Electrochemical measurement.

The mass of PTh in PTh-TNT NFs supercapacitor electrode was determined by the difference in weight before/after electropolymerization using a Sartorius BP211D balance with an accuracy of 0.01 mg. After electropolymerization, the samples were first dried and were weighed. As the supercapacitive property of only TiO_2 nanotubes (TNTs) was extremely poor, the specific capacitance is negligible (as shown in Figure 9a) compared to the PTh-TNT NFs. In the present work, the specific capacitance was calculated by considering the mass of PTh only. The specific capacitance was obtained from the CV and charge-discharge curves according to the following equations 1 and 2.

$$C_{sp} = \frac{1}{ms\left(V_f - V_i\right)} \int_{V_i}^{V_f} I\,(V) dV \qquad (1)$$

$$C_{sp} = \frac{I \times \Delta t}{m \times \Delta V} \qquad (2)$$

Where I is the discharge current (A), m is the mass of the electroactive material in the electrode (g), s is the potential scan rate (V s^{-1}), ΔV is the potential window, and Δt is the discharge time (s). [References: *Chem. Sci.*, 2016, 7, 5704; *Nat. Commun.* 2013, 4, 1894, *Acc. Chem. Res*., 2008, 41, 699].

Figure S1

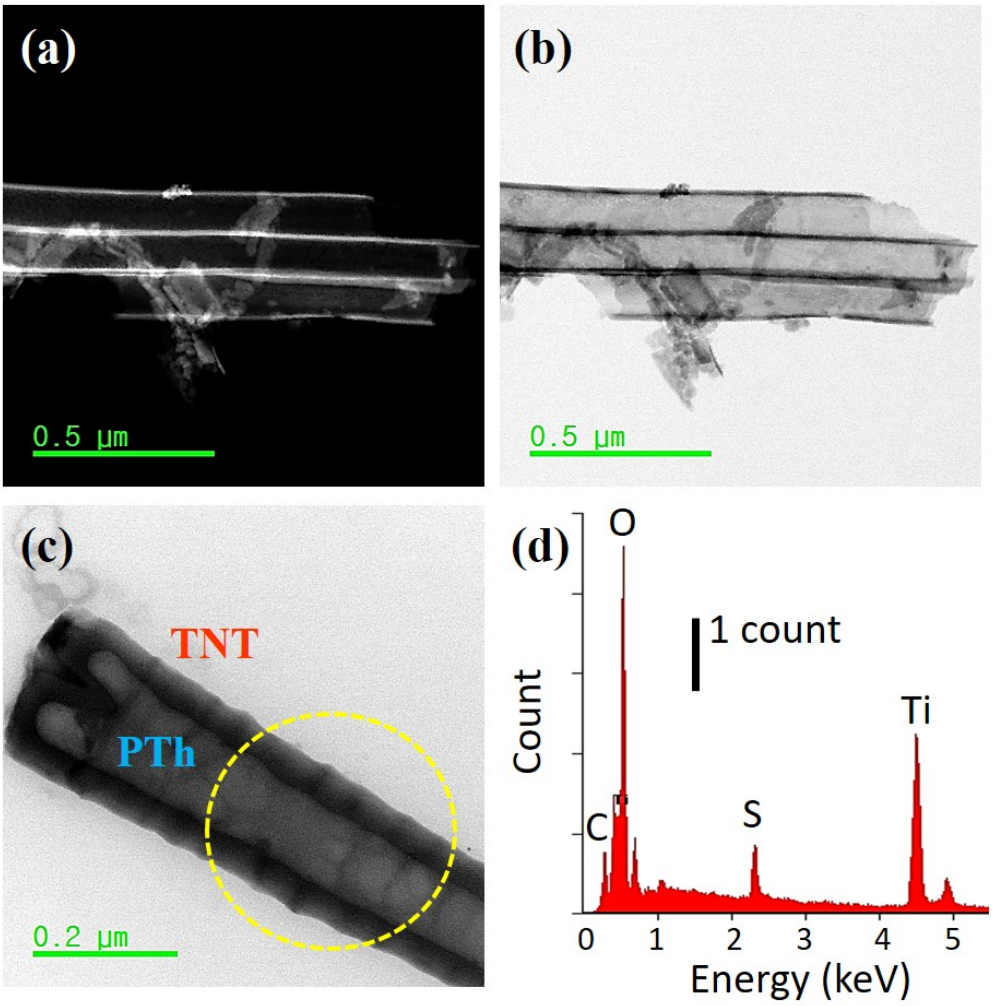

Figure S1 (a) Bright field, and (b) dark field images of TNTs. (c) TEM image of PTh-TNT NFs and (d) EDX spectrum are taken from the yellow circle of (c).

