TiO₂ fibers with oxidant were dried and ground to facilitate the monomer vapor flowing through. The ground fibers were spread on a piece of filter paper, which was fixed over a petri dish containing 100 µL EDOT at the bottom. The preparation was heated in an oven at the given polymerization temperature, either 50 or 110 °C. After the TiO₂ fibers were exposed to EDOT vapor for 1 hour, the sample

was removed to terminate the polymerization. To remove the Fe(PTS)_3 oxidant, pyridine, residual EDOT and TiO_2 fibers not coated with PEDOT, the TiO_2 fibers after vapor-phase polymerization of PEDOT were soaked in ethanol for 30 minutes under vigorous stirring, then the supernatant suspension was removed and blue solid material was retained. The rinsing process was repeated 4 times to ensure the removal of undesired materials was complete. The PEDOT was spontaneously oxidized during the polymerization process and *p*-toluenesulfonate ions were incorporated with the p-doped PEDOT to maintain charge neutrality. The sample was dried at 60 °C overnight before characterization or being used as the electrode material. To simplify the narration, all the samples are named with the polymerization temperature and calcination temperature. For example, the VPP PEDOT/ TiO_2 composite fibers prepared by vapor-phase polymerization held at 50 °C using TiO_2 fibers calcined at 450 °C as the substrate is denoted as 50 PEDOT-450 TiO_2 , similarly hereinafter.

2.3. Characterization

The chemical composition of the electrode materials and polymorphs of TiO_2 fibers were studied with a DXR xi Raman imaging microscope with the laser wavelength of 532 nm from Thermo Scientific. The calculated rutile fractions were obtained with powder X-ray diffraction (XRD) using a Bruker D8 advance diffractometer equipped with a $\text{Cu K}\alpha$ tube ($\lambda = 1.54178\text{\AA}$) and a LYNXEYE XE detector. The data were collected in the range of $2\theta = 20\text{--}60^\circ$ with a step size of 0.02° while spinning the sample to minimize preferred orientation. The surface morphology was investigated with Zeiss Supra 55 field emission scanning electron microscope (FESEM). The weight percentage of PEDOT was determined by thermogravimetric analysis (TGA) with thermogravimetric analyzer Q50 from TA Instruments, and the tests were run at a heating rate of

20 °C min⁻¹ from room temperature to 600 °C under air. The diffuse reflectance spectra were recorded using UV-2600 UV-Vis spectrophotometer with ISR-2600 integrating sphere attachment from Shimadzu from 200-800 nm with a data interval of 1 nm. The symmetrical supercapacitor cells were fabricated with 1 mg of the VPP PEDOT/TiO₂ composite fibers as the electrode material for each electrode and a piece of 3×3 cm² filter paper as the separator. Solution of 3 M EMI-BF₄ in PC was employed as electrolyte. All the electrical tests were conducted with two-electrode system in ambient room conditions. Cyclic voltammetry (CV) and galvanostatic charge-discharge (CD) tests were run with a VMP multichannel potentiostat (Biologic) to evaluate specific capacitance of the electrode materials. The voltage window for CV was -0.5 to 0.5 V, and 0 to 1 V for CD. The Nyquist plots were obtained from electrochemical impedance spectroscopy using a Solartron Impedance Analyzer to investigate the electrochemical processes. Nitrogen adsorption isotherms were measured for calcined TiO₂ fibers using a Micromeritics 3Flex Surface Characterization Analyzer at 77 K. Prior to analysis, each material was activated overnight at 100 °C under a flow of dry nitrogen. Brunauer–Emmett–Teller (BET) modeling was performed to obtain the specific surface areas.

3. Results and discussion

3.1. Characterization of TiO₂ fibers and VPP PEDOT/TiO₂ composite fibers

Figure 2

TiO₂ fibers were successfully fabricated by the calcination of polymer composites containing PMMA and TTIP that had been electrospun as previously described [33]. The electrospinning of pre-calcined polymer fibers was carried out using a high voltage Spellman SL 30 generator to apply the high electrical potential across the syringe needle attached to a copper wire and the

