Supporting Information

Introduction of Fe^{2+} in $Fe_{0.8}Ti_{1.2}O_4^{0.8-}$ nanosheets via photo reduction and its enhanced electrochemical performance for lithium ion battery anode

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Experimental details

Preparation of $K_{0.8}Fe_{0.8}Ti_{1.2}O_4$ and $H_{0.8}Fe_{0.8}Ti_{1.2}O_4$

Layered titanate $K_{0.8}Fe_{0.8}Ti_{1.2}O_4$ was prepared by a solid state method, as was reported previously. K_2CO_3, Fe_2O_3 and TiO_2 is mixed at a molar ratio of 0.4: 0.4: 1.2, K_2CO_3 was added in an excess amount of 5% to compensate for the volatilization of potassium. Then the mixture was heated to 1373K for 24h. The products were filtered, washed with deionized water (named KFTO). KFTO was converted into protonic titanate by reacting $K_{0.8}Fe_{0.8}Ti_{1.2}O_4$ with 0.5mol/L HCl (solid/liquid=1g:100mL) under constant stirring at ambient temperature for 24h.The color of KFTO changes from red to yellow immediately with the addition of HCl. The ion-exchange was carried out for two times to completely exchange the K^+ with H^+, The obtained samples were filtered, washed with a large amount of water to remove the excess acid, and finally dried in air (named HFTO).

Exfoliation of $H_{0.8}Fe_{0.8}Ti_{1.2}O_4$

$Fe_{0.8}Ti_{1.2}O_4^{0.8-}$ nanosheets were performed by treating 0.4g $H_{0.8}Fe_{0.8}Ti_{1.2}O_4$ in 100mLof tetrabutylammonium hydroxide under stirring for more than 7 days. The colloid suspensions were centrifuged at a speed of 1000rpm to separate incompletely exfoliated samples and obtain the suspension containing well-dispersed exfoliated $Fe_{0.8}Ti_{1.2}O_4^{0.8-}$ nanosheets. The incompletely exfoliated samples were washed with water for several times to remove the excess TBAOH on the surface of nanosheets (until the pH of solution attain nearly neutral), and then dried using a freeze drier.

Decomposition of TBA^+ and remove of water molecules

The obtained nanosheets were redispersed in water under UV illumination for several hours to decompose the TBA^+ and then heat-treated at 200°C for 3 h to remove of water molecules in the interlayer. The obtained sample was named as yellow nanosheets.

The preparation of Fe^{2+} self-doped $Fe_{0.8}Ti_{1.2}O_4^{0.8-}$ nanosheets (Fe^{2+}-doped FTO nanosheets)

The preparation procedure of Fe^{2+} self-doped $Fe_{0.8}Ti_{1.2}O_4^{0.8-}$ nanosheets was as follows: 0.1g of $Fe_{0.8}Ti_{1.2}O_4^{0.8-}$ nanosheets powders were first dispersed in 30 mL of methanol solution in a quartz tube using a magnetic stirrer, and then the suspension was exposed to UV light for several hours. The color of the suspension turned from yellow to grey with the prolonging of irradiation time. TBA^+ and water molecules were also removed under UV irradiation in methanol. The samples were centrifuged and dried using a vacuum drier and named as Fe^{2+}-doped FTO nanosheets.

Preparation of electrode

Prior to electrode preparation in a helium-filled glovebox, samples were dried at 200°C for 3 h to remove the water in the gallery. The active material was mixed with acetylene black and polyvinylidene fluoride (PVdF) binder together at a weight ratio of 7:2:1 in N-methylpyrrolidone (NMP) to form a slurry and pasted on copper foil. Then it was dried in a vacuum oven at 110 °C for 48 h and punched into small disks with a diameter of 15.8 mm. Electrochemical measurements were performed using CR2032 half cells, which were assembled in argon-filled glove box (Mbraun, Germany, O_2 and H_2O contents <0.5 ppm). Pure Li foil was used as the counter electrode and microporous polypropylene film as the separator. The electrolyte was a solution containing 1 m LiPF6 dissolved in a mixture of ethylene carbonate, ethyl methyl carbonate, and DMC (1:1:1 in volume).

Characterization

The crystal structure of the sample was investigated using a powder X-ray diffractometer (XRD, Rigaku D/max-2200PC) with Cu Ka (λ= 0.15418 nm) radiation. The size and morphology of the particles were observed using a field-emission scanning electron microscope (Hitachi, FE-SEM, S-4800). Transmission electron microscopy (TEM) observation and selected-area electron diffraction

(SAED) were performed on a Tecnai G2F20STWIN system at 200 kV, and the powder sample was supported on a microgrid. X-ray photoelectron spectroscopy (XPS) measurements were done on an Axis Ultra XPS instrument with an Mg Ka source. The Fourier transform infrared (FTIR) spectra were measured in Bruker infrared spectrometer (VERTE70) with the KBr disk technique.

