Supporting Information

Substitutional Carbon-Modified Anatase TiO_2 Decahedral Plates Directly Derived from Titanium Oxalate Crystals via Topotactic Transition

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Material characterization: X-ray diffraction patterns of the titanium oxalate and TiO_2 samples were obtained with a Rigaku diffractometer using Cu Kα irradiation (λ = 1.54056 Å). The morphology and microstructures of the samples were studied by scanning (Nova NanoSEM 430) and transmission electron microscopy (FEI Tecnai-F30). The chemical states of the samples were determined by X-ray photoelectron spectroscopy (Thermo Escalab 250, using a monochromatic Al Kα X-ray source). All binding energies were referred to the C 1s peak (284.8 eV) that arises from adventitious carbon. The optical absorption spectra were recorded on a UV-visible-infrared diffuse reflectance spectrophotometer (Jasco V-770). Cathodoluminescence spectra were obtained on a scanning electron microscope (Hitachi SU-70) equipped with a CL system (Horiba MP-32S) at room temperature. Electron Spin Resonance spectra of the powders were obtained at 140 K using a JES-FA200 ESR spectrometer (130K, 9.058 GHz, X-band), with microwave power of 1 mW, sweep width range from 274 to 374 mT, modulation frequency of 100 kHz and modulation amplitude of 0.35 mT. I-V curves of a single plate of TiO_2 and $TiO_{2-x}C_x$ were measured at room temperature using a scanning electron microscope (FEI, NanoSEM 430) equipped with a four-probe micromanipulator (Kleindiek MM3A-EM) in its vacuum chamber at room temperature. A silicon wafer was used as a substrate to support the plates, which were ultrasonically dispersed in an ethanol solution prior to dropping them onto the substrate. For picking up the plates and measuring its I-V curves, two probes were connected to a Keithley 4200–SCS

semiconductor characterization system. Commercial tungsten probes were used to pick up the plates because of their sufficient hardness and sharpness. Prior to loading the plates, two tungsten probes were manipulated to achieve tip-to-tip contact and then subjected to Joule heating by applying a voltage scan from 0 to 10 V several times in order to fully remove the surface tungsten oxide layer on the probes.

Photocatalysis activity measurement: 10 mg of the TiO_2 or $TiO_{2-x}C_x$ sample was suspended in 80 mL of an aqueous solution containing 10 mM NaOH and 3 mM terephthalic acid. The suspension was stirred in the dark for 20 min to reach adsorption saturation before exposure to light ($\lambda > 420$ nm). 5 mL of the solution was collected from the reaction solution every 20 min and centrifuged to determine the concentration of the 2-hydroxy terephthalic acid by photoluminescence spectroscopy. The light source used in photocatalytic reactions was a 300 W Xe lamp (Beijing Perfectlight Co. Ltd, PLS-SXE). Visible light was obtained using a cut-off filter of 420 nm to remove UV light.

Electrochemical lithium ion storage measurement: The electrochemical properties of TiO_2 and $TiO_{2-x}C_x$ as anode materials for lithium ion batteries were evaluated by a galvanostatic charge/discharge technique. The working electrodes were prepared by mixing the active material, carbon black (Super-P), and poly(vinylidene difluoride) at weight ratios of 80:10:10 that was then pasted onto a copper foil, and pressed and dried under vacuum at 120 °C for 12 h. Coin cells were assembled in an argon-filled glove box, with metallic lithium as the counter electrode, a mixture of 1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate (1:1 vol) as the electrolyte, and Celgard 2400 polypropylene as the separator. The electrochemical tests were performed between 1-3 V versus Li^+/Li. The C-rate currents used were calculated based on an anatase TiO_2 capacity of 168 mA h g^{-1} ($Li_{0.5}TiO_2$). The AC impedance spectrum was measured by a Solatron 1287/1260 Impedance Analyzer in the frequency range 10 mHz to 100 kHz with a potential perturbation of 10 mV.