collector screen. A Lindberg/Blue MTM tube furnace from Thermo Scientific was employed for calcination. The calcinations were carried out in air for 4 hours at 450, 550 or 700 °C, and then used as the substrates for VPP PEDOT growth. The VPP PEDOT was grown at different temperatures, 50 and 110 °C, in order to assess the role of heat in the polymer growth. The chemical composition changes were tracked with Raman spectroscopy, as shown in Figure 2. In Figure 2a, the pre-calcined polymer fibers showed peaks at 1450, 1730, 2950, and 3000 cm⁻¹, characteristic of PMMA. There was no significant peak observed lower than 750 cm⁻¹. After calcination, the peaks assigned to PMMA were no longer observed, which suggested the complete decomposition of PMMA during the calcination [40]. New peaks were observed below 750 cm⁻¹, and the peak positions varied with the calcination temperatures. The characteristic peaks for the anatase phase at 143, 397, 514 and 635 cm⁻¹ were observed with the 450 °C calcined TiO₂ fibers, and the peaks at 235, 443 and 608 cm⁻¹ for rutile were observed with the 700 °C calcined TiO₂ fibers. The 550 °C calcined TiO₂ fibers showed a transitional spectrum between the TiO₂ fibers calcined at 450 and 700 °C. Under the calcination temperatures studied, the rutile fraction increased as the calcination temperature increased, which is consistent with prior reports [37]. Raman spectra of VPP PEDOT/TiO₂ composite fibers are shown in Figure 2b. All the fibers retained the characteristic peaks of TiO₂ observed before vapor-phase polymerization, and the peak intensity didn't change significantly. This suggested the polymorph of TiO₂ fibers was stable through the polymerization temperature treatment. Meanwhile, the moderate intensity peaks at 1420 and 1510 cm⁻¹ appeared. These two peaks were assigned to C_α=C_β symmetric stretching and C_α=C_β asymmetric stretching from PEDOT, respectively. Other characteristic peaks of PEDOT, including 1250 cm⁻¹ peak for C_α-C_α' stretching and 1360 cm⁻¹ peak for C_β-C_β stretching, were also observed in the Raman spectra. Therefore, it was concluded

that, when the VPP PEDOT/TiO₂ composite was prepared with the procedures mentioned above, the effect of polymerization temperature on TiO₂ polymorph was negligible.

Figure 3

The XRD patterns of pre-calcined polymer fibers and TiO₂ fibers calcined at 450, 550 and 700 °C in air for 4 hours are shown in Figure 3. No distinct peak was observed on pre-calcined polymer fibers, indicating the amorphous phase before calcination. The characteristic diffraction peaks of anatase were found with TiO₂ fibers calcined at 450 °C. The 2θ peaks at 25.3, 37.9, 48.1 and 54.5° were assigned to the Miller indices (101), (004), (200) and (105) planes of anatase as illustrated in Figure 2. Also a weak 2θ peak appeared at 27.5°, which corresponded to the (110) plane of rutile. According to the XRD patterns, the TiO₂ fibers calcined at 450 °C were mostly anatase phase. As the calcination temperature increased to 550 °C, the TiO₂ fibers were still a mixture of anatase and rutile phases, however the rutile peaks intensified greatly, indicating the increasing percentage of rutile phase. As the calcination temperature increased to 700 °C, the characteristic peaks of rutile appeared at 27.5, 36.1, 39.2, 41.3, 44.1, 54.4, 56.6°, assigned to (110), (101), (200), (111), (210), (211) and (220) planes, respectively. To quantify the weight fraction of rutile phase in the calcined TiO₂ fibers, the equation of $W_R = 1/[1 + 0.8(I_A/I_R)]$ [39] was employed. I_A is the X-ray intensity of the (101) reflection of anatase at 25.3° and I_R is that of the (110) reflection of rutile at 27.5°. The calculated results were consistent with the trend observed from the XRD patterns, and the weight percentages of rutile in the TiO₂ fibers calcined at 450, 550 and 700 °C were 18.8%, 75.0% and 95.9% respectively.

Figure 4

The morphology of the pre-calcined polymer fibers, calcined TiO₂ fibers and VPP PEDOT/TiO₂ composite fibers prepared by vapor-phase polymerization at 50 or 100 °C with TiO₂ fibers as substrates are shown in Figure 4. The average diameters of all the fibers were calculated basing on the measurement of at least 20 fibers from each sample, as listed in Table 1. The pre-calcined polymer fibers (Figure 4a) were long with the average diameter of 260±49 nm, and the surface was slightly wrinkled. After the calcination, the sizes of the calcined TiO₂ fibers decreased compared to the pre-calcined polymer fibers, the diameters were 208±29, 191±33 and 156±25 nm for the TiO₂ fibers calcined at 450, 550 and 700 °C respectively. Based on these results, we hypothesize that the decrease in fiber diameter was a result of both the loss of PMMA and the increase in the fraction of the denser rutile phase with increasing temperature [40]. This was consistent with the Raman and XRD results presented above.

