Electronic Supporting Information (ESI)

Polythiophene Infiltrated TiO₂ Nanotubes as a High-Performance Supercapacitor Electrode[†]

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Experimental Details

All chemicals including thiophene monomer, tetrabutyl ammonium tetrafluoroborate (Bu_4NBF_4), acetonitrile and titanium foils (0.127 mm thick, 99.95%) were purchased from Sigma-Aldrich and were used as received without further purification.

Preparation of TiO₂ Nanotubes

Ti-sheet was degreased by successive 20 min ultra-sonication in acetone, isopropanol and ethanol, respectively. After rinsing with deionized (DI) water and drying in nitrogen, substrates were anodized immediately. All reagents were of analytical grade. TiO₂ nanotubes (TNTs) were fabricated by the two step anodization process as prepared in our previous work.¹ Briefly, the vertically oriented nanotubular TiO₂ were prepared via potentiostatic anodization at a two electrode-electrochemical cell. Cleaned titanium strips and graphite plate were used as anode and cathode, respectively. In order to effectively reduce effects on the surface, samples were preanodized in a 0.5 wt % NH₄F ethylene glycol solution at 50 V for 3 h, and then the TNTs were removed via ultrasonication in a 1 M HCl aqueous solution. The samples were anodized for a second time at 50 V for 30 min to obtain nanoporous TNTs. Nanotube arrays thus fabricated were highly ordered and the outer tube walls of individual nanotubes were nearly in contact with each other which hardly leaves a space in between the nanotubes in the array. Such nanotubular arrangement in the array prevents the current leakage through the pores other than the nanotubes (i.e., the pores in between the nanotubes), which enables to direct the successful electrodeposition preferentially inside the nanotubes.^{1(e)} After anodization, the samples were soaked in and washed with methanol before being dried in air. Finally, the samples were annealed at 450 °C.

Electrochemical Polymerization and measurements

In a typical interfacial synthesis, 4% (v/v) thiophene and 0.1 M Bu₄NBF₄ were dissolved in acetonitrile, respectively. The two solutions were mixed together under constant stirring to form a static organic/inorganic interface. The concentration of Bu₄NBF₄ was optimized to obtain the desired crystallinity of PTh. As explained by Li *et al.*², with increasing salt concentration in the acetonitrile solution, the film surfaces become more and more compact leading to a high crystallinity. Since the supercapacitor electrodes demand high porosity, we maintained the concentration of Bu₄NBF₄ at a minimum to avoid high crystalline polymeric films.

All electrochemical measurements including cyclic voltammetry, galvanostatic charge/discharge measurements and electrochemical impendence spectroscopy (EIS) were performed using an Autolab-PGSTAT100 program operating on a potentiostat-galvanostat electro-chemical workstation in one compartment and a three-electrode cell at room temperature. The highly ordered array of TNTs and a flat Ti metal foil used to deposit PTh served as working electrodes. The reference electrode was an Ag/AgCl electrode, and all potentials in this paper are given with respect to the Ag/AgCl reference. The electrochemical polymerization process was carried out at 25 mV s⁻¹ in the potential range of 0 to 2 V. The mass of supercapacitor electrode material was determined by difference in weight before/after electropolymerization. For this, the samples were first dried in a stream of N₂ and were weighed using a Sartorius BP211D balance. As the supercapacitive property of only TNTs was extremely poor and the specific capacitance was negligible compared to the PTh/TNTs, the specific capacitance in the present investigation was calculated by considering the mass of PTh only. Prior to voltammetric scanning, all solutions were deaerated by nitrogen bubbling. This avoids possible degradation of the polymer and any side reactions between the electrolytes and electrodes due to over oxidation. After polymerization, the samples were cleaned and dried in air before being used prior to characterization.

Characterization

Crystallographic information of all as prepared samples was obtained using X-ray diffraction (XRD) on a PANalytical X-pert diffractometer operating at 30kV and 20mA with a CuKa radiation (λ = 1.5405 Å) collected in the 2 θ (twice the Bragg angle) range of 10–80° at a scan speed of 1° min⁻¹ using a step size of 0.04°. The intensity distributions of the XRD data were fit using JADE software from JADE Software Corporation, CA. The morphologies of the bare TNTs, PTh/TNTs and PTh/Ti foil electrodes were studied using a Hitachi S-4700 field emission scanning electron microscope (FE-SEM) coupled with energy-dispersive X-ray (EDX) spectroscopy. Transmission electron microscopy (TEM) images were obtained by JOEL JEM-2010 microscope operated at an acceleration voltage at 200 kV. The chemical bonding characteristics of the samples were characterized by Fourier transform infrared spectroscopy (FT-IR, Shimadzu FT-IR-8700) using a standard potassium bromide pellet technique. Each FT-IR spectrum was collected after 32 scans at a resolution of 2 cm⁻¹ from 4000 to 600 cm⁻¹. Xray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Analytical Probe (A Shimadzu Group) system equipped with a monochromatic (Al/Mg) X-ray source (1486.6 eV). XPS measurements were also carried out with a twin anode and a charge neutralizer, testing the electronic binding energy of the samples. Conductivity measurements were done using a four point probe setup, on freestanding samples.



