

Supporting information

Preparation of 1D ultrathin niobate nanobelt by the liquid exfoliation as a photocatalyst for hydrogen generation

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Experimental section

Materials and preparation

The parent rod-like oxide RbNbO_3 (RNO) was prepared by solid-state reaction. Nb_2O_5 (>99.9 %) and Rb_2CO_3 (>99.9 %) were selected as raw materials. The mixture of these raw materials were weighed and ground thoroughly in an agate mortar with a pestle, and then calcinated in air at 850 ~ 950 °C for 24 h in an alumina crucible. An excess of 2 mol% Rb_2CO_3 was added to compensate the Rb loss due to its volatilization. RNO powder is extremely hydrophilic and decomposes to an amorphous powder after exposed in the air for a few minutes. Therefore, the obtained powder was stored in a glovebox with dry argon atmosphere until the subsequent exfoliation experiments.

The RNO powder (~0.1 g) was dispersed in 100 ml deionized water. Then the suspension was dealt with by ultrasonic homogenizer for 30 min to form a milky colloid two times. After the colloid was kept to stand for 3 days, the supernatant containing the $\text{H}_x\text{Rb}_{1-x}\text{NbO}_3$ (HRNO) nanobelts was collected, named as the nanobelt supernatant. The nanobelt concentration (~0.5 g/L) was calculated from the powder weight obtained by slow drying the nanobelt supernatant at 400 °C for 30 min.

The above preparation process indicates that the ultrathin 1D niobate nanobelts are easily acquired in pure water and no other impurity phases are introduced.

Characterization

The crystal phase was examined by powder X-ray diffraction (XRD) on a Rigaku D/Max-2400 diffractometer with a $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The data in the 2θ range of 5 - 40° were collected in a step of 0.02° with the remaining time 8°/min under the tube conditions 40 kV and 100 mV. The characterizations of the transmission electron microscopy (TEM) and selected area electron diffractions (SAED) were performed on a JEOL JEM-2100F transmission electron microscope operating at 200 kV. The particle/nanobelt morphologies and the compositions of the products were examined with a field-emission scanning electron microscope (FESEM, Hitachi S-4800) at an accelerating voltage of 5 kV with an energy dispersive X-ray spectrometer (EDS). Tapping-mode atomic force microscopy (AFM; Seiko Instruments SPA400) with a silicon-tip cantilever (20 N m⁻¹) was used to characterize the lateral size and thickness of exfoliated nanobelts deposited on a silicon substrate. Thermogravimetric differential thermal analysis (TG/DTA) was performed using a thermal analyzer (SDT-Q600, TA) with a heating rate of 2 °C/min in the ambient atmosphere. All ¹H magic angle spinning (MAS) solid-state nuclear magnetic resonance (NMR) spectra, operating at 9.4 Tesla, were obtained at a proton resonance frequency of 400 MHz using a 4 mm H/X MAS NMR probe (Bruker Avance III 400), MAS speed was 12 kHz. The spectra were acquired using 5 s delay, 128 scans and $\pi/2$ pulse of 2.5 μs . For the NMR data collection, the nanobelt powder (it contained ~8 wt% water according to TG data) was

loaded into MAS NMR rotor in the ambient atmosphere, while for the blank control sample RNO, the loading operation was conducted in the glovebox with the dried argon atmosphere. The compositions of the ultrathin nanobelts were also analyzed by inductively coupled plasma - atomic emission spectroscopy (ICP-OES). UV-vis DRS were performed on a UV-Vis-NIR spectrophotometer (UV-3600 Plus, Shimadzu), and BaSO₄ served as a reference standard.

Pt deposition

HRNO nanobelts: The reaction system was consist of 40 mL nanobelt supernatant which containing 20 mg photocatalyst (HRNO nanobelts) and 10 mL methanol (20 vol% methanol aqueous solution). Suitable amount Pt(NH₃)₄Cl₂ (98 %, Heowns) was added into the above system. After irradiated under the 300 W Xe lamp for 3 h, Pt(NH₃)₄Cl₂ was decomposed into Pt and deposited as the co-catalyst on the HRNO nanobelts (Pt : nanobelts = 0.5 wt%). After the co-catalyst Pt was loaded, 0.02 M HCl aqueous solution (~15 mL) was added into the system with constant stirring. The surface charge of the nanobelts was changed by adding the HCl solution, which resulted in the nanobelt aggregation. The aggregated nanobelts were washed using the deionized water and centrifuged for several times to remove residual Rb⁺ and H⁺, and the nanobelt paste (named photocatalyst Pt-nanobelt), was obtained for photocatalytic activity evaluation without drying.

