Supplementary Information

Direct Synthesis of Pure Single-Crystalline Magnéli Phase Ti$_8$O$_{15}$ Nanowires as Conductive Carbon-Free Material for Electrocatalysis

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**Schematic diagram of apparatus**

**Figure S1** (A) Schematic diagram of the experimental apparatus for growth of Ti$_8$O$_{15}$ NWs, the temperature decreases gradually from centre to the right, giving two temperature regions: high (H.T.) and low temperature (L.T.), (B) Digital pictures of Ti substrate before and after experiment.

Since no catalyst was used in the process of the growth of the Ti$_8$O$_{15}$ NWs, suggesting that the growth mechanism of the KTi$_8$O$_{16}$ NWs may not dominated by the vapor-liquid-solid (VLS) mechanism, which is is frequently employed to explain the growth of nanowires and nanoarchitectures.$^{S1,S2}$ Instead, we propose a possible growth mechanism for the formation of the KTi$_8$O$_{16}$ NWs based on the modified vapor-solid (VS) mechanism.$^{S3,S4}$ A two-step path reaction process was proposed in our synthesis process of KTi$_8$O$_{16}$ NWs, showing as follow:

(a) The TiO$_2$ powders in the quartz boat at the center of the tube (the high temperature
region, H.T.) were reduced to form H₂O (g):

\[ TiO_2 + H_2 \xrightarrow{H.T.} TiO_H + H_2O(g) \]

(b) The H₂O (g) reacted with the Ti on the Ti substrate (the low temperature region, L.T.) to form oxygen-deficient tetragonal phase of KTi₈O₁₆ NWs in H₂ atmosphere.

\[ H_2O(g) + Ti + H_2(g) \xrightarrow{L.T.} Ti_8O_{15}(nanowires) + H_2(g) \]

**Additional experimental data**

**Calculation Details**

![Figure S2](image)

**Figure S2** Supercell models of (A) anatase TiO₂, (B) the site of oxygen vacancy,(C) Magneli phase Ti₈O₁₅.

Anatase TiO₂ has a tetragonal structure with lattice parameters \( a = b = 3.776 \text{ Å} \), \( c = 9.486 \text{ Å} \). To calculate anatase TiO₂, a 2×2×1 supercell was constructed with 16 Ti and 32 O atoms, as shown in Figure 1(A). The calculate modle of Ti₈O₁₅ was constructed from removed two O atoms from anatase TiO₂ supercell and optimized the atomic structure, as shown in Figures 1(B)–1(C).
**Figure S3** Energy-band diagram, total density of states and partial density of states of anatase TiO$_2$(A,B,C) and Magneli phase Ti$_8$O$_{15}$(D,E,F).

First-principles calculations were performed using the CASTEP module in Materials Studio 5.0 developed by Accelrys Software Inc. Electron-ion interactions were modeled using ultrasoft pseudopotentials in the Vanderbilt form. The states Ti: 3s$^2$ 3p$^6$ 3d$^2$ 4s$^2$ and O:2s$^2$ 2p$^4$ were treated as valence states. The wave functions of the valence electrons were expanded through a plane wave basis-set and the cut off energy was selected as 500 eV. The Monkhorst-Pack scheme Kpoints grid sampling was set at $7 \times 7 \times 7$ in the supercells. The convergence threshold for self-consistent iterations was set at $5 \times 10^{-7}$ eV. The lattice parameters and atomic positions for each supercell system were first optimized using the generalized gradient approximation (GGA) together with the method. The optimization parameters were set as follows: energy change = $5 \times 10^{-6}$ eV/atom, maximum force = 0.01 eV/Å, maximum stress = 0.02 GPa, and maximum displacement tolerance = 0.005 Å.
The electronic structure of magneli phase titanium suboxide Ti$_8$O$_{15}$ are studied by using the plane-wave ultrasoft pseudopotential method based on the density functional theory. The band structure reveals that the energy band gap of Ti$_8$O$_{15}$ is reduced a lot compared with that of anatase TiO$_2$, which is due to the fact that O2p, Ti3p and Ti3d of Ti$_8$O$_{15}$ shift toward the left compared with those of TiO$_2$, and a new electron energy level formed by the redundant electrons of Ti3d and Ti3p of Ti$_8$O$_{15}$ due to the lack of oxygen atom in lattic. The results from density of states (DOS) analysis show that electron distribution near the Fermi level of Ti$_8$O$_{15}$ is different from that of anatase TiO$_2$, contribution of O2p to Fermi level decrease and that of Ti3d increase, compared with anatase TiO$_2$ which only has high electrical conductivity, because its narrow forbidden band width results in the Transitions of Electron from the valence band to the conduction band energy required to reduce.

**Conductivity Measurements**

To measure the conductivity under conditions of low energy and bias voltages, a voltage ramp of 0–0.05 V was applied across split electrodes in steps of 0.025 V for two-probe measurements using a source meter (Keithley 2400). For each measurement, after allowing the exponential decay of the transient ionic current, the steady-state electronic current for each voltage was measured every second over a minimum period of 100 s using a Labview data acquisition program (National Instruments). The time-averaged current for each applied voltage was calculated to create the current–voltage (I–V) characteristics. For the two-probe measurement, the
linearity of the I–V characteristics was maintained by applying an appropriate low voltage/current. The dissipative power was kept under $1 \times 10^{26}$ W to eliminate self-heating effects.

Figure S4. (A) Schematic diagram of the conductivity measuring experiment, (B) SEM image of Ti$_8$O$_{15}$ nanowire electrode, (C) I–V characteristics of a single Ti$_8$O$_{15}$ nanowire at room temperature.
Microscopic morphological characteristics

**Figure S5.** SEM image of club-shaped Ti$_8$O$_{15}$ nanoparticles, which were formed in the initial stage of the growth of Ti$_8$O$_{15}$ NWs.
Electrochemical performance

![Cyclic voltammograms of Pt/C and Pt/Ti$_8$O$_{15}$ NWs in 0.5mol L$^{-1}$ H$_2$SO$_4$](image)

**Figure S6.** Cyclic voltammograms of Pt/C and Pt/Ti$_8$O$_{15}$ NWs in 0.5mol L$^{-1}$ H$_2$SO$_4$ with the scan rate of 20 mV s$^{-1}$ at 30°C

Microscopic morphological characteristics

![TEM images of Pt/Ti$_8$O$_{15}$ NWs after 6,000 cycles](image)

**Figure S6.** (A,B)TEM images of Pt/Ti$_8$O$_{15}$ NWs after 6,000 cycles.
References