All the calcined TiO₂ fibers were shorter than the pre-calcined polymer fibers due to the brittle texture of the calcined TiO₂ fibers resulting in breaking upon losing mechanical support of the PMMA matrix. The surfaces of the TiO₂ fibers showed more folding after calcination, especially those calcined at 550 and 700 °C. The morphology of VPP PEDOT/TiO₂ composite fibers were shown in Figure 4e-4j. The wrinkles and edges of the result fibers were indefinite compared to the bare TiO₂ fibers, and it was observed no significant amount of PEDOT separated from TiO₂ fibers. Most of the PEDOT generated by vapor-phase polymerization grew on the surface of TiO₂ fibers instead of blending PEDOT and TiO₂. This close combination benefited the capacitive behavior which is shown below. However, there was no significant increase in diameter of fibers after the vapor-phase polymerization (listed in Table 1), meaning the fraction of PEDOT in the composite fibers could be low.

Table 1

Figure 5

TGA was used to quantify the mass fraction of PEDOT in the VPP PEDOT/TiO₂ composite fibers, shown in Figure 5. There was no noticeable weight loss appearing before 200 °C or after 550 °C. PMMA couldn't remain in the samples since PMMA decomposes quickly after the temperature reaches around 285 °C and is found to have been completely removed at around 370 °C (see Figure S4), whereas the calcination temperatures were all higher than that and were held for 4 hours [41]. According to the TGA curve of Fe(PTS)₃·6(H₂O) (see Figure S5), the decrease in weight of Fe(PTS)₃·6(H₂O) was more than 80% before 400 °C. According to literature, the doping level of PEDOT is about 0.33 [42], meaning the mass fraction of toluenesulfonate ions is about 28% calculated with the molecular weight of EDOT and counter ion. It is reasonable to believe that the actual doping levels of the samples in this study were no higher than 0.33, as reported in the literature, since ethanol could have de-doped the samples to a certain extent during the rinsing process. The small amount of oxidant residue after 550 °C is negligible for the total mass of PEDOT. Hence PEDOT was the only component causing the weight loss in the range of 200 to 500 °C. As calculated from the TGA curves, the weight percentage of PEDOT in 50 PEDOT-450 TiO₂ was 5.5 %, 50 PEDOT-550 TiO₂ 4.7 %, 50 PEDOT-700 TiO₂ 3.2%, 110 PEDOT-450 TiO₂ 7.8%, 110 PEDOT-550 TiO₂ 6.3 % and 110 PEDOT-700 TiO₂ 7.8 %. The PEDOT weight percentages indicated that the VPP PEDOT/TiO₂ fibers prepared with vapor-phase polymerization process at 50 °C had less PEDOT than the ones prepared at 110 °C. It was hypothesized that the higher vapor concentrations and the faster reaction rates at higher temperature led to the greater yield of PEDOT. Nevertheless, the highest weight percentage of PEDOT in these composites was still lower than 10%. As a result, the PEDOT did not add significantly to the diameter of the composite fibers, consistent with the SEM images in figure 4.

For the composite fibers prepared with the vapor-phase polymerization at the same temperature, there was no relationship between the amount of PEDOT and the anatase/rutile ratio of the TiO_2 fibers. Since the amount of bare TiO_2 fibers rinsed off after polymerization of PEDOT was not able to be controlled precisely, and the percentage of PEDOT was only used to calculate the specific capacitance in this research, here the comparison between the three composite fibers prepared with the same polymerization conditions was neither practicable nor needed, although this could be an interesting direction for further study.

3.2. Capacitive behaviors of VPP PEDOT/ TiO_2 composite fibers

Figure 6

The supercapacitor cells assembled with VPP PEDOT/ TiO_2 composite fibers as the electrode materials were studied by cyclic voltammetry (CV) at 10 mV s^{-1} as shown in Figure 6, additional scan rates can be found in the supporting information. The pure TiO_2 fibers showed very low capacitance in control experiments. The TiO_2 fibers calcined at 550°C are shown as an example with the dash line CV curves in Figure 6a and 6b. The capacitance of the TiO_2 fibers was found to be negligible. All the VPP PEDOT/ TiO_2 composite fibers exhibited a rectangular shape on the CV curves, suggesting good reversibility for cycling and low internal resistance of the electrode materials. The introduction of TiO_2 fibers to PEDOT did not result in a severe decrease in the conductivity of the electrode or affected the redox behavior. The specific capacitance was calculated as reported previously [8] and normalized by the weight fraction of PEDOT. The specific capacitance values from the CV results 68.2 , 87.9 and 64.7 F g^{-1} were for 50 PEDOT-450 TiO_2 , 50 PEDOT-550 TiO_2 and 50 PEDOT-700 TiO_2 , and 58.3 , 66.9 and 66.7 F g^{-1} for 110 PEDOT-450 TiO_2 , 110 PEDOT-550 TiO_2 and 110 PEDOT-700 TiO_2 , respectively. Compare to

