Electronic Supplementary Information (ESI):

Facile synthesis of freestanding Si nanowire arrays by one-step template-free molten salt electro-deoxidation of SiO_2

Ji Zhao,[a,b] Jun Li,[a] Pinliang Ying,[a] Wenhua Zhang,[a] Lijian Meng[a,c] and Can Li*[a]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, 116023, Dalian, China*

[b] *University of Chinese Academy of Sciences, 100049, Beijing, China.*

[c] *Departamento de Física, Instituto Superior de Engenharia do Porto，Instituto Politécnico do Porto , Rua Dr. António Bernardino de Almeida, 431, 4200-072, Porto, Portugal/Centro de Física, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal.*

Fax: +86 411 84694447; Tel: +86 411 84379070; E-mail: canli@dicp.ac.cn;

Experimental details

In a typical synthesis process, 220 g $CaCl_2$ (analytical reagent, Sinopharm, China) was used for the electrolytic bath. It was dried in a muffle furnace at 150 °C for 5 hours and then 350 °C for 10 hours to remove residue water before use. A cylindrical graphite crucible (1.8 $g \cdot cm^{-3}$, 0.005% ash, JA Carbon ltd. China) was used to hold the electrochemical cell (inner height 160 mm, outer diameter 65 mm and wall thickness 7.5 mm). The graphite crucible was heated in vacuum at 180 °C for 10 hours before use. After being filled with $CaCl_2$ salt, the crucible was placed inside a quartz glass tube which was attached in a stainless steel reactor in a vertical furnace. All the

experiments were carried out under Ar atmosphere in this stainless steel reactor which was sealed by flange structure at 850 °C.

The graphite crucible was screwed on the top edge by a Mo rod (3mm in diameter, 99%, Tongli Metal Ltd. China) to serve as the counter electrode. A working electrode was composed of a quartz glass plate, 2 pieces of nickel net and 2 kinds of Mo wires. In a typical working electrode, a rectangular thin quartz glass plate (20*10*1 mm, 99.9% SiO_2, Changda Quartz, China) was bounded with 2 pieces of Ni net (20*10 mm 20 mesh, Shenghua Nets, China) and a folded Mo wire (1 mm in diameter, Alfa Aesar) by a small amount of Mo thin wire (0.25 mm in diameter, Alfa Aesar) to form a sandwich-like electrode. Electrical contact was formed by binding the working electrode to a 3 mm diameter Mo rod with 0.25 mm diameter Mo wire.

Electro-deoxidation experiments were performed with a Princeton Parstat 263 A potentiostat/galvanostat. Samples were prepared by electrolysis (electro-deoxidation) at a constant cell voltage in a range of 1.7 V ~ 2.2 V. When the reaction finished, the sample was cooled down in Ar atmosphere in the reactor. Later the sample was washed. Firstly rinsing was done by distilled water tenderly to remove the salt. After that, the Mo wires and Ni nets were peeled off carefully. Then the sample was washed by 0.1 mol L^{-1} hydrochloric acid until no gas emitting. At last the sample was washed with water and ethanol to remove the final residues of acid and salt. Then after filtering, the sample was dried at 60 °C and collected.

SEM images were taken on FEI Quanta 200F scanning electron microscope, with a working voltage of 20 kV. EDX accessory is Ametec Quanta 200 FEG 132-10, Detecting Unit PV7760/68ME.

X-ray diffraction (XRD) was carried out using a Rigaku Rint D/MAX-2500/PC, operated at 40 kV and 30 mA. Samples were scanned at 5 °/min 2θ under ambient conditions.

Transmission electron microscopy (TEM) images were digitally acquired using a FEI Tecnai G2 Spirit transmission electron microscope operated at 100 kV. TEM samples were prepared by scratching a piece of Si NWAs by sharp razor blade and 10 min ultrasonic dispersion in ethanol, then drop-casting onto 200 mesh lacey carbon copper TEM grids.

HRTEM image and SAED image were acquired using FEI Tecnai G2 F30 S-Twin, operated at Accelerate Voltage of 300kV.

