Supplementary Information for:

Insight into the reversible conversion-(de)incorporation of redox-active dopants inside polymer-based electrode

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Experimental Section

Chemicals and materials. 1,3,5-tri(9-carbazolyl)benzene (TCB, 98%), tetrabutylammonium perchlorate (TBAP, 99%), 1,2-dichloroethane($\geq$99.0%), hydroquinonesulfonic acid potassium salt (HQS, $\geq$98%), Ammonium phosphate tribasic (($NH_4)_3PO_4$), lithium perchlorate ($LiClO_4$, 98%) were all purchased from Aladdin and used as received. Lithium trifluoromethanesulfonate salt (LiOTf, 98%), lithium bis(trifluoromethylsulfonyl)imide salt (LiTFSI, 99%) and dimethyl sulfoxide (DMSO, 99.9%) were purchased from Aladdin as well, and dried before use. Ultra-light carbon nanotubes film (CNT film) was purchased from Jiedi, Suzhou, China, and cut into pieces as the electropolymerizing substrate of TCB with the radius of 0.6 cm, loading area of 1.13 cm^2 and the weight of about 0.2 mg.

Synthesis of CNT@pTCB. The 1,3,5-tri(9-carbazolyl)benzene (TCB) monomers were electropolymerized through cycle voltammetry method on Biologic electrochemical workstation at room temperature for 10 cycles at a scan rate of 100 mV s^{-1} and potential range of -0.5V to 1.5V. A 15 ml 1,2-dichloroethane solution with 10 mg of TCB and 0.1M tetrabutylammonium perchlorate (TBAP) was employed as electrolyte. The procedure was done in a three-electrode system, where CNT film with the area of 1.13 cm^2 was used as working electrode, Pt plate was used as counter electrode and Ag electrode was used as reference electrode. The self-supporting CNT@pTCB electrode was obtained after 10 steady cycles of polymerization, and was dried in vacuum oven at 60℃ overnight.

Electro-doping of dopants. The assist dopant $(NH_4)_3PO_4$ was doped via potentiostatic method at 1.1V vs Ag^+/Ag for 15 min in 0.1M aqueous solution at room temperature. HQS was doped via potentiostatic method at 0.15V vs Ag^+/Ag for 10 min in 0.1M HQS/DMSO solution at room temperature. All procedures were performed on Biologic electrochemical workstation.

Preparation of electrolyte and electrode. The preparation of LiTFSI-DMSO electrolyte was done in an Ar-filled glovebox, with 3M LiTFSI mixed in DMSO then stirred at 70℃ for over 3h until a transparent viscous liquid was obtained.The preparation of LiOTf-LiTFSI-DMSO electrolyte was done with 1M LiOTf and 3M LiTFSI mixed in DMSO then stirred at 70℃ for over 3h until a transparent viscous liquid was obtained. The electrolytes were cooled down to room temperature before use. CNT and CNT@pTCB films was soaked in saturated HQS/DMSO solution then rested in Ar-filled glovebox overnight. For CNT@pTCB+HQS+PO electrode, the soaking procedure was applied after PO electro-doping.

Half-cell tests. The prepared electrodes were used without further purification. The working electrode, the polypropylene (PP) separator, and lithium foil anode were packaged in a CR2032-type coin cell using different electrolytes as prepared in an Ar-filled glovebox. Galvanostatic charge/discharge tests were performed in the voltage ranging from 2.4 to 3.8 V (vs Li^+/Li) at different current densities on a LAND test system.

Electrochemical quartz crystal microbalance (EQCM) tests. The EQCM tests were carried out in a special gas-flow enabled three-electrode cell (QE 401 Electronics Unit), in which the Au disk

was used as the working electrode, coordinating with a platinum counter and a Ag^+/Ag reference electrode. The quartz crystals were QSX 301 gold sensor, with a surface area of 0.785 cm^2. Crystal impedance measurements and cyclic voltammetry tests were performed using QSense Explorer System. The mass change per unit area (Δm/ng cm^{-2}) is determined via the resonant frequency change (Δf/Hz) on the basis of the well-known Sauerbrey equation:

$$\Delta f = - \frac{2f_0^2 \Delta m}{A(\rho_q \mu_q)^{\frac{1}{2}}} \quad (\Delta m = - S\Delta f)$$

Where f_0 is the resonate frequency of the unload crystal, A is the electrochemically active area of Au electrode, ρ_q is the density of quartz and μ_q is the velocity of the acoustic wave in quartz. When performing pTCB electro-polymerization, the potential was set to -0.5V to 1V. When performing CV test, the potential range was set to -0.3 to 0.7V.