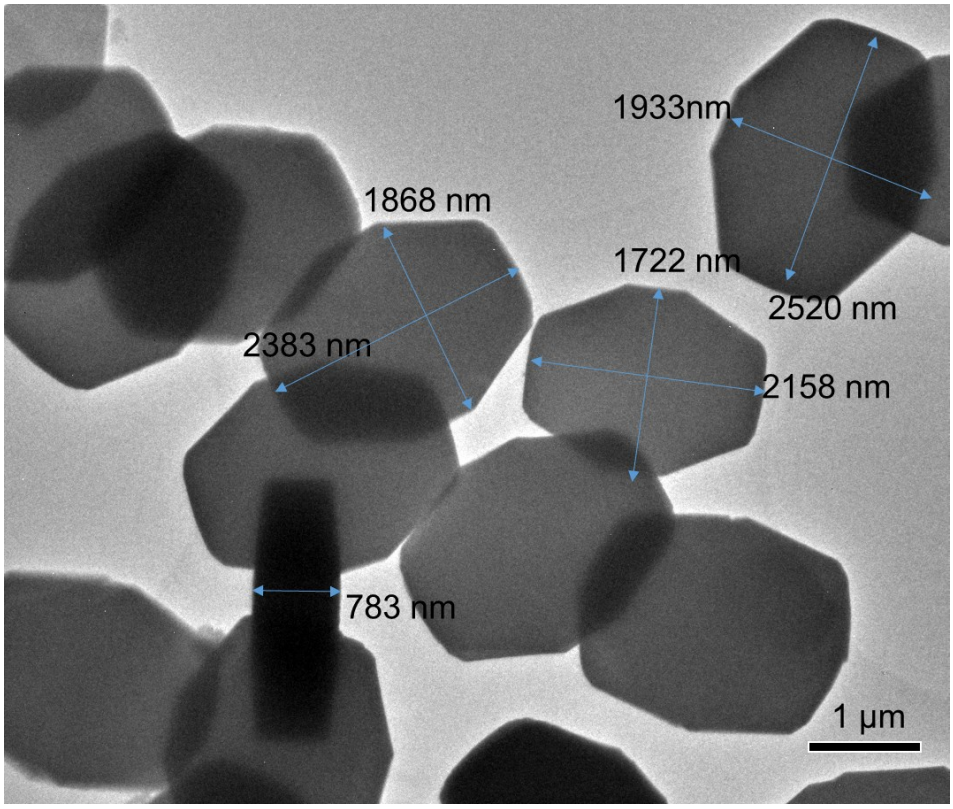

Figure S1 TEM image of the titanium oxalate decahedral plates synthesized.

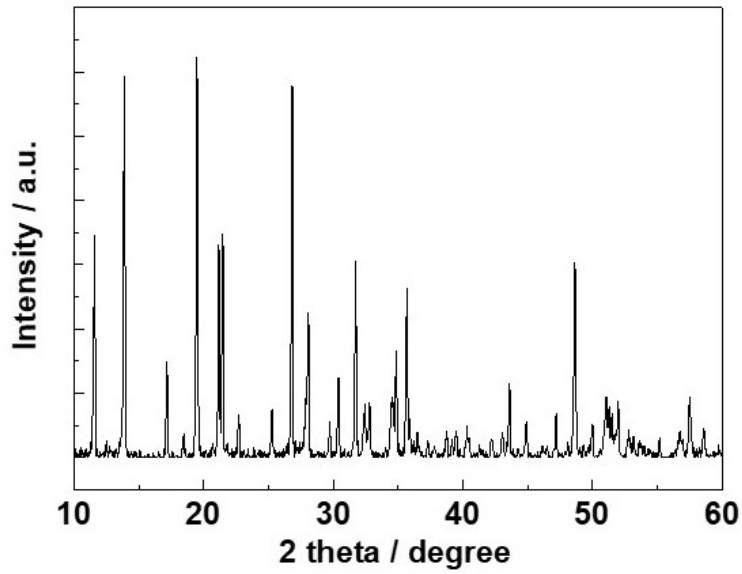

Figure S2 XRD pattern of the synthesized titanium oxalate decahedral plates.

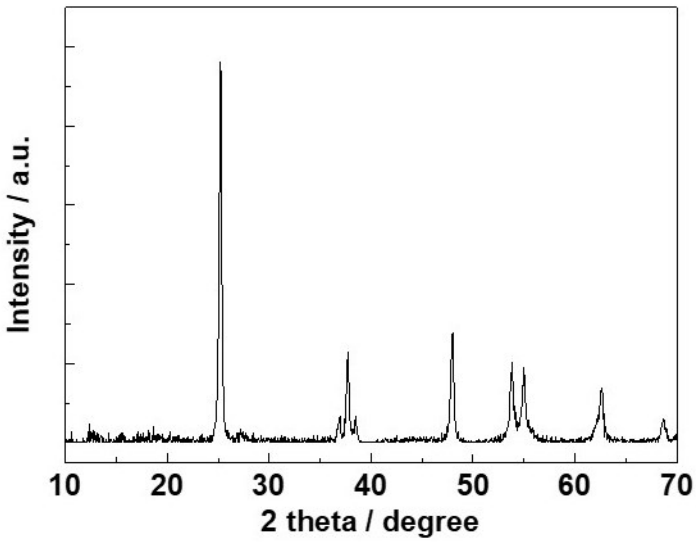

Figure S3 XRD pattern of the anatase TiO_2 derived from titanium oxalate by heating in air.