XPS test was done by Shimadzu Amicus XPS spectrometer. The thickness of the oxide layer was determined by comparing the relative areas of the peak at 99.4 eV (assigned to Si^{0}) and the peak at 103.5 eV (assigned to Si^{4+}). (See the reference cited in the text)

Calculation of the energy cost for the Si NWAs synthesis

Origin data of Si NWAs:

Charge, C	863	1259	1411	1520	2131	2159

Thickness of Si NWAs, μm	120	200	180	220	300	350

Fitting: linear

$$Y\ (\mu m) = 0.1598\ X\ (C) - 20.536 \quad (1)$$

$r = 0.970$

intercept：Y=0， X= 128.5

The quartz electrode area: ~ 4 cm^2 (20*10*0.5 quartz glass)

Thus for unit area (1 cm^2), the equation is:

$$Y\ (\mu m) = 0.6392\ X\ (C) - 20.536 \quad (2)$$

intercept：Y=0， X= 32.1

According to the equations (2),

$\Delta Y = 1$, $\Delta X = 1/0.6392 = 1.56$ (C)

i.e., for 1 μm growth of silicon nanowire arrays of 1 cm^2, the electricity needed is 1.56 C. The electricity needed for the beginning of the growth is 32.1 C.

Suppose U = 2.2V, the power for 1 μm growth of silicon nanowire arrays per cm^2 is

1.56 C * 2.2V = 3.4 J.

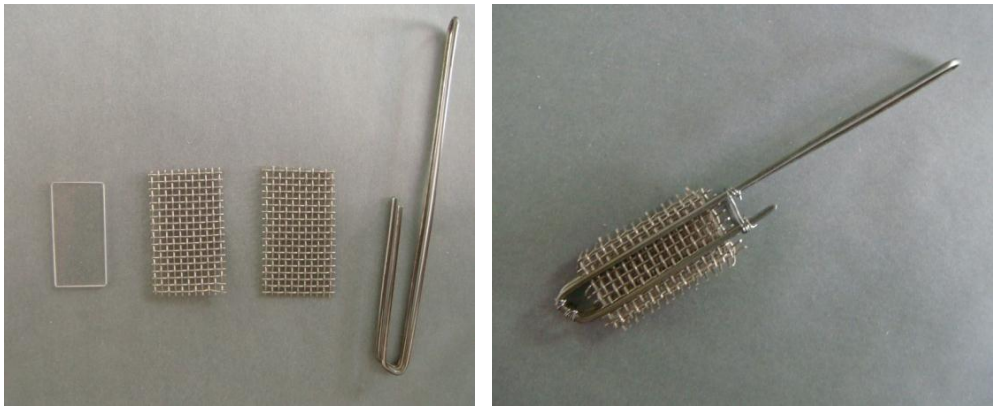

Figure S1. Photographs of the sandwich structured electrode.