Scheme 1. Schematic representation of the infiltration of electropolymerized PTh into the matrix of the TNTs.



Scheme 2. Synthesis mechanism of Polythiophene



Figure S1. Cyclic voltammograms of electropolymerization of thiophene on (a) Ti foil, (b) TNTs and (c) acetonitrile solution with Bu_4NBF_4 without thiophene at a scan rate of 25 mV s⁻¹.



Figure S2. XRD patterns of (a) Bare Ti foil, (b) Bare TNTs, (c) PTh/TNTs and (d) PTh/Ti foil.

Fig. S2 shows the XRD patterns of the bare Ti foil, bare TNTs, PTh/TNTs, and PTh/Ti foil. The XRD patterns of Ti foil and bare TNTs are in good agreement with previous reports.^{3,4} The peak centered at $2\theta = 20^{\circ}$ clearly confirms the presence of PTh.⁵ The peak centered at 25° is attributed to the diffraction arising from the TNTs .^{3,4} Obviously, this peak was not found in the XRD spectrum of PTh/Ti foil (Fig. S2d), which however exhibited a prominent peak centered at $2\theta = 20^{\circ}$ attributing to PTh.

FT-IR

The FT-IR spectra of the bare TNTs, PTh/TNTs, and PTh/Ti foil are presented in Fig. 2 of the main content. The prominent peaks at 2957 cm^{-1} observed in Spectra (b) and (c) are due to the presence of C-H bonds and 3460 cm⁻¹ which is due to OH stretching vibrations resulting from the hygroscopic nature of the dopant in PTh. Several low intensity peaks seen in the range of 2800-3100 cm⁻¹, can be collectively attributed to the C–H stretching vibrations.⁵ The absorption in this region is obscured by the bipolaron absorption of the doped PTh. The range of 600-1500 cm⁻¹ is the fingerprint region of the PTh. The strong peak at 1622 cm⁻¹ is usually accredited to the aromatic C=C stretching band.⁵ The C-S bending mode was identified at approximately 724 cm^{-1} , which indicates the presence of a thiophene monomer.⁵ The peak around 1310 cm⁻¹ was attributed to the C-C stretching vibration mode of the thiophene ring.⁶ The absorption peaks at 1033, and 785 cm^{-1} indicated a C_{ss}-H out-of-phase and an in-phase bending vibrations, respectively. The polymerization of thiophene monomer effects in polythiophene with three different conjunctions, *viz* α - α conjunction, α - β conjunction, or β - β conjunction (Scheme 2). The IR spectrum achieved for polymerization of thiophene on TNTs showed absorption peaks of C_{α} - C_{α} conjunction at 1428, 1112, 1033 and 785 cm⁻¹, which confirms additionally that the thiophene monomer was successfully polymerized into PTh. Moreover, the strong intensity of these 1428, 1112, 1033 and 785 cm⁻¹ bands which is characteristic of the 2, 5-disubstituted thiophene ring, indicates that the electrochemical coupling of the thiophene ring occurred preferentially at the 2, 5 position (i.e. $\alpha - \alpha$ linkage).⁶ It is well documented that the α -position in the monomer is more reactive than the β -position; therefore $\alpha - \alpha$ conjunction is predominant in the polymer chain. Additionally the α - α conjunction has a good conductivity.⁵ Interestingly, the intensity of the peak at 785 cm⁻¹ is more predominant in the PTh/TNTs than in the PTh/Ti foil. Also, more peaks at 1428, 1033 and 1112 cm⁻¹ attributing to C_{α} - C_{α} conjunction were clearly observed in PTh/TNTs but not at all in PTh/Ti foil. These findings strongly suggest that the PTh/TNT electrode is more electroactive than the PTh/Ti foil. The IR spectrum of the bare TNTs (Figure 2a) demonstrates interactions between Ti ions and molecular water at 1630 cm⁻¹ and 3380 cm⁻¹ and is in well accordance with as reported earlier.⁷



Figure S3. Cross-sectional FESEM of (a) Bare TNTs, (b) PTh/TNTs (c) PTh/Ti foil and (d) EDX of PTh/TNTs.



Figure S4. TEM images of PTh/TNTs at (a) open and (b) closed ends of TNTs.



Figure S5. (a) UV absorption spectra of TiO_2 nanoparticle, (b) Cyclic voltammogram for electropolymerization of thiophene on TiO_2 nanoparticle, (c) Cyclic voltammogram of PTh/TiO₂ nanoparticle at different scan rates and (d) Specific capacitance variation of PTh/TiO₂ nanoparticle electrode at different scan rates.