Figure S2

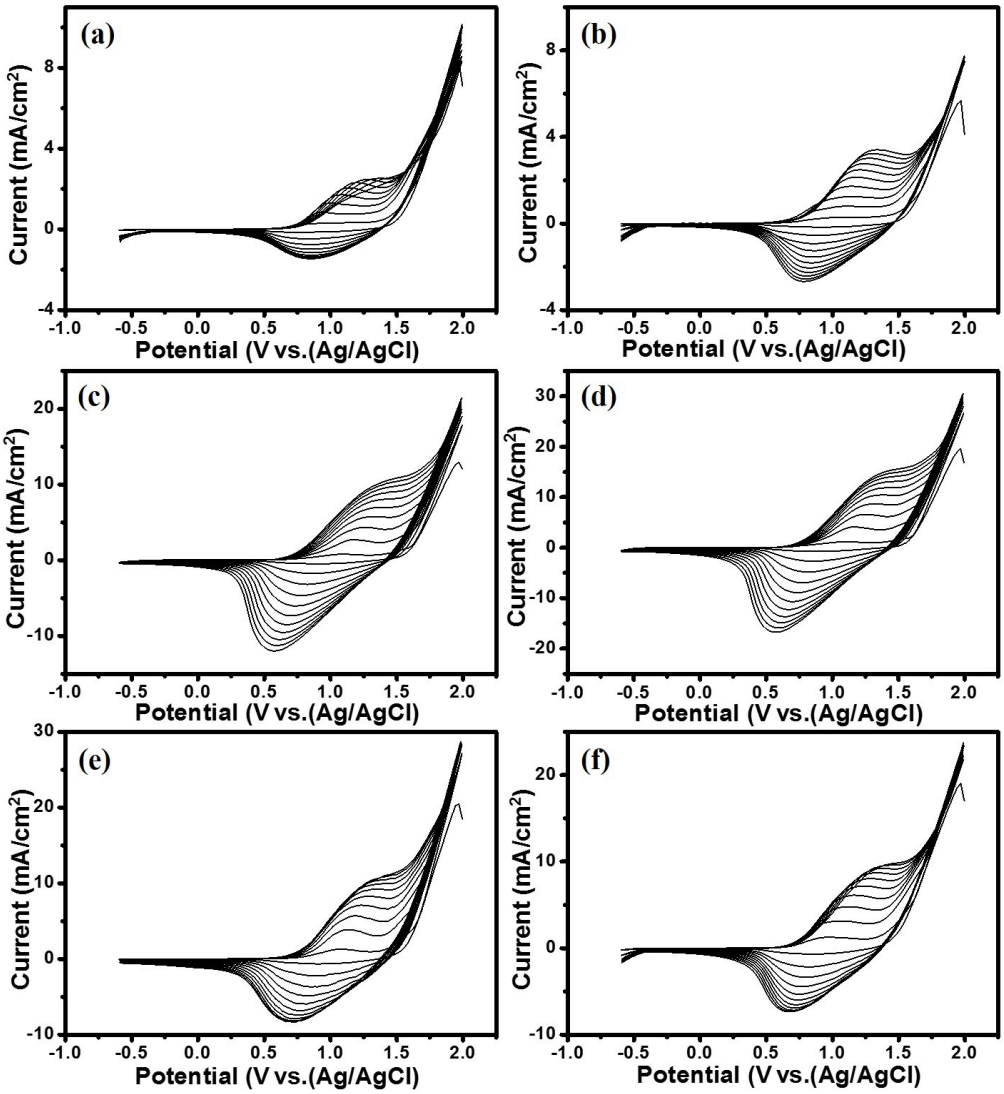

Figure S2 Cyclic voltammograms of electropolymerization of thiophene (0.5 M) on TNTs at different scan rates; (a) 5 mV s^{-1}, (b) 10 mV s^{-1},, (c) 15 mV s^{-1}, (d) 25 mV s^{-1}, (e) 50 mV s^{-1}, and (f)100 mV s^{-1}.