***In situ* Fourier transform infrared spectroscopy (*in-situ* FTIR) tests.** A modified battery was charged and discharged by a LAND test system when the FTIR (Thermo Scientific Nicolet iS50) test performed, which was assembled similarly as the coin cell. The FTIR information were recorded per minute automatically with the model of attenuated total reflection (ATR).

Other characterizations. TCB monomer, CNT film and CNT@pTCB film were characterized by Fourier transform infrared (FTIR, Thermo Scientific Nicolet iS50). The prepared electrodes and cycled Li anodes were characterized by X-ray photon spectroscopy (XPS, Perkin-Elmer PHI 550) with Al Kα as the X-ray source, Transmission Electron Microscope (TEM, JEM-2100f) and Scanning Electron Microscope (SEM, Hitachi S4800).
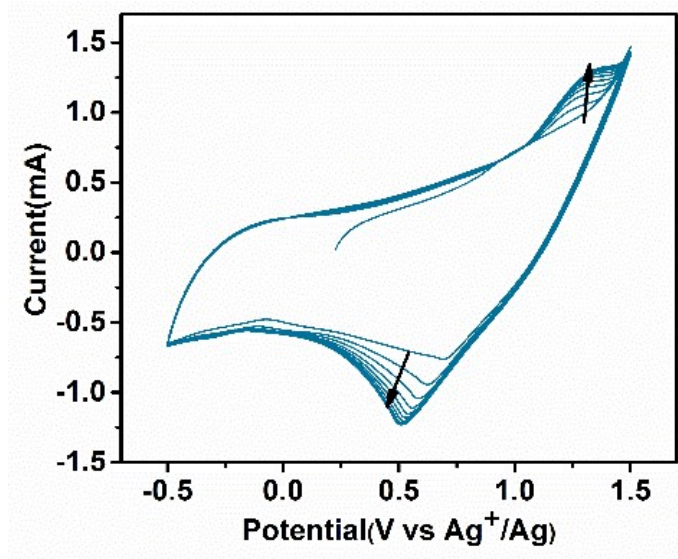
Supplementary Figures

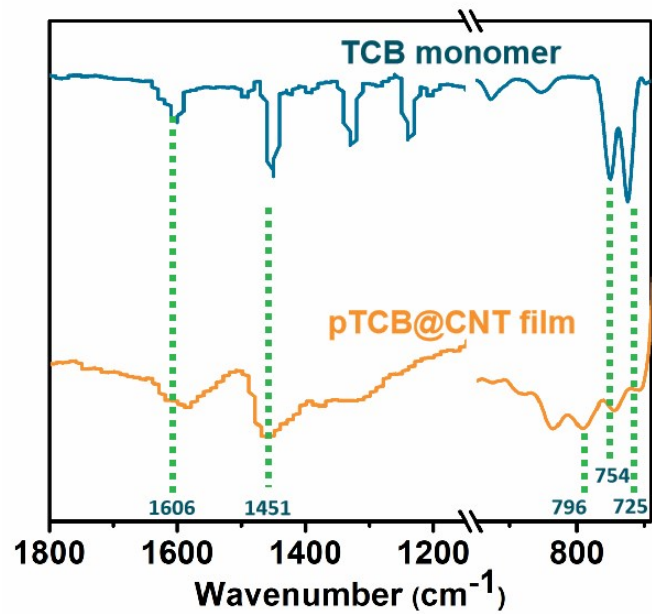**Figure S1**. CV curves of pTCB polymerization on CNT film at 100 mV s^{-1} for 10 cycles.