Electrical measurement

The galvanostic charge/discharge tests were conducted using a battery testing system (Shenzhen, Neware, China) under different current density with a voltage range of 0.01～3 V (vs Li/Li+). The cyclic voltammetry was conducted between 0.01 and 3.0 V at a scan rate of 0.1 mV $s^{-1}$and electrochemical impedance spectroscopy were performed using a CHI660E electrochemistry workstation (Shanghai Chenhua, China).

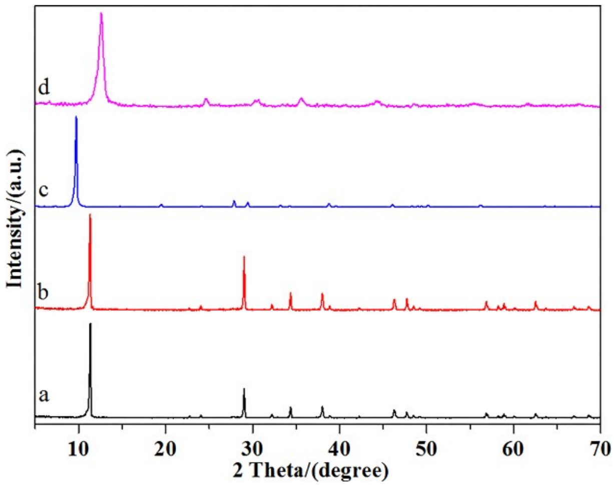

Figure.S1 XRD patterns of (a) KFTO, (b) KFTO heat-treated at 200℃, (c) HFTO and (d) HFTO heat-treated at 200℃

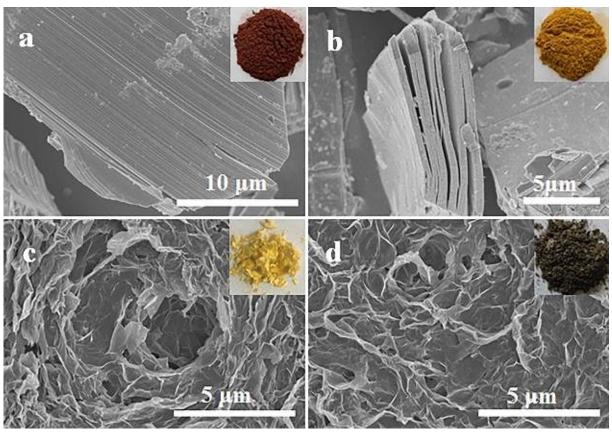

Figure.S2 SEM images and optical photos of (a)KFTO, (b)HFTO, (c) FTO nanosheets and (d) Fe^{2+}-doped FTO nanosheets

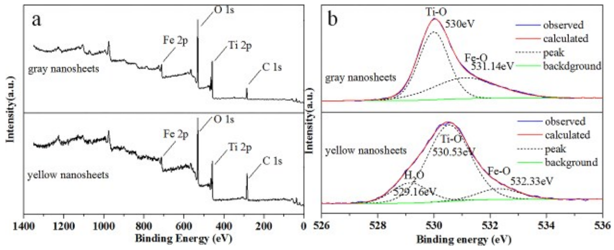

Figure.S3 Overall XPS spectrum(a) and O1s XPS spectrum(b) of FTO nanosheets and Fe^{2+}-doped FTO nanosheets

Table. S1 content of Fe^{2+} and Fe^{3+} calculated from the Fe 2p XPS spectrum

Name	Position	FWHM	Area	%Area
Fe^{2+}	710.8	1.048	2221.36	6.82
Fe^{2+}	724.5	1.926	1638.86	5.03
Satellite of Fe^{2+}	714.7	2.599	1938.75	5.95
Fe^{3+}	711.9	3.282	14731.59	45.23
Fe^{3+}	725.5	4.774	8915.89	27.37
Satellite of Fe^{3+}	719.5	3.324	3125.13	9.59

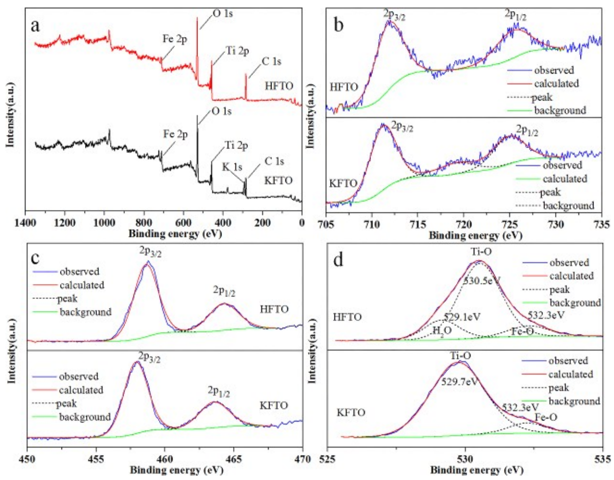

Fig.S4 Overall XPS spectrum(a), Fe2p XPS spectrum(b), Ti2p XPS spectrum(c) and O1s XPS spectrum(d) of KFTO and HFTO