Figure S6. High resolution XPS spectrum of PTh/TNTs, (a) C1s, (b) S 2p, (c) Ti 2p and (d) O1s spectra of PTh/TNTs. (Dotted line: experimental curve; solid line: deconvolution curve.)



Figure S7. XPS survey spectra of (a) Bare Ti Foil, (b) Bare TNTs, (c) PTh/Ti foil, and (d) PTh/TNTs electrode.

Our findings were strongly supported by the X-ray photoelectron spectroscopy (XPS) data of our PTh/TNT samples. XPS results for PTh/TNT composites in terms of C 1s, S 2p, Ti 2p and O 1s core levels are shown in Fig S6.a-d, respectively. More significantly, electropolymerized polythiophene shows a peak at 285.2 eV due to C1s from the bulk. The peak at 285.2 eV (Fig. S6a) is attributed to α -carbon in the thiophene ring.⁸ This is very much in accordance to what we have observed in our FT-IR results. The S 2p core level from PTh displays a peak at 164 eV, typical for thiophene sulfur.⁹ The deconvoluted peaks at 164.2 eV and 164.4, 164.6, 164.9 eV arise from neutral S2p3/2 and oxidized S2p1/2, respectively (Fig. S6b).¹⁰ This result indicates that the neutral and oxidized sulfur species were mainly produced in the polymer backbone when thiophene monomer was electropolymerized for 5 cycles at the scan rate of 25 mV s⁻¹. The chemical bonding states of the Ti and O peaks arising from the TNT substrate were also observed (Fig. S6 c & d). The peak intensities of the Ti–O component 459.2 eV 11 in the Ti 2p3/2 spectra along with 464.45 eV, 465.3 eV, 465.7 eV, 466 eV in the Ti 2P1/2 and the Ti-O component 532.4 eV, 532.77 eV in the O 1s spectra were observed. We ascribe this to the possible formation of new surface hydroxyl groups on the surface of the TNTs after subjecting them to electropolymerization. Such alterations at the surface usually contribute to an increase in the hydrophilicity, and the binding of organic molecules to the surface of the TNTs leads to a higher migration of ions effecting into increased supercapacitance in PTh/TNTs.¹²



Figure S8. Cyclic voltammogram of (a) Bare TNTs, and (b) PTh/Ti foil at different scan rates in 1 M H₂SO₄.



Figure S9. Charge/discharge curves of (\blacksquare) Bare TNTs and (\bullet) PTh/Ti foil at a current density of 2 A g⁻¹ in 1 M H₂SO₄.



Figure S10. (a) Nyquist plot of (■) bare TNTs, (●) PTh/Ti foil (▲) PTh/TNTs electrode, (b) Magnified image of PTh/Ti foil and (c) An equivalent circuit used for fitting the Nyquist plots.

Nyquist plots of all electrodes: bare TNTs, PTh/TNTs, and PTh/Ti foil in the frequency range of 1 Hz to 10 kHz and a constant potential of 0.1 V are shown in Fig S10 (a) and (b). At lower frequency, the imaginary part of impedance increases, which shows the capacitive behavior. The impedance behavior of bare TNTs comes closer to an ideal capacitor. On the other hand, PTh/Ti foil electrode shows deviation from ideal capacitor and exhibits much lower impedance than the bare TNTs. It is obvious that, as the frequency increases, more inclined features of the spectra are observed due to the more pronounced surface redox reactions at the electrode-electrolyte interface. In the high frequency region, the semicircle represented in Fig S10b, is charge transfer resistance at the interfaces between electrode and electrolytes. Although the equivalent circuit model of the impedance of PTh/TNTs composite electrode may be different with that of PTh/Ti 15 foil and bare TNTs film and the semicircles is not well shown in Nyquist plots due to low applied voltage, the estimated charge transfer resistances judging from the slopes of the curves in the low frequency region are approximately 75 Ω , 51.6 Ω , and 9.7 Ω for bare TNTs, PTh/Ti foil, and PTh/TNTs electrodes, respectively. A prominent semicircular arc was observed in the PTh/Ti foil electrode (Fig. S10b) is indicative of charge transfer limiting process, which is usually a result of internal resistance and capacitance. The low value of charge transfer resistance for the PTh/TNTs with a narrow diameter indicates that the electrolyte ions penetrate into the polymer and access the inner layer of the polymer with greater ease. Overall, the EIS measurements indicated that the PTh/TNTs possess a reduced ion diffusion resistance and charge transfer resistance and charge transfer resistance.



Figure S11. Variations in specific capacitance with respect to number of cycles (a) Bare TNTs and (b) PTh/Ti foil electrode.



Figure S12. Specific capacitance variations of (a) Bare TNTs (b) PTh/Ti foil and (c) PTh/ TNTs electrode at different scan rate.

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