Figure S2. FTIR spectra of TCB monomer and CNT@pTCB electrode. The peaks at 1606 cm^{-1}, 1451 cm^{-1}, 754 cm^{-1} and 725 cm^{-1} are attributed to substituted benzene ring.[1]
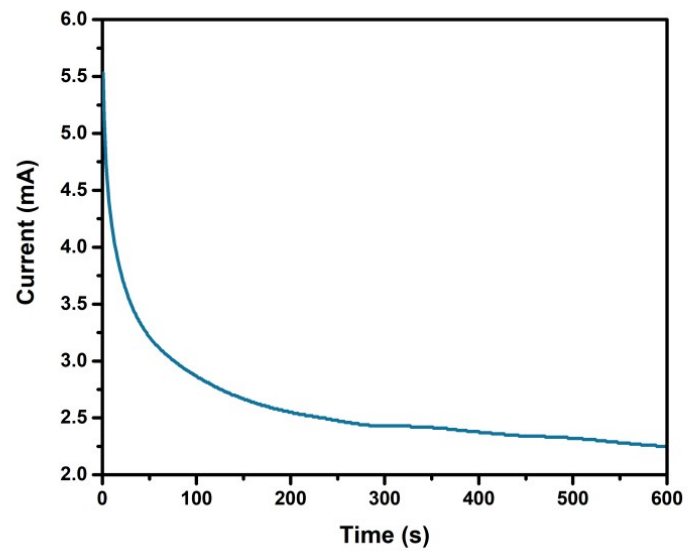
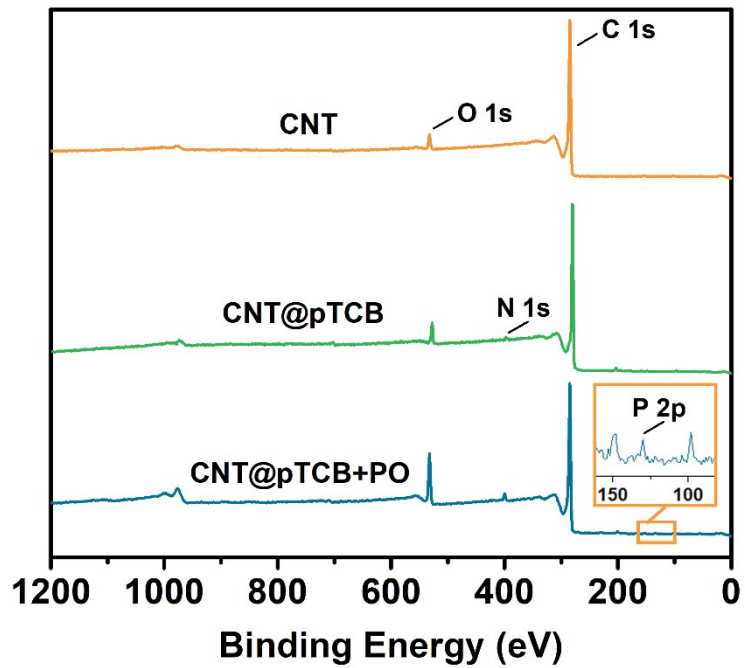**Figure S3**. Potentiostatic curves of electro-intercalating processes for PO at 1.1 V vs Ag$^+$/Ag for 10 min.

Figure S4. The XPS spectra of CNT, CNT@pTCB, and CNT@pTCB+PO. The atomic percentage of P element is 0.50%, suggesting that only tiny amount of PO is inserted into the pTCB matrix. Therefore, adequate space for HQS doping afterwards is ensured.
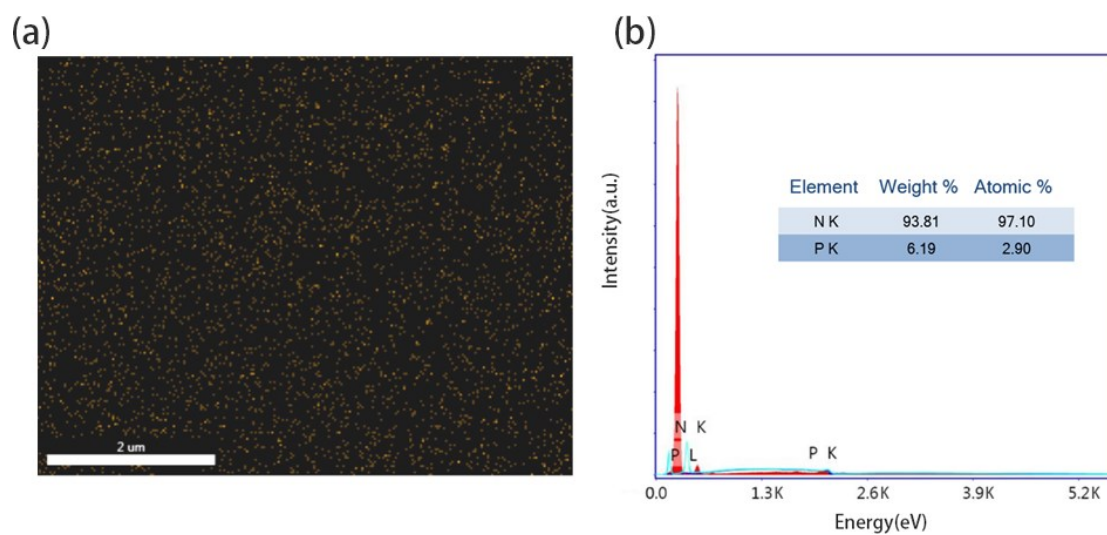
Element	Weight %	Atomic %
N K	93.81	97.10
P K	6.19	2.90

