Structural characterization of TiO$_2$ arrays

X-ray diffraction (XRD) patterns were recorded at room temperature using a Rigaku D/MAX 2000 PC diffractometer with Cu Kα radiation (λ=1.5406Å). 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 TiO$_2$ 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 LiPF$_6$/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.

![EDS result of the as-cleaned nanorods array](image)

**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.$^{51-54}$ (2) Tailoring the pH value of the reaction solution preventing the corrosion of Cu substrate by high concentration of Cl$^{-}$.

![SEM image](image)

**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:

\[(\text{NH}_2)_2\text{CO} + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 \cdot \text{H}_2\text{O} + \text{CO}_2\] (1)

\[\text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-\] (2)

And the chemical process of the formation of TiO$_2$ is:

\[\text{Ti}^{3+} + \text{H}_2\text{O} \rightarrow \text{TiOH}^{2+} + \text{H}^+\] (3)

\[\text{TiOH}^{2+} + \text{O}_2 \rightarrow \text{Ti(IV) oxo species} + \text{O}_2 \rightarrow \text{TiO}_2\] (4)

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.$^\text{S1}$ Then, with the
slow generation of OH\,-, [Ti(OH)$_2$(Cl)$_2$(OH)$_2$]$^{10}$ complex was formed,$^\text{S2}$ leading the growth of
rutile TiO$_2$ by oxolation (the formation of oxo bridges by the elimination of water).$^\text{S3-S4}$
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,$^\text{S5-S7}$ 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**

(S1) Y. B. Zhang, X. J. Feng, L. Jiang, *Sci China Ser B-Chem.*, 2007, **50**, 175-178