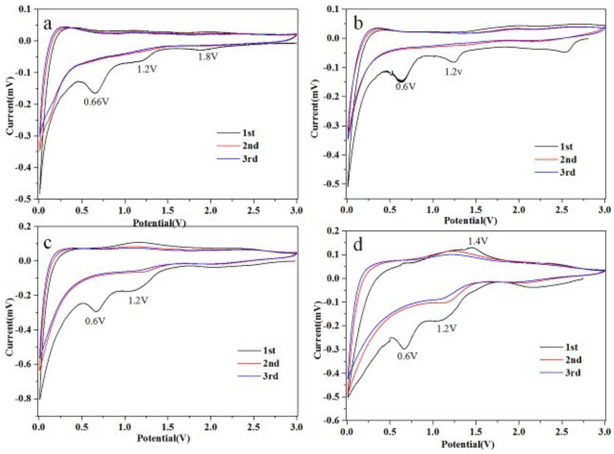

Fig.S5 Cyclic voltammetry curves of KFTO(a), HFTO(b), FTO nanosheets (c) Fe^{2+}-doped FTO nanosheets(d)

KFTO, HFTO, FTO nanosheets and Fe^{2+} doped FTO nanosheets exist a reduction peak at 0.6V, which is attributed to the formation of solid–electrolyte interface (SEI) film, and the reduction peak at 1.2V is due to the Li^+ insertion. The cathodic peaks observed at 1.8 V in Fig. S5a may be the reduction of Fe^{3+} to Fe^{2+}. The anodic peak at 1.4 V in Fig. S5d can be attributed to the deintercalation of Li^+.

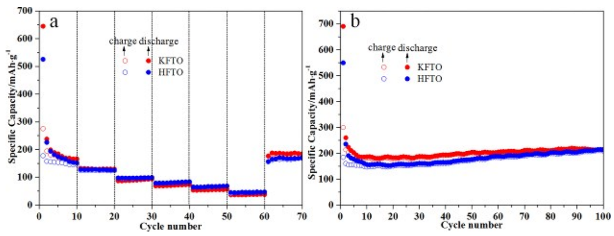

Fig. S6 Electrochemical performance of KFTO and grey HFTO (a) rate capability from 100 to 5000 mA g^{-1} (b) cycling performance at 100 mA g^{-1}

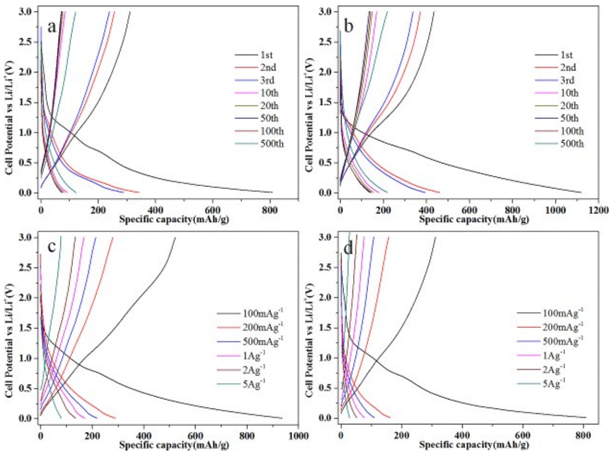

Fig. S7 voltage profiles under the current density of 100 mA g^{-1} at different cycles (a) FTO nanosheets and(b) Fe^{2+}-doped FTO nanosheets; voltage profiles under different current density (c) FTO nanosheets and (d) Fe^{2+}-doped FTO nanosheets.

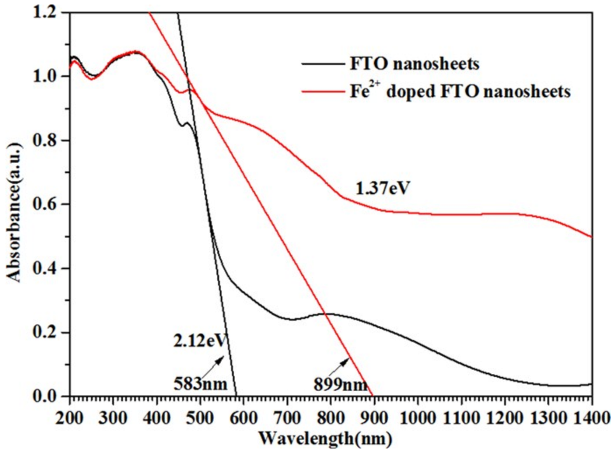

Fig.S8 UV–vis diffuse reflectance spectra of FTO nanosheets and Fe^{2+} doped FTO nanosheets

For the spectra, it can be seen that FTO nanosheets have a band gap of 2.12eV while Fe^{2+} doped FTO nanosheets have a lower band gap of 1.37 eV, suggesting that the electrical conductivity of Fe^{2+} doped FTO nanosheets is superior to FTO nanosheets.