Figure S3

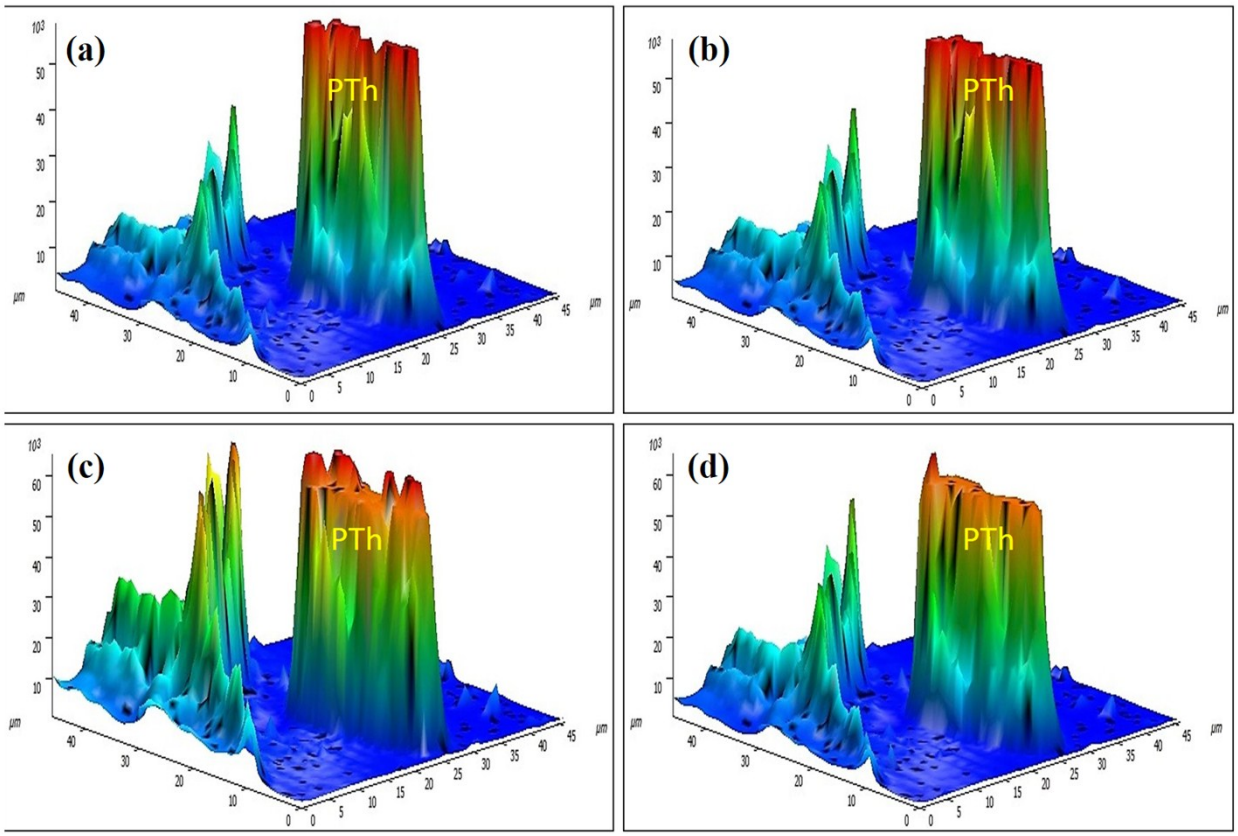

Figure S3 3D Raman maps at bands (a) 1203 cm^{-1}, (b) 1276 cm^{-1}, (c) 1452 cm^{-1}, and (d) 1597 cm^{-1} of PTh-TNT NFs.