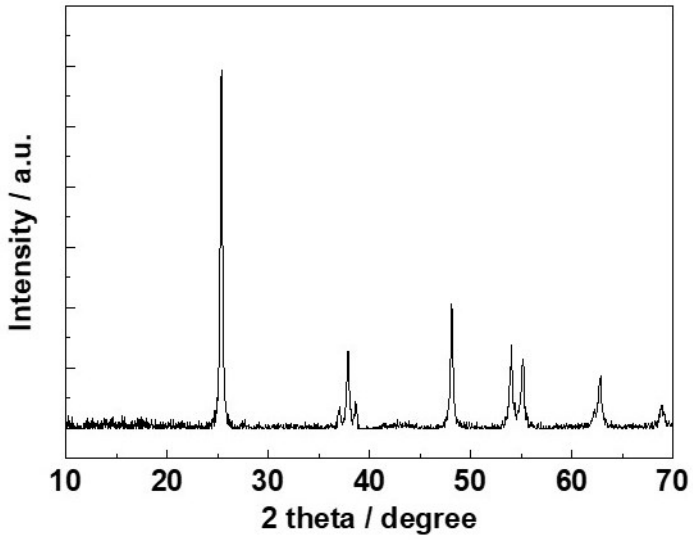

Figure S4 XRD pattern of the anatase $TiO_{2-x}C_x$ derived from titanium oxalate in the atmosphere of argon.

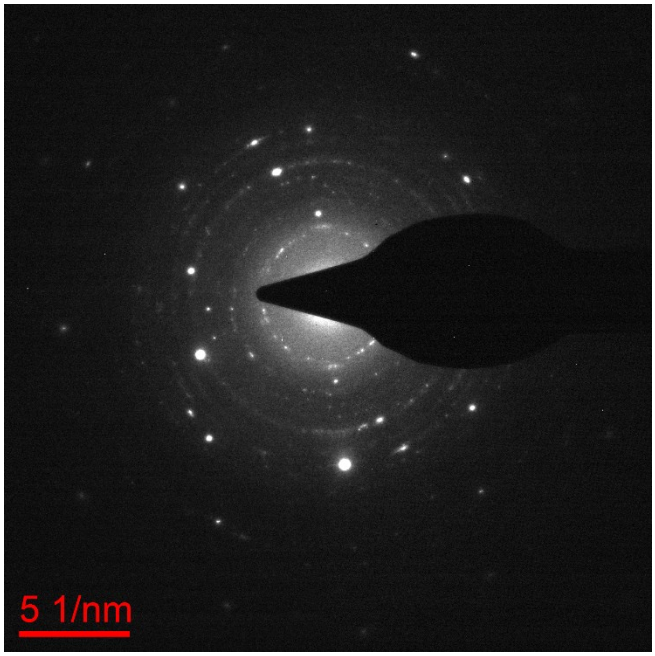

Figure S5 Electron diffraction patterns recorded from the $TiO_{2-x}C_x$ sample in Figure 3c. The light spots are originate from the crystalline Si substrate. The rings are from the $TiO_{2-x}C_x$ sample supported by Si substrate.

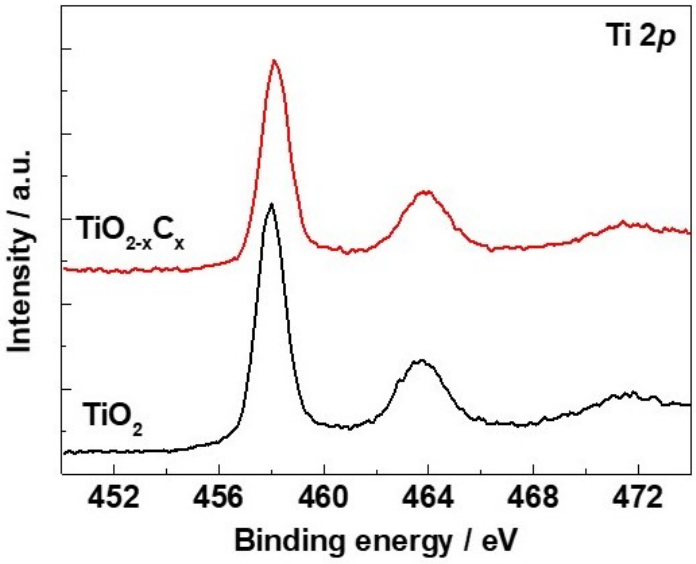

Figure S6 XPS Ti 2*p* spectra recorded from the pristine surfaces of TiO_2 and $TiO_{2-x}C_x$.