Figure S5. (a)The EDS elemental mappings of P in CNT@pTCB+PO. (b)The EDS spectra of N element and P element.
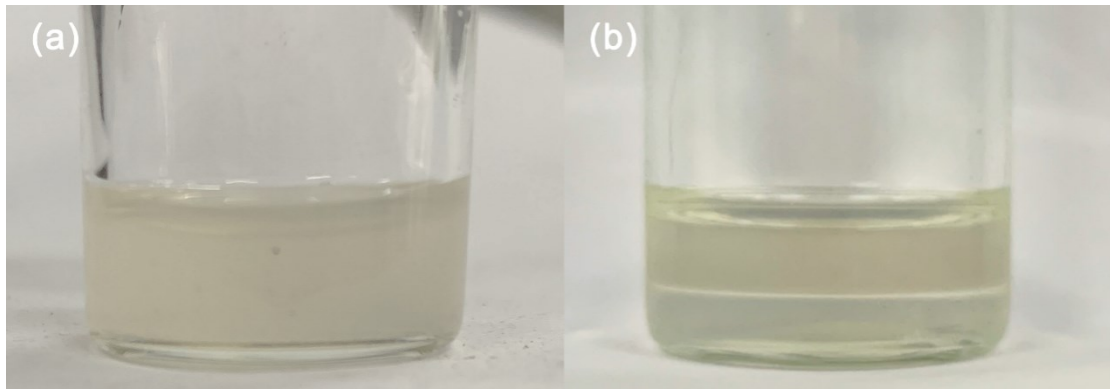
Figure S6. The digital picture of HQS/DMSO solution added in (a)LiTFSI-DMSO electrolyte and (b)LiOTf-LiTFSI-DMSO electrolyte.
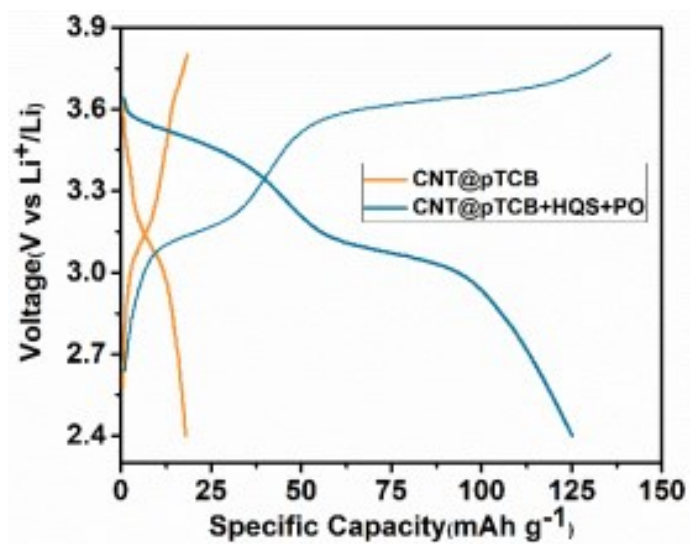
Figure S7. Galvanostatic charge/discharge curves of CNT@pTCB and CNT@pTCB+HQS+PO at the first cycle in LiOTf-LiTFSI-DMSO electrolyte at 0.3C.
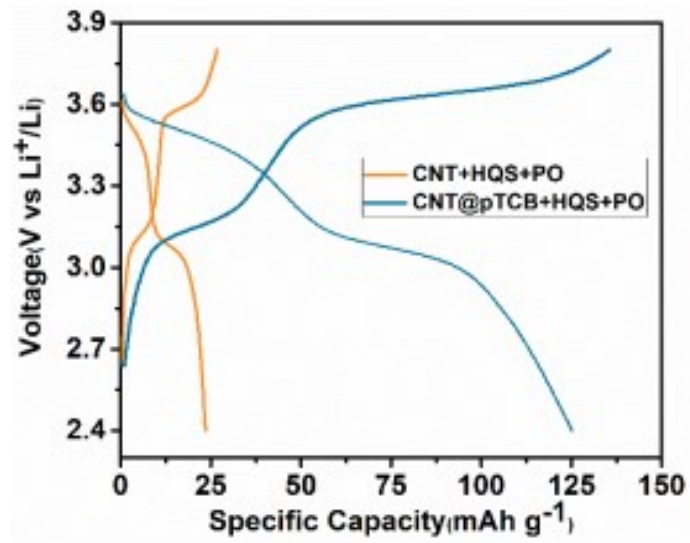
Figure S8. Galvanostatic charge/discharge curves of CNT+HQS+PO and CNT@pTCB+HQS+PO at the activating cycle in LiOTf-LiTFSI-DMSO electrolyte at 0.3C.
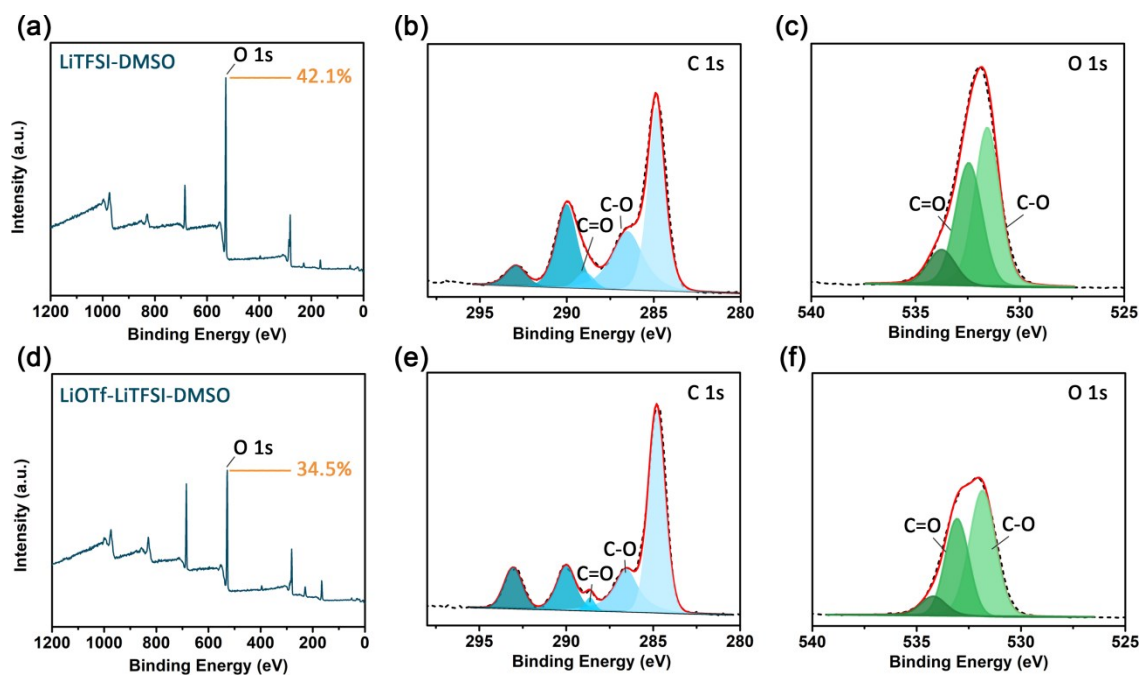