the specific capacitance 23.2 F g^{-1} of *in situ* PEDOT (Procedures to prepare *in situ* PEDOT are stated in supporting information) at 10 mV s^{-1} shown in Figure 6 with dot lines, the capacitive performance of the PEDOT on all the composite fibers got enhanced greatly. The PEDOT on the composite fibers prepared with vapor-phase polymerization at 50°C were with higher specific capacitance than the ones at 110°C due to the increased load of PEDOT. The PEDOT film on TiO_2 fibers prepared through vapor-phase polymerization could block the ion diffusion further into the electrode material, causing the inferior ability of redox reaction of the inner portion of PEDOT. Hence the calculated specific capacitance values of the composite fibers prepared at 50°C were higher.

Figure 7

The galvanostatic charge-discharge (CD) curves of the supercapacitors with VPP PEDOT/ TiO_2 composite fibers as the electrode materials were measured at 0.5 A g^{-1} as shown in Figure 7, additional current densities can be found in the supporting information. The specific capacitance values 75.6 , 83.8 and 73.1 F g^{-1} were for the PEDOT on 50 PEDOT-450 TiO_2 , 50 PEDOT-550 TiO_2 and 50 PEDOT-700 TiO_2 , and 56.4 , 69.3 and 69.3 F g^{-1} for 110 PEDOT-450 TiO_2 , 110 PEDOT-550 TiO_2 and 110 PEDOT-700 TiO_2 respectively, summarized in Figure 7c. These results are consistent with the results from CV curves. IR drop appearing in the CD curves can be mostly attributed to the resistance of TiO_2 fibers [43]. According to the specific capacitance values obtained from CV and CD, the TiO_2 fibers calcined at 550°C were the best substrates for the composite fibers prepared with polymerization of PEDOT at 50°C ; and for the samples prepared with polymerization of PEDOT at 110°C , the TiO_2 fibers calcined at 550 and 700°C showed similar performance and both better than the TiO_2 fibers calcined at 450°C . This could be explained by the nature of anatase and rutile phase of TiO_2 . The greater surface area of

anatase and the lower band gap energy of rutile together can both benefit the capacitive behaviors of the composite fibers. The proper mixture of the two phases could exhibit optimal combination of the two properties. For the composite fibers fabricated by polymerization of PEDOT at 50 °C, the highest capacitance among the three samples tested was obtained with the composite fibers prepared on the TiO₂ fibers calcined at 550 °C, which contained 75.0% rutile. For the ones at 110 °C, similarly, 110 PEDOT-550 TiO₂ exhibited the highest capacitance. Besides, the capacitance of 110 PEDOT-700 TiO₂ was very close to that of 110 PEDOT-550 TiO₂. With the higher yield of PEDOT compared to the samples prepared at 50 °C, the high percentage of rutile impacted positively on the capacitance due to the lower band gap energy of rutile relative to anatase. The sample with the highest specific capacitance 50 PEDOT-550 TiO₂ was employed to study the cycling performance at the current density of 0.5 A g⁻¹. After 1000 cycles, the capacitance retention was 90.2%, exhibiting excellent cycling stability.

The linear relationship between discharge potential and time shows the low internal resistance of the system and the sufficient conductivity of the electrodes. There was some non-linearity around the voltage limits (1 V) on the CD curves. This result is consistent with previous reports describing the de-doping of the anode and cathode which occurs at the potential limit [33].

