Supporting information

1. Material and methods

1.1 Preparation of C&N-Ts

All chemicals were used as received without further purification.

Preparation of C&N co-doping TiO_2 nanospheres (C&N-Ts):

Tetra-n-butyl Titanate (purchased from Alfa Aesar Co. Ltd.), placed parallel with a dosage of 17 mL, were dissolved into 200 mL ultra-pure ethanol, named solution A. Later, 4 g $(NH_2)CO$ added into 50 mL H_2O, named solution B. Solution B was intruducted into solution A under vigorous machine stirring to promote the hydrolysis of Tetra-n-butyl Titanate, and then a white colloid solution appeared in the reactor. The colloid solution was air dried at 323 K for 24 h. After that, the products were calcined at 773 K for 4 h with a heating rate of 1 K min^{-1} under a nitrogen atmosphere in a tube furnace. Finally, black-yellow mesoporous C&N co-doped TiO_2 nanospheres were abtained.

The another three compared products were prepared in the same way:

N doping TiO_2 (N-Ts): the yellow products were calcined the sample at 773 K for 4 h under the air.

C doping TiO_2 (C-Ts): the black products were calcined at 773 K for 4 h under the nitrogen flow but without introduced the $(NH_2)_2CO$.

No doping TiO_2 (Ts): the white products were calcined at 773 K for 4 h under the air and without introduced the $(NH_2)_2CO$.

Electrode fabrication

The electrochemical rate-capability and cycling performance of samples were carried out with coin-shaped cells using a metallic lithium film as both the counter and reference electrodes. The mass of the Li metal was typically 15 mg, whereas the mass of samples ranged from 3 mg to 6 mg. The anode was prepared by a coating method, a slurry of 80% (weight percent) active material (the blue powder was ground and sieved before used), 10% conducting carbon black (Super P), and 10% polyvinyli-dene fluoride (PVDF) binder homogeneously mixed in N-methyl pyrrolidinone (NMP) were prepared into viscous slurries for efficient deposition. After the slurries was stirring on a magnetic stirring apparatus until the powder mixed uniformity. The slurries was coated on the copper foil by an automatic film editor, then dried in a vacuum oven at 393 K for 12 h, and cut into circular sheet. Then the sheet was dried in a vacuum oven at 393 K for 12 h again. The cells were assembled into CR2016 coin cells in a glove box filled with pure argon, in which the moisture and oxygen was strictly controlled to less than 1 ppm. Microporous polypropylene film (Celgard2400) was used as the separator. The electrolyte was 1.0 mol L^{-1} $LiPF_6$ in a mixture of diethyl carbonate (DEC) and ethylene carbonate (EC) in the ratio of 1:1(w : w). The cells had a configuration of Li metal (−) | electrolyte | LTO (+), with a liquid electrolyte.

2.3 Measurement and Characterization

The obtained products were characterized by X-ray powder diffraction (XRD) using a X ‘Pert-ProMPD (Holand) D/max-γA X-ray diffractometer with Cu Kα radiation (λ ＝0.154178 nm). The XRD measurement conditions: the scanning current is 40 mA, the scanning voltage is 40 KV, the scanning step is 0.026 ^{o} and the scanning rate is 0.2626 ^{o} s^{-1}. Scanning electron microscopy (SEM) images and EDX were taken on a FEI-quanta 200F scanning electron microscope with acceleration voltage of 30 kV. Transmission electron micrographs (TEMs) were taken on a FEI-Tecnai F20 (200 kV) transmission electron microscope (FEI). X-ray Photoelectron Spectroscopy (XPS) was obtained by using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatised Mg Kα X-ray (hν = 1283.3 eV). XPS samples were prepared by drying a dispersion of micro-crystals on a piece of silicon wafer. Nitrogen adsorption-desorption isotherms were obtained using a ASAP2050 (Micromeritics Industrument Corp.) surface area & porosity Analyzer at 77 K. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated by the Barret-Joyner-Halenda (BJH) method.

2.4 Electrochemical characterization

All the tests were carried out at room temperature.

The electrochemical properties of products were tested in CR2016 coin cells. All the measurements were controlled and recorded automatically by the LAND CT2001C charge–discharge detector (China, Wu han). Cyclic voltammetry (CV) tests were performed over the potential range of 0.01 - 3.00 V using a CHI1000B electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was performed in a three-electrode system, with metallic lithium as the reference electrode. The applied frequency of the EIS test covered a range from 100 KHz to 10 mHz under an open circuit. The electrochemical analysis was tested with an electrochemical working station with impedance modules (CHI660D electrochemical workstation).