Figure S9. (a, d) XPS spectra from the surface of cycled Li anode in (a) LiTFSI-DMSO electrolyte and (d) LiOTf-LiTFSI-DMSO electrolyte. (b, c) XPS spectra of (b) C 1s and (c) O 1s from the surface of Li anode cycled in LiTFSI-DMSO electrolyte. (e,f) XPS spectra of (e) C 1s and (f) O 1s from the surface of Li anode cycled in LiOTf-LiTFSI-DMSO electrolyte. In the C 1s spectra, the peaks at 286.8 and 289.2 eV are assigned to C-O and C=O, respectively. In the O 1s spectra, The peaks at 531.5 and 533.2 eV are assigned to C-O and C=O, respectively.[2]
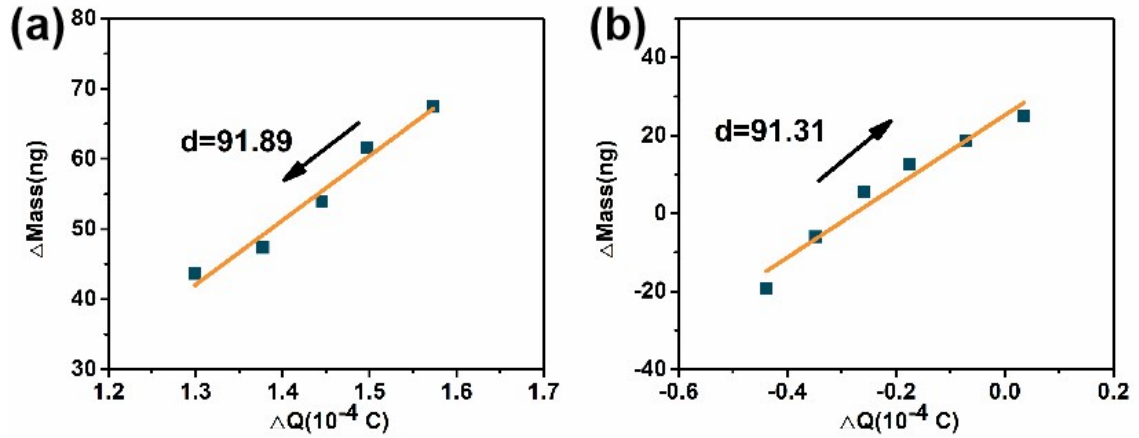
Figure S10. The mass-charge curve of the electro-polymerized pTCB on Au disk at 100 mV s^{-1} for one cycle in a potential range of 0.1 V to 0.6 V while (a) charging and (b) discharging. The transportation of anion and cation follows the Faraday's law:

$$Q = \frac{nmF}{M}$$

where m/Q is the slope d of the line above, n is the number of electrons (set to be 1 in this case) and F is Faraday constant (9.65×10^4 C mol^{-1}).
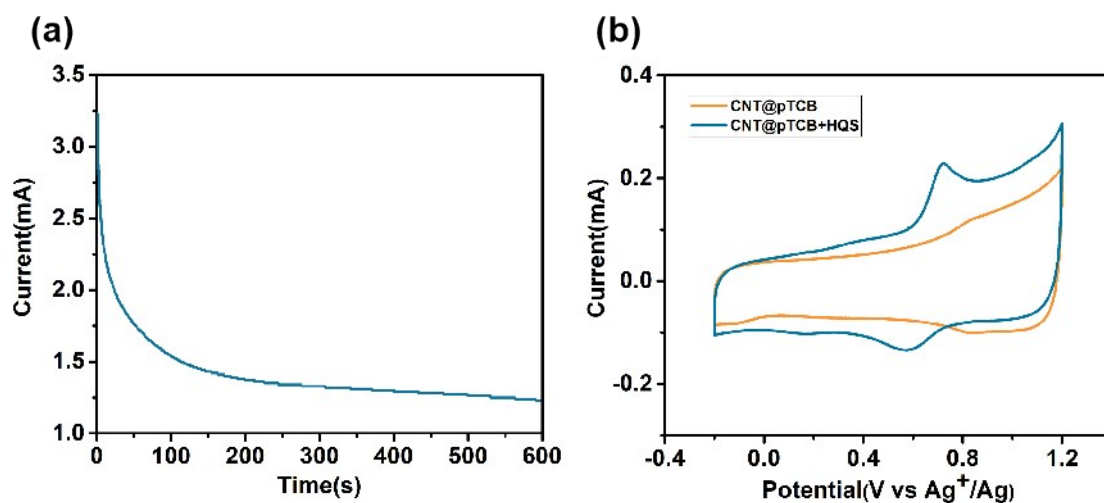
Figure S11. (a) Potentiostatic curves of electro-doping processes for HQS at 0.15 V vs Ag$^+$/Ag for 10 min. (b)CV curves of CNT@pTCB and CNT@pTCB+HQS in 0.1M LiClO$_4$/acetonitrile solution at 20 mV s^{-1}

References:

1.Y. S. Mary, K. Raju, T. E. Bolelli, I. Yildiz, H. I. S. Nogueira, C. M. Granadeiro and C. Van Alseony, *J. Mol. Struct.*, 2012, **1012**, 22-30.

2.W. Stickle; T. Stickle, Propylene Carbonate - XPS Reference Spectra. *Surf. Sci. Spectra (USA)* 2014**, 21(1)**, 28-34.