Figure 8

Nyquist plots of supercapacitor cells constructed with VPP PEDOT/TiO₂ composite fibers as the electrode materials are shown in Figure 8a and 8b. The approximate linear portion at low frequencies and the semi-circle at high frequencies can be observed. The linear portion is almost parallel with the imaginary axis, indicating quasi ideal capacitive behavior at low frequencies. As the inset shown in Figure 8a and 8b, the electrolytic resistances (the intercept on the real axis) of all the VPP PEDOT/TiO₂ composite fibers were close since the supercapacitor cells were all

constructed with the same configuration and the structures of all the composite fibers were similar. The semi-circle is associated with the doping/de-doping process which occurs at the interface between PEDOT and the electrolyte solution. The radius of the semi-circle reflects the resistance of charge transfer. For the composite fibers prepared with polymerization of PEDOT at 50 °C, the charge transfer resistance of 50 PEDOT-550 TiO₂ was the lowest and the that of 50 PEDOT-450 TiO₂ was the highest. For the samples prepared with polymerization of PEDOT at 110 °C, 110 PEDOT-550 TiO₂ and 110 PEDOT-700 TiO₂ had similar charge transfer resistance and both lower than that of 110 PEDOT-450 TiO₂. This was consistent with the capacitance measurements: the composite fibers showed lower charge transfer resistance exhibited higher capacitance. The differences between the samples could be explained by the band gap energy and surface area of the composite fibers. Rutile phase of TiO₂ has lower band gap energy than anatase, the band gap energy of the composite could be modified to a lower value with the increasing fraction of rutile phase, which could benefit the charge transfer process. The higher specific surface area of anatase probably led to higher specific surface area of the composite fibers, which provided more doping/dedoping sites for PEDOT redox reactions. [This is consistent with the observation that the samples produced by calcination at 550 °C led to the best capacitive performance of the PEDOT/TiO₂ composite fibers.](#)

Figure 9

Diffuse reflectance UV-Vis measurements for the VPP PEDOT/TiO₂ composite fibers were performed with the integrating sphere attachment for solid sample. In Figure 9, the optical band gaps are shown in Tauc plots with $(\alpha h\nu)^2$ as the y-axis for the direct band gap of the composite fibers. For 50 PEDOT-450 TiO₂, 50 PEDOT-550 TiO₂ and 50 PEDOT-700 TiO₂ (Figure 9a), the band gap energy values were 3.13, 3.09 and 3.07 eV, for 110 PEDOT-450 TiO₂, 110 PEDOT-

550 TiO₂ and 110 PEDOT-700 TiO₂ (Figure 9b) were 3.16, 3.12 and 3.08 eV respectively. This confirmed the hypothesis drawn from the impedance data. As the rutile fraction increased, the band gap energy of the composite decreased. The similar pattern was observed in the previous work on the TiO₂ fibers [37]. All the band gap values were close to those of TiO₂ fibers [37] due to the abundance of TiO₂ according to TGA data. The band gap energy values of the composite fibers prepared with polymerization of PEDOT at 50 °C were slightly lower than those of the ones with polymerization of PEDOT at 110 °C, probably due to the different band gap energy values of the PEDOT prepared at different temperatures.

Figure 10

If the band gap energy values of VPP PEDOT/TiO₂ composite fibers were considered only, the samples prepared with the TiO₂ fibers calcined at 700 °C were supposed to exhibit the best specific capacitance. However, 50 PEDOT-550 TiO₂ showed highest specific capacitance among the composite fibers fabricated through vapor-phase polymerization at 50 °C, and 110 PEDOT-550 TiO₂ and 110 PEDOT-700 TiO₂ were very close and both better than 50 PEDOT-550 TiO₂. The surface area of the calcined TiO₂ fibers was another factor to affect the capacitive behaviors of these VPP PEDOT/TiO₂ composite fibers. According to the existing work [37], the TiO₂ fibers with higher fraction of rutile phase had a lower specific surface area. Given the parameters of the vapor-phase polymerization, the low specific surface area of TiO₂ fibers led to the low specific surface area of PEDOT, resulting in the low specific capacitance of the final composite fibers. Consider both band gap energy and surface area, it was reasonable that the TiO₂ fibers calcined at 550 °C were the optimal substrates. For the composite fibers fabricated through vapor-phase polymerization process at 110 °C, the high yield of PEDOT reduced the difference between 110 PEDOT-550 TiO₂ and 110 PEDOT-700 TiO₂.

4. Conclusion

VPP PEDOT/TiO₂ composite fibers were fabricated by vapor phase polymerization of PEDOT with TiO₂ fibers as the substrate. Three calcination temperatures were applied, producing different polymorphs of TiO₂ fibers with the rutile fraction increased as the calcination temperature increased from 450 °C to 700 °C. Two different polymerization temperatures were also studied for optimal capacitive performance of the composite fibers. As a result VPP PEDOT/TiO₂ composite fibers exhibited much higher specific capacitance than the PEDOT produced by in-situ method. Both calcination temperature and polymerization temperature affected the capacitive behavior of the supercapacitor cells assembled with the composite fibers as electrode materials by adjusting the rutile fraction in TiO₂ fibers and the amount of PEDOT loaded respectively. The highest specific capacitance to date 87.9 F g⁻¹ was obtained with the composite fibers prepared by vapor-phase polymerization at 50 °C with the TiO₂ fibers calcined at 550 °C as the substrates.