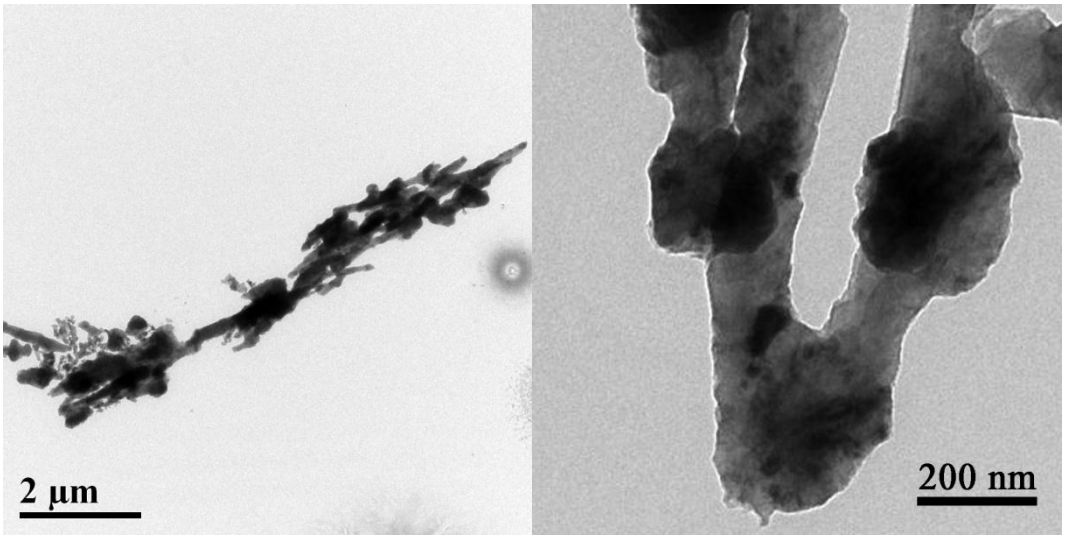

Figure S2. TEM images of two fragments of Si NWAs.

