

Supporting Information

Fabrication of Rutile TiO₂ Nanorods Arrays on Copper Substrate for High-performance Lithium-ion Batteries

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Structural characterization of TiO₂ arrays

X-ray diffraction (XRD) patterns were recorded at room temperature using a Rigaku D/MAX 2000 PC diffractometer with Cu K α radiation ($\lambda=1.5406\text{\AA}$). Scanning electron microscopy (SEM) images were obtained on a HITACHI S4800 microscope. Detailed structural properties of the obtained product were investigated by transmission electron microscopy (TEM, JEM-2010, JEOL).

Electrochemical measurements

The electrochemical performance of the TiO₂ nanorods array on Cu substrate was studied by Swagelok-type two-electrode assembled in an Ar-filled glove box (MB-10-G with TP170b/mono, MBRAUN) using lithium foil as anode, 1M LiPF₆/EC+DEC (1:1 in volume) as electrolyte, and Celgard 2300 membrane as separator. For these experiments, no additives such as binder agent and conductive agent were used. The galvanostatic charge/discharge cycle was performed using a battery test system (NEWARE BTS-610, Neware Technology Co., Ltd) at a constant current density, with cut off voltage of 2.6–1.0V (vs. Li/Li⁺). A three-electrode electrochemical cell was employed for cyclic voltammetry measurements in which Li metal disk served as the reference and counter electrodes. Cyclic voltammetric (CV) tests were conducted between 1.0-2.6V with scan rate of 0.1, 0.5 and 1.0 mV · s⁻¹ (IM6ex, Zahner elektrik).

S1: In order to confirm that the nanorods contain Ti and O without any chlorides, which probably influence the electrochemical test, energy-dispersive X-ray spectrometry (EDS) analysis is introduced. The peaks of Si, C and Cu are donated by the TEM equipment and copper grid, respectively.

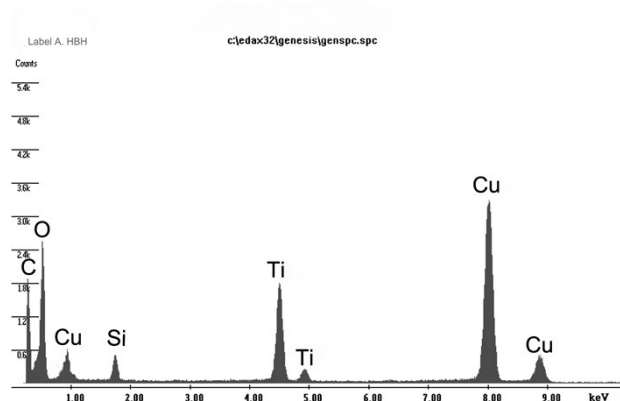


Figure S1. EDS result of the as-cleaned nanorods array

S2: Urea here plays an important role for the growth of nanorods. (1) Slow down the hydrolysis of Ti^{3+} and afford simultaneously hydrolysis–condensation by olation of the Ti^{3+} , which can control the nucleation progress.^{S1-S4} (2) Tailoring the pH value of the reaction solution preventing the corrosion of Cu substrate by high concentration of Cl^- .

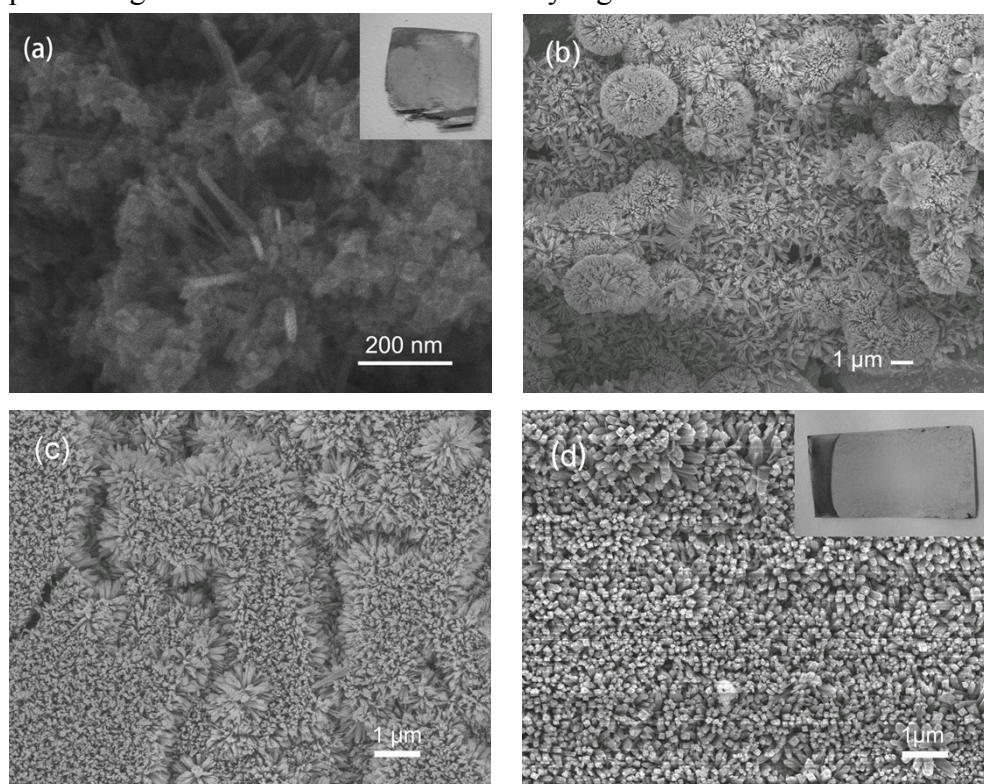
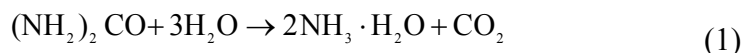
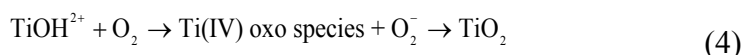


Figure S2 SEM image of (a) sample prepared with absence of urea (b) sample prepared with addition of 0.05g urea, (c) sample prepared with addition of 0.1 g urea, and (d) sample prepared with addition of 0.3 g urea

It is well known that urea decomposes in hot water and produces ammonia and carbon dioxide. The reaction is as follows:



And the chemical process of the formation of TiO_2 is:



The hydrolysis of Ti^{3+} was slow down firstly because of the coordination between Ti^{3+} and ammonia ligands, resulting in the change of composition or coordination structure of the growing unit, and induced the heterogeneous nucleation on the Cu substrates.^{S1} Then, with the slow generation of OH^- , $[\text{Ti}(\text{OH})_2(\text{Cl})_2(\text{OH}_2)_2]^0$ complex was formed,^{S2} leading the growth of rutile TiO_2 by oxolation (the formation of oxo bridges by the elimination of water).^{S3-S4} Furthermore, it is widely known that copper can be corroded badly by Cl^- , especially with the presence of H^+ , and the high pH value is benefit of preventing copper corrosion,^{S5-S7} which was achieved by the hydrolysis of urea.

Figure S2a shows TiO_2 nanoparticles are produced with observation of only a few nanorods in the absence of urea, and the copper substrate is badly corroded. With the addition of urea, dandelion-like structures assembled by nanorods generate (Figure S2b). As is shown of Figure S2d, uniform TiO_2 nanorods array was prepared when the content of urea is up to 0.3g, and the corrosion of Cu substrate is prevented.

Supporting References

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