Supplementary file

(S1)

XPS analysis (figure S1 shown below) indicates the presence of Ti-O on TiC particle surface, and the negative-charge may originate from de-protonated hydroxyl groups (Ti-O<sup>-</sup>). A schematic presentation of the possible interaction between TiC and PPy through hydrogen bonding is illustrated in Fig. S2.



Fig. S2: Schematics of possible TiC-PPy interaction through hydrogen bonding.

(S2) Experimental:

## CP composites preparation:

PPy(pTS) nanocomposite polymer was formed on the surface of TiC via chemical polymerization at 0 °C. After the addition of 5 wt% TiC nanoparticles, 0.02 mole pyrrole (98%; Aldrich) monomer and 0.02 mole *p*-toluenesulfonate (pTS; 95%; Aldrich) into 80 vol% aqueous methanol solution, the resulting solution was treated in an ultrasonic bath for 30 min. As an oxidant, 0.0466 mole FeCl<sub>3</sub> (97%, Aldrich) was dissolved separately in the methanol solution and then added to the prepared pyrrole monomer/*p*TS/TiC solution drop-wise, followed by stirring for 20 min at 0 °C. The reaction product was filtered and washed thoroughly with deionized water and methanol until the filtrate was colorless and the sample was dried under vacuum for more than 12 h at room temperature.

## Materials characterization

Particle morphology was examined by both scanning electron microscopy (SEM; JEOL JSM-7600F) and transmission electron microscopy (JEOL JEM-1230), while crystal structure and phase composition were identified by X-ray diffraction (XRD) on a diffractometer (Rigaku Ultima IV) with Cu Kα X-ray radiation. Elemental analysis was carried out by the combustion-based (C,N,H,S) elemental analyzer (Elementar VarioEL-III). X-ray photoelectron spectroscopy (XPS) analysis was conducted on PHI 5000 VersaProbe (ULVAC-PHI), which employed a focused X-ray

source of 30 W.

## **Electrochemical characterization**

For electrochemical characterization, the electrodes were made of CP-containing powder and PTFE binder with a weight ratio of 10:1 (without conductive carbon additive) on an Al current collector. After drying at 50 °C in vacuum oven for 24 hr, the electrode sheets were punched into disks, 1.2 cm in diameter, for assembly. The active material loading of the electrodes is ca.1.0 mg/cm<sup>2</sup>. The coin cell consisted of a CP-containing electrode, a Li foil disk as the counter electrode, and electrolyte of 1M LiPF<sub>6</sub> in a 1:1:1 v/v mixture of ethylene carbonate (EC), ethylmethyl carbonate (EMC), dimethyl carbonate (DMC) with 5% propylene carbonate (PC). A polypropylene porous membrane was used as the separator. All cells were assembled in a dry room where the dew point was maintained between -40 and -45 °C. The cells were tested between 2.0 and 3.8 V. The electrochemical impedance spectroscopy analysis was conducted at the open-circuit voltage of the tested cell. The amplitude was 10 mV, and the frequency ranged from 200 kHz to 10 mHz.

## (S3) Electrochemical Impedance spectroscopy analysis:

The following figure (Fig. S3) compares the Nyquist plots of the three electrodes taken at their open-circuit voltages. All the plots show a (distorted) semi-circuit in the medium frequency range. The diameter of the semi-circuit, as delineated by the dashed lines, approximately gives the overall resistance of charge transfer. As shown, the semi-circle width is the largest for PPy(pTs) electrode, and smallest for the TiC@PPy(pTS). The data are consistent with the rate performance shown in Fig. 4.



Fig. S3: Nyquist plots of the PPy-containing electrodes at open-circuit voltage.