ACKNOWLEDGMENT

The work was supported by the National Science Foundation (NSF) (IIP-1318202 and REU-DMR1263004), the NY State Technology Accelerator Fund, and the Army Research Office (ARO) W911NF1310235. We thank Dr. Stanley Whittingham for the access to the VMP multichannel potentiostat and Dr. Alok Rastogi for the Solartron Impedance Analyzer.

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Figure 1. Schematic showing preparation of VPP PEDOT/TiO₂ composite sub-micron fibers.

Figure 2. (a) Raman spectra of pre-calcined polymer fibers, TiO₂ fibers calcined at 450, 550 and 700 °C in air for 4h respectively, and (b) the VPP PEDOT/TiO₂ composite fibers prepared by vapor-phase polymerization at 50 or 110 °C with the calcined TiO₂ fibers mentioned above.

Figure 3. XRD patterns of pre-calcined polymer fibers and TiO₂ fibers calcined at 450, 550 and 700 °C in air for 4 hours respectively. The “A” and “R” labels denote the anatase and rutile phases of TiO₂.

Figure 4. (a) SEM images of pre-calcined polymer fibers; TiO_2 fibers calcined at 450 (b), 550 (c) and 700 °C (d) in air for 4 hours; (e) 50 PEDOT-450 TiO_2 ; (f) 50 PEDOT-550 TiO_2 ; (g) 50 PEDOT-700 TiO_2 ; (h) 110 PEDOT-450 TiO_2 ; (i) 110 PEDOT-550 TiO_2 ; (j) 110 PEDOT-700 TiO_2 .

Figure 5. TGA curves of VPP PEDOT/ TiO_2 composite fibers. The tests were run under stepwise isothermal mode in air, with heating rate of 20 °C/min.

Figure 6. Cyclic voltammetry (CV) curves of supercapacitor cells assembled with VPP PEDOT/TiO₂ composite fibers as the electrode materials, obtained with scan rate of 10 mV s⁻¹. The dash lines are CV curves of TiO₂ fibers calcined at 550 °C, and the dot lines are of *in situ* PEDOT, both measured with 10 mV s⁻¹.

Figure 7. Galvanostatic charge-discharge (CD) (a and b) curves of supercapacitor cells assembled with VPP PEDOT/TiO₂ composite fibers as the electrode materials, obtained with current density of 0.5 A g⁻¹. (c) The specific capacitance comparison between the composite fibers was plotted basing on the CD data. (d) The cycling performance of 50 PEDOT-450 TiO₂ at the current density of 0.5 A g⁻¹.

Figure 8. Nyquist plots for the supercapacitor cells assembled with VPP PEDOT/TiO₂ composite fibers as the electrode materials with the high frequency region as the inset. (a) 50

PEDOT-450 TiO₂, 50 PEDOT-550 TiO₂ and 50 PEDOT-700 TiO₂; (b) 110 PEDOT-450 TiO₂, 110 PEDOT-550 TiO₂ and 110 PEDOT-700 TiO₂.

Figure 9. Plot of $(\alpha h\nu)^2$ versus photon energy for calculating band gap energy of VPP

PEDOT/TiO₂ composite fibers. (a) 50 PEDOT-450 TiO₂, 50 PEDOT-550 TiO₂ and 50 PEDOT-700 TiO₂; (b) 110 PEDOT-450 TiO₂, 110 PEDOT-550 TiO₂ and 110 PEDOT-700 TiO₂.

Figure 10. The specific surface area of TiO₂ fibers determined by BET plotted relative to the rutile weight fraction determined by XRD [adapted from reference 34].

Table 1. Average diameters of pre-calcined polymer fibers, calcined TiO₂ fibers and VPP PEDOT/TiO₂ composite fibers.

Polymerization Temp. TiO ₂ Calcination Temp.	No PEDOT	50 °C	110 °C
No calcination	260±49 nm		
450 °C	208±29 nm	211±59 nm	213±55 nm
550 °C	191±33 nm	198±36 nm	200±35 nm
700 °C	156±25 nm	170±45 nm	170±42 nm