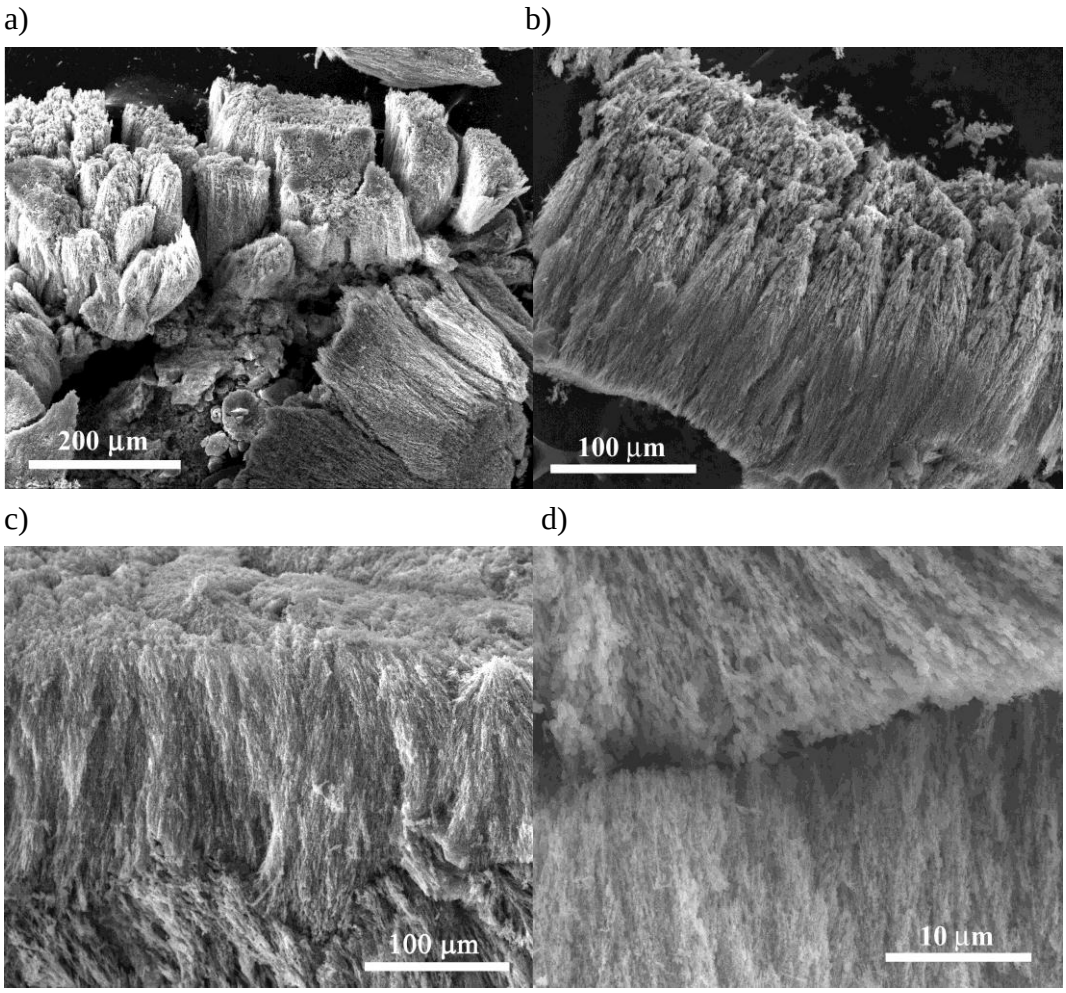

Figure S3. (a) SEM image of one layer Si NWAs. (b) SEM image of one layer Si NWAs in side-view, showing the disordered Si layer exists on top of the wheatear-like structure of the Si NWAs. (c) Low magnification SEM image of double-layered Si NWAs in side view. (d) Higher magnification SEM image of double-layered Si NWAs, showing the boundary between the two layers.

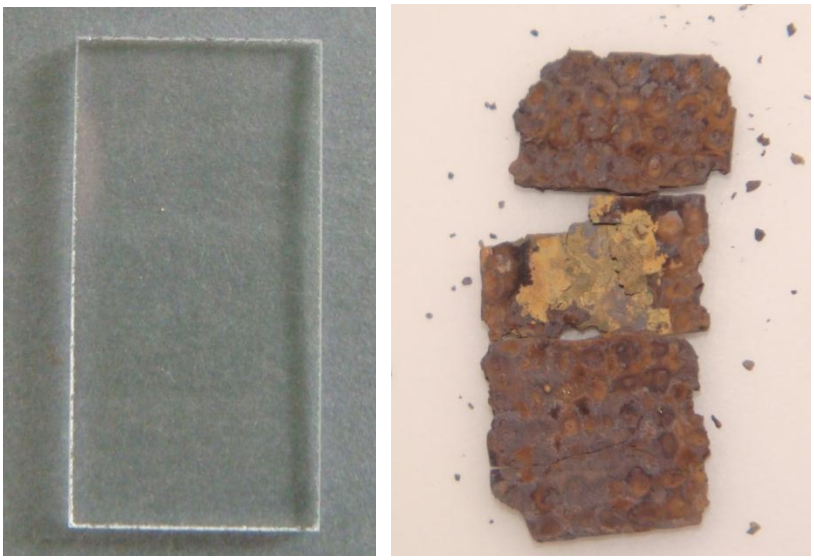

Figure S4. Photographs of the pristine quartz glass (20*10*0.5 mm) and the as synthesized Si NWAs.

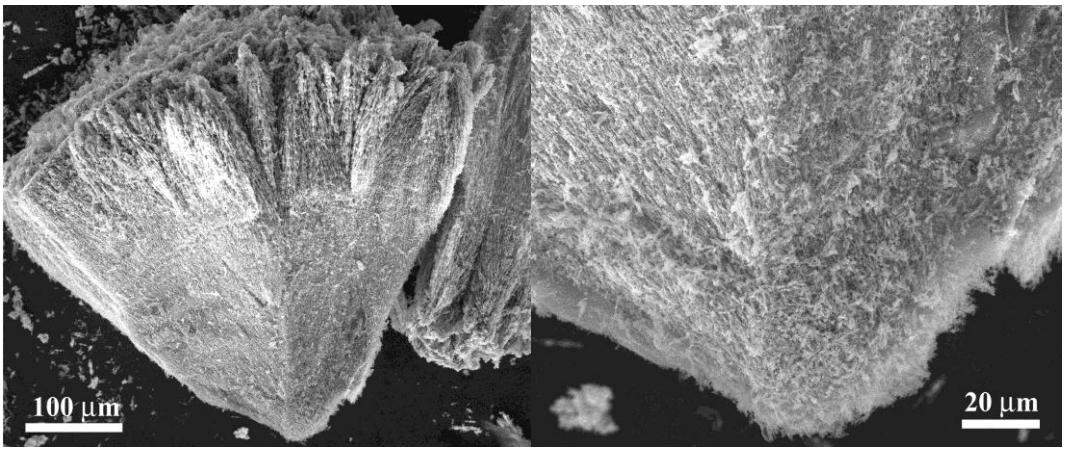

Figure S5. SEM images of cone-shape Si NWAs.