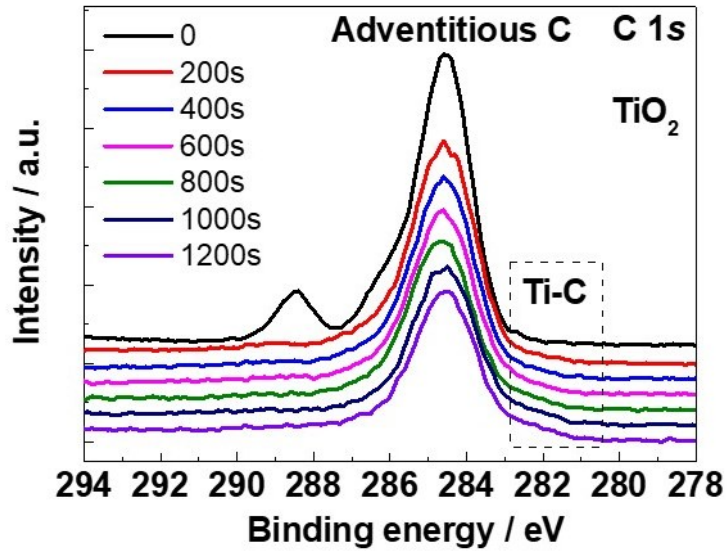

Figure S7 Sputtering time dependent XPS spectra of the C 1*s* state for sample TiO_2.

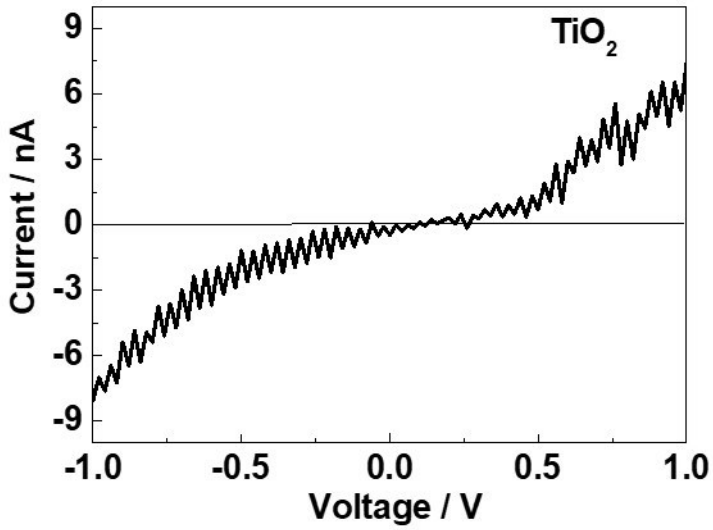

Figure S8 Current-voltage curve measured from a single TiO_2 particle.

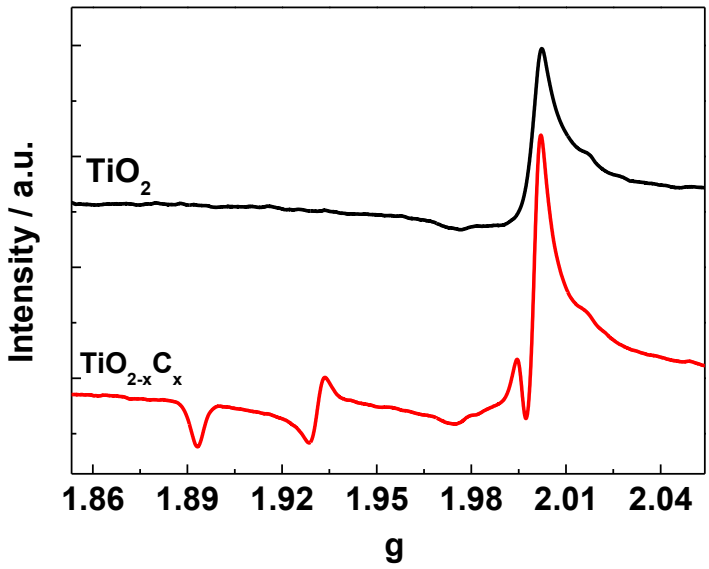

Figure S9 Electron spin resonance spectra of TiO_2 and $TiO_{2-x}C_x$ measured at 140 K.

Table S1 Comparison of lithium storage capacity at rates of 10 and 15 C of $TiO_{2-x}C_x$ with reported TiO_2 samples.

Sample	Capacity at 10 C	Capacity at 15 C	Reference
TiO_2 microspheres with {001} facets	47.5	37.3	*Adv. Mater. 2015, 27, 3507*
TiO_2 microspheres with {010} facets	12.4	9.2	*Adv. Mater. 2015, 27, 3507*
N/S codoped TiO_2 nanoparticles	64	/	*Chem. Commun. 2013, 49, 3461*
$TiO_{2-x}C_x$ decahedral plate	91.5	78.5	This study