Figure S4

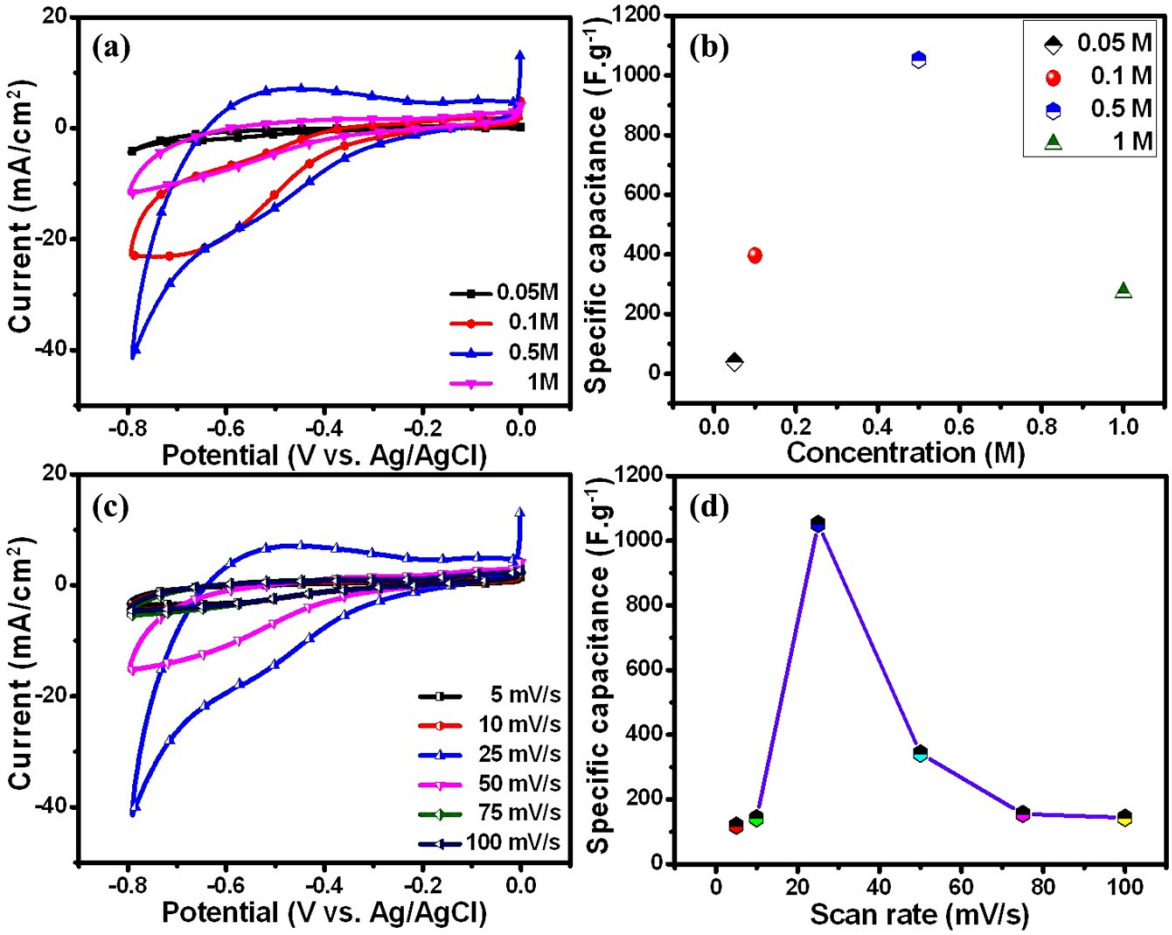

Figure S4 (a) CV curves, and (b) specific capacitance variation of PTh-TNT NFs with different concentrations of thiophene. (c) CV curves and (d) specific capacitance variation with optimized thiophene monomer (0.5 M) concentration at various electropolymerization scan rates. All the CVs are measured in 1 M aqueous H_2SO_4 electrolyte within the potential window from -0.8 to 0.0 V (*vs.* Ag/AgCl) at a gradual scan rate of 5 mV s^{-1}.