Other catalysts: 20 mg catalyst of each RNO, anatase TiO₂ or P25 was added into the 50 ml 20 vol.% methanol aqueous solution, and then the same amount of Pt(NH₃)₄Cl₂ as that for the HRNO nanobelt experiment was added into each reaction system. Pt was deposited on the catalysts under the irradiation of the 300 W Xe lamp for 3 h and the photoatalysts (Pt-RNO, Pt-anatas TiO₂ and Pt-P25) were obtained.

Photocatalytic reactions

20 mg of photocatalyst (Pt-nanobelt, Pt-RNO, Pt-anatas TiO₂ or Pt-P25) was dispersed into the 50 mL of 20 vol.% methanol aqueous solution, which was held in a 100 mL quartz reactor connected with an automatic sampling equipment (SUNCAT Instruments PGS-15, China). Prior to starting reaction [switching on the 300 W Xe lamp (CEL-HXF 300E, Beijing CEL Tech. Co., Ltd) for irradiation], the reactor was sealed and then vacuumed to remove the gas. The reaction processed at room temperature and the liquid in the reactor was constantly stirred. The generated H₂ was automatically measured through a gas chromatography (Agilent, GC-7890B).

Table S1 The relative percentages of protons and Rb cations for the four $H_{1-x}Rb_xNbO_3$ samples, analyzed by EDS.

Element	Sample 1	Sample2	Sample 3	Sample 4	Sample 5
Nb	1	1	1	1	1
Rb	0.39	0.40	0.41	0.42	0.45
H	0.61	0.60	0.59	0.58	0.55

* The data are represented in decimal format, rather than percentage format. H can be calculated as $1 - x$, x is the content of Rb

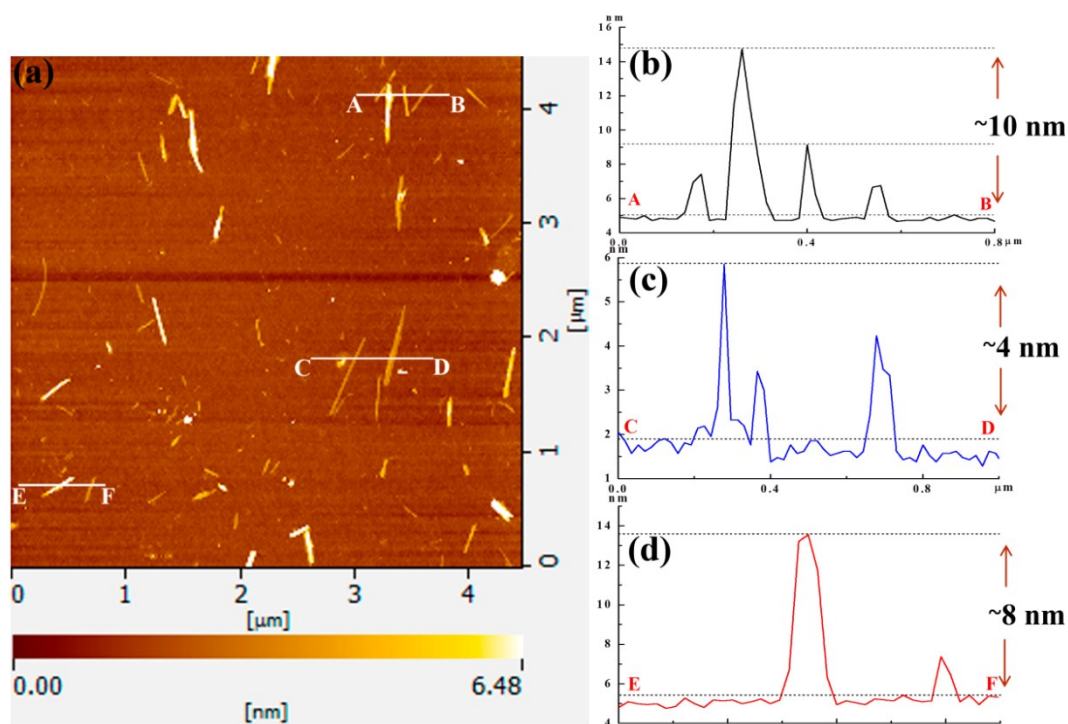


Fig.S1. (a) AFM image of the HRNO nanobelts and the corresponding cross-sectional profiles of ultrathin nanobelts along the lines marked on (a): (b) line AB; (c) line CD and (d) line EF, respectively.