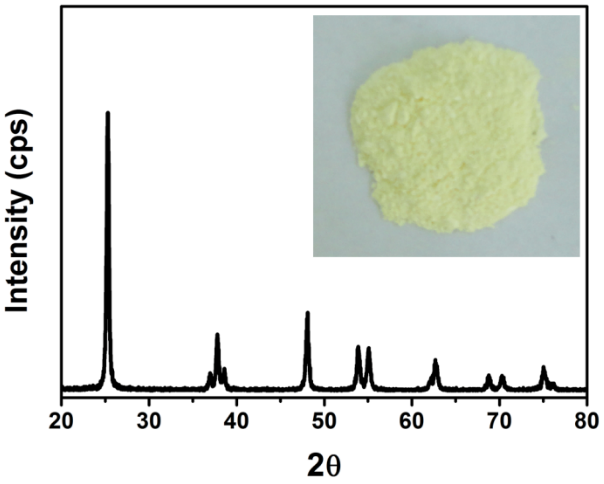

Fig. S1 XRD pattern and digital image of N-Ts.

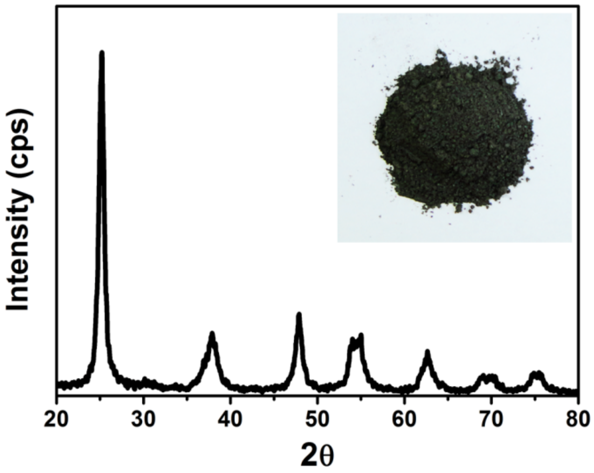

Fig. S2 XRD pattern and digital image of C-Ts.

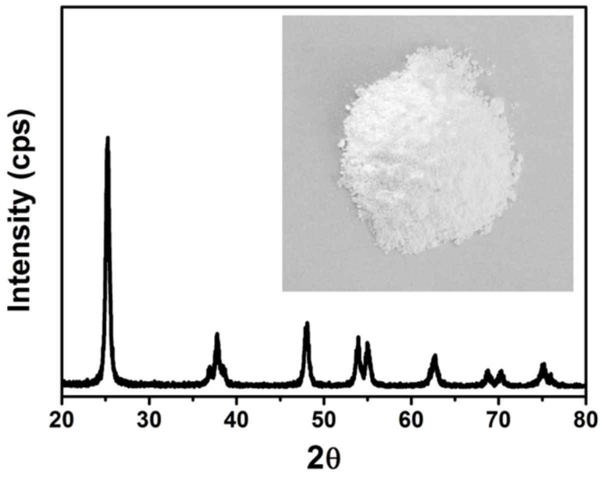

Fig. S3 XRD pattern and digital image of Ts.

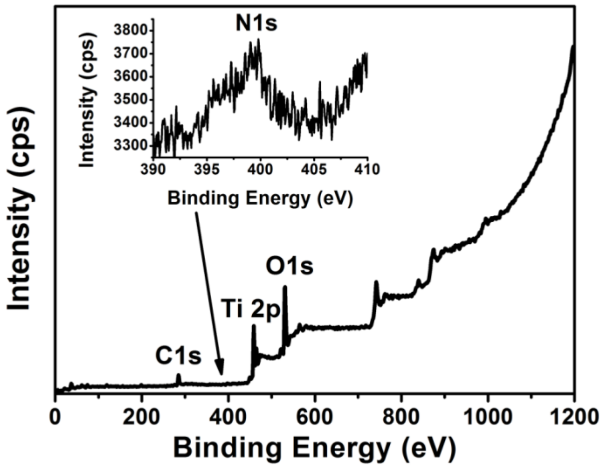

Fig. S4 XPS full spectrum of the C&N-Ts.

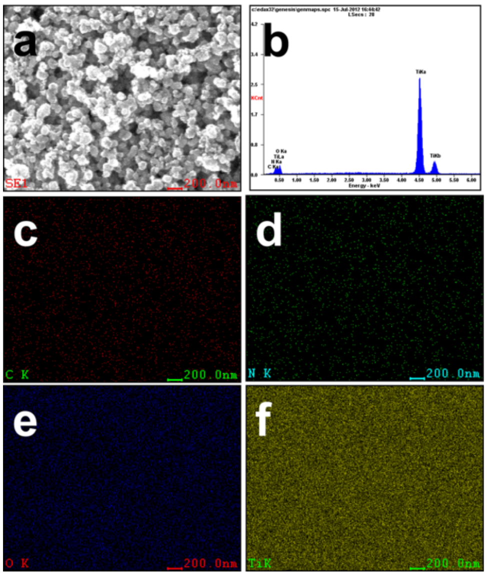

Fig. S5 EDX spectrum and elemental mapping of C&N-Ts.