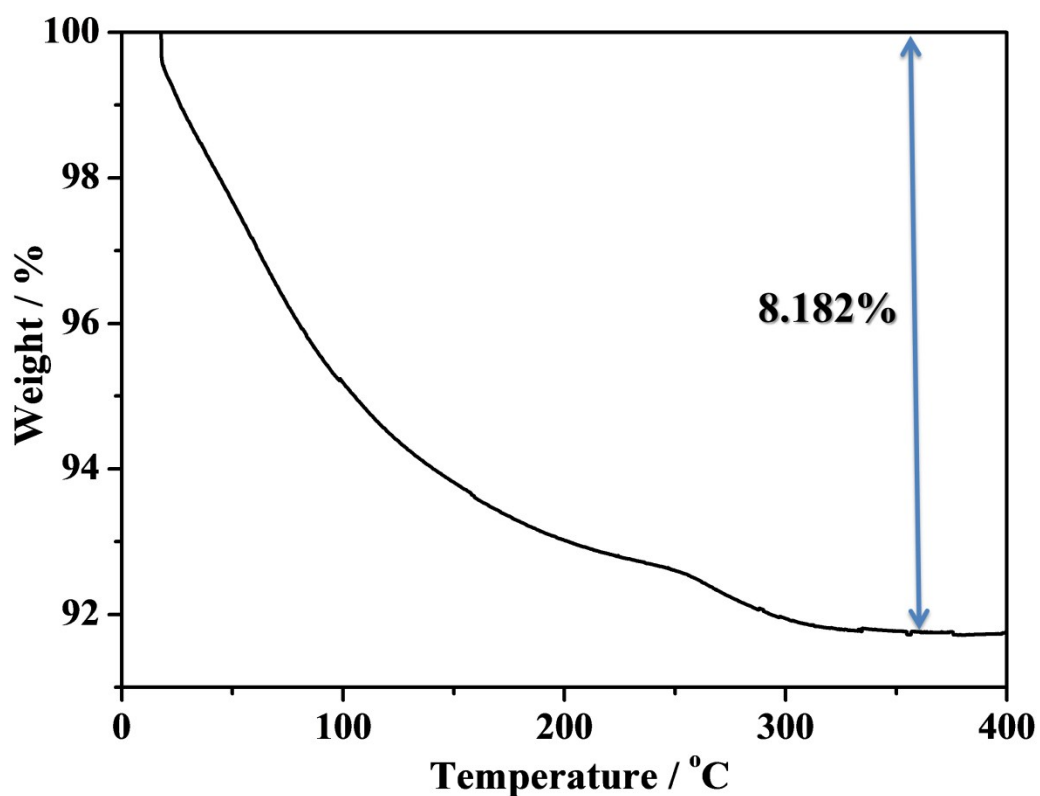


Fig. S2. TG profile of HRNO nanobelts from room temperature to 400 °C at a heating rate of 2 °C/min under ambient atmosphere.

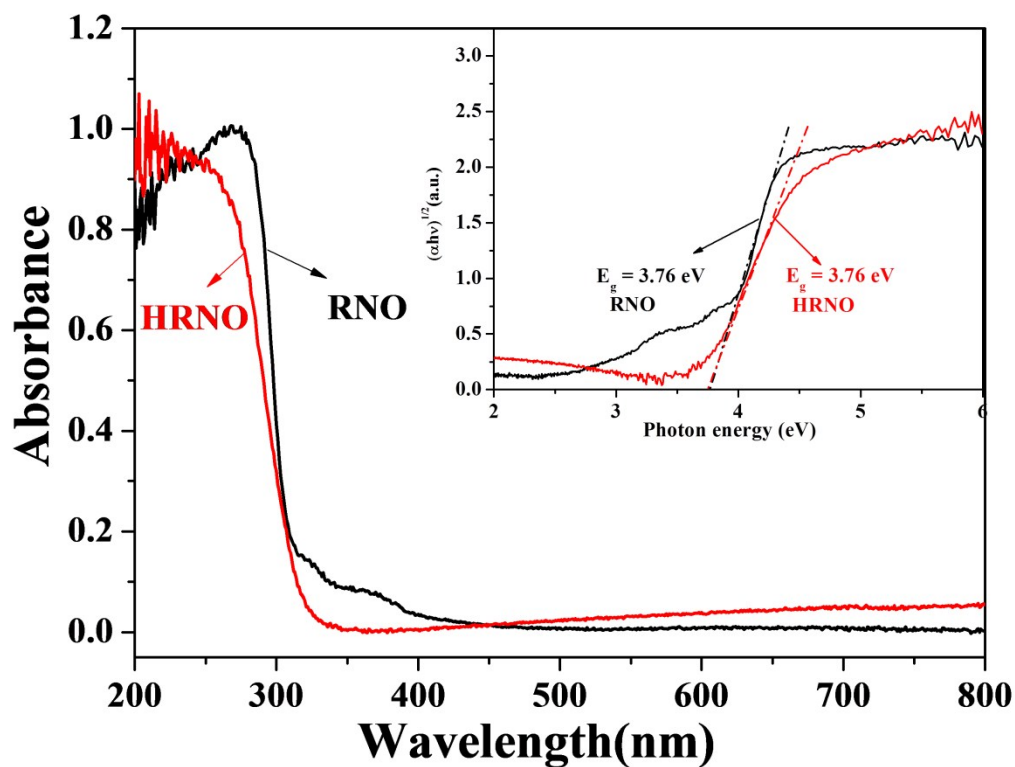


Fig. S3. The absorption spectra of the RNO and HRNO and the inset shows their estimated band gap energy.

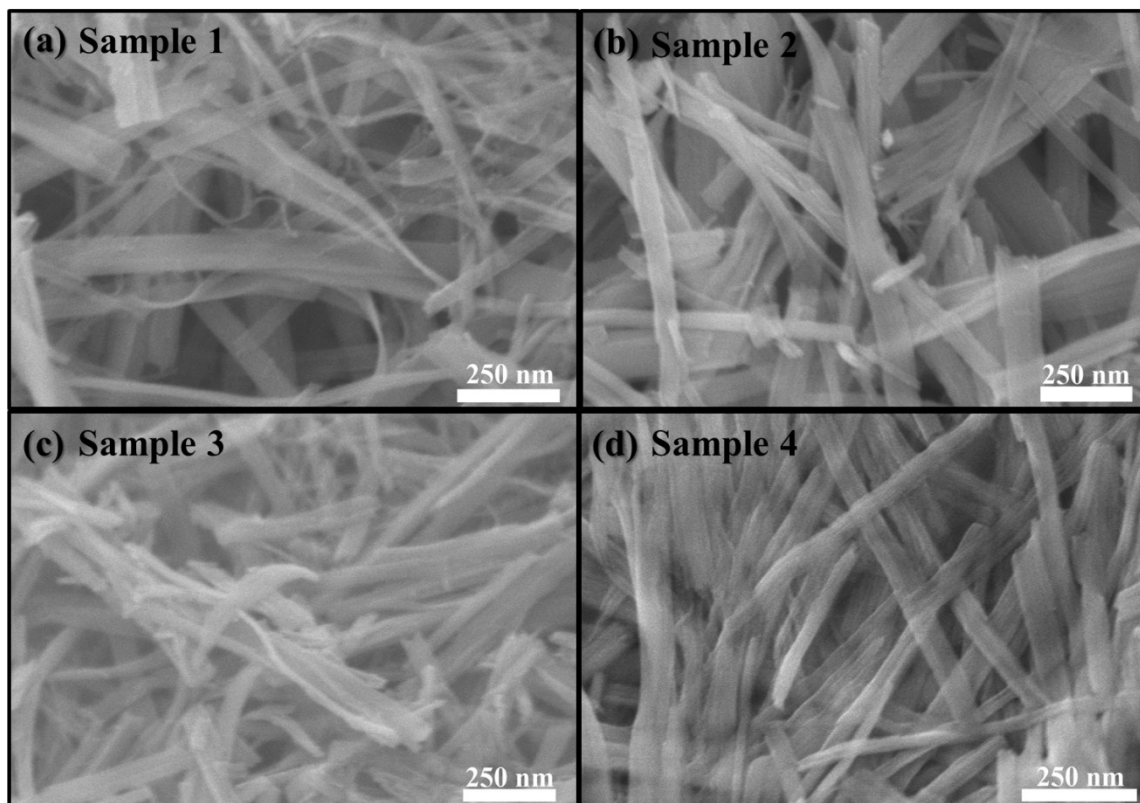


Fig. S4 The SEM images of the four HRNO colloid powders, which were acquired under the similar experimental conditions.

Table S2 The relative percentages of protons and Rb cations for the four samples, prepared in the similar experimental conditions, analyzed by ICP-OES.

Element	Sample 1	Sample 2	Sample 3	Sample 4
H	0.61	0.58	0.59	0.53
Rb	0.39	0.42	0.41	0.47