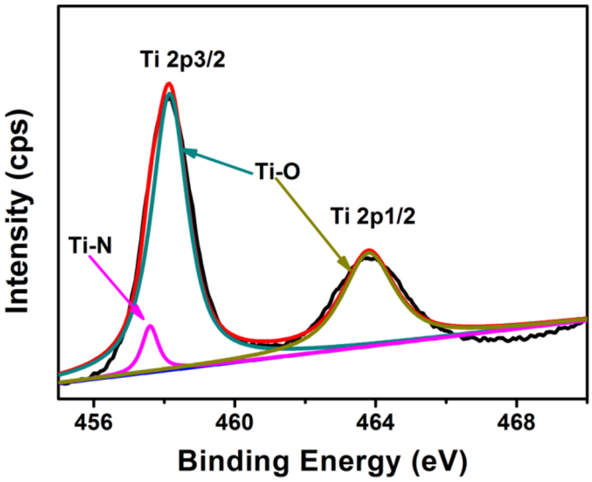

Fig. S6 XPS high-resolution spectra of the Ti2p regions of the as-prepared C&N-Ts.

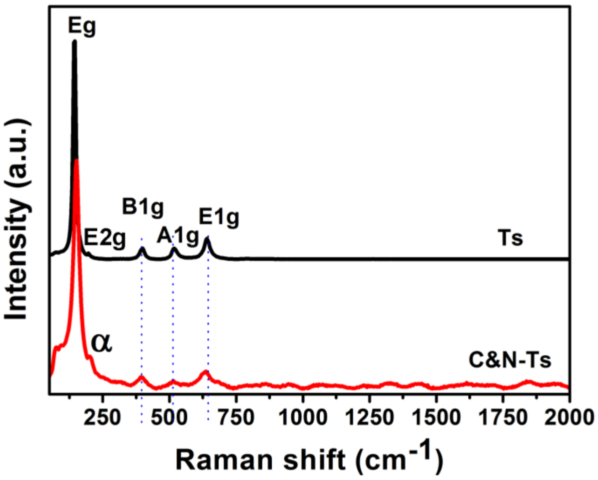

Fig. S7 Raman spectra (λ_{ex} = 633 nm) of the C&N-Ts and Ts.

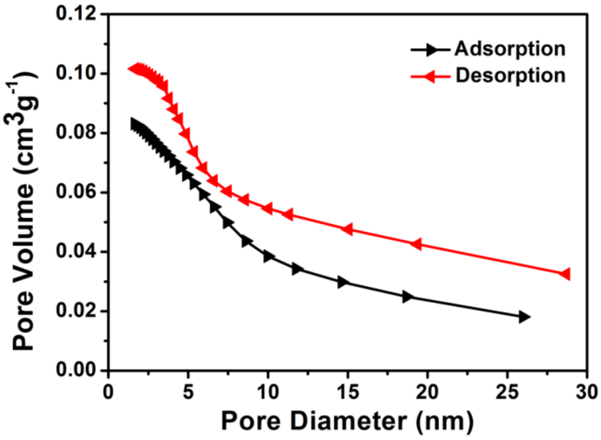

Fig. S8 BJH cumulative pore volume of C&N-Ts.

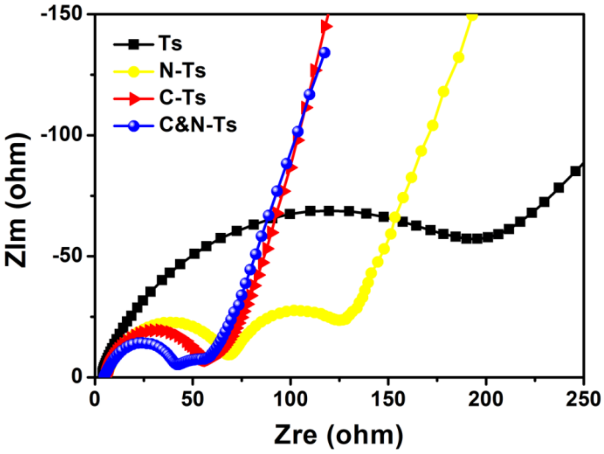

Fig. S9 Nyquist plots of the C&N-Ts, N-Ts, C-Ts and Ts composite electrode.