Supplementary information

Layered lithium niobium (III) oxide - LiNbO₂ as a visible-light-driven photocatalyst for H₂ evolution

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Synthesis of lithium niobate LiNbO₂

Li₃NbO₄ was used as a precursor and was prepared by calcining a homogenized mixture of Li₂CO₃ (Aldrich 99.9%) and Nb₂O₅ (Alfa Aesar 99%) according to stoichiometry. Ball milling followed by hand grinding were employed for a thorough mixing. The typical calcining temperature was 900°C and reaction time was around
10 hours. Intermediate grindings was performed in order to eliminate any secondary phases.

The freshly prepared Li$_3$NbO$_4$ precursor was thoroughly mixed with Nb$_2$O$_5$ (Alfa Aesar 99%) and Nb (Alfa Aesar 99% 325 mesh) in a proper ratio. Hand grindings using a mortar and a pestle were performed for at least 40 minutes to guarantee a homogeneous mixing. The admixtures were pressed into pellets under a pressure of 50 MPa using a 13 mm diameter die. The resulting pellets were then wrapped in a molybdenum foil and calcined at 1250 °C for 20 hours in a flowing Ar atmosphere.

**Supplementary Figure 1**

Observed and calculated X-ray powder diffraction patterns of synthesized LiNbO$_2$. Schematic crystal structure model of LiNbO$_2$ is shown in the image inserted.
Supplementary Figure 2

SEM images of LiNbO$_2$ before (a) and after (b) ball-milling.
High resolution TEM analysis of LiNbO$_2$ loaded with 1wt% Pt as a co-catalyst. Pt nanoparticles (~10 nm) can be easily identified according to the difference in image contrast compared to LiNbO$_2$. Selective area energy-dispersive X-ray spectroscopy
(EDX) also confirmed the “black dot” to be Pt nanoparticle. Pt peaks in EDX was labelled by red bars.

**Supplementary Figure 4**

Action spectrum of photocatalytic hydrogen production for LiNbO$_2$. Experiments were performed with 0.1 g powders dispersed in oxalic acid solution (0.025M). The light source was a 300 W Xe lamp (Beijing Trusttech Co.Ltd., PLS-SXE-300UV). The incident monochromatic light in the photocatalytic reactions was achieved by using corresponding monochromatic filters.
Linear sweep voltammogram of LiNbO$_2$ thin film electrode in 0.2M Na$_2$SO$_4$ aqueous solution (pH = 7) under chopped monochromatic light (400 nm).
Photocurrent action spectrum (IPCE vs wavelength) for LiNbO$_2$ thin film electrodes, measurements were performed in 0.2M Na$_2$SO$_4$ aqueous solution under bias potential 0.6 V vs Ag/AgCl. UV-Vis absorption spectrum was also displayed for comparisons.
Repeated time courses of hydrogen evolution for ball-milled LiNbO$_2$ under full range irradiation. Experiments were performed on 0.05 g catalyst with 1wt% Pt as a co-catalysts. Methanol aqueous solution (10 vol%) was used as sacrificial agent and the reactor was purged with pure Ar at the end of first experiment (24 hours irradiation).
Supplementary Figure 8

XRD patterns of LiNbO$_2$ before and after photocatalytic reaction.
SEM image of LiNbO$_2$ before (a) and after (b) photocatalytic reaction, particles with layered morphology were maintained.
X-ray photoelectron spectroscopy (XPS) of Nb 3d before and after photocatalytic reaction, the binding energies were referenced to the adventitious C 1s peak (284.6 eV). The peaks located around 203.5 eV, 206.6 eV and 209.4 eV can be attributed to 3d_{5/2} and 3d_{3/2} doublets of Nb^{2+} and Nb^{4+} species, respectively\textsuperscript{1-4}. 
Total density of states (DOS) and partial density of states (PDOS) of individual atoms of LiNbO$_2$: ↑ spin-up densities and ↓ spin-down densities.
Supplementary Figure 12

Mott-Schottky plot of LiNbO$_2$ electrode.
Supplementary Table 1

Photocatalytic hydrogen production rate for balled milled LiNbO$_2$ with different sacrificial agents. Measurements were performed upon 0.05 g powders loaded with 1wt% Pt as a co-catalyst under full range irradiation.

| Sacrificial agent                                      | $\text{H}_2$ evolution rate ($\mu$mol/h) |
|--------------------------------------------------------|-----------------------------------------|
| Methanol aqueous solution (10 vol%)                     | 116.6                                   |
| Sodium sulfite aqueous solution (0.05M)                 | 29.1                                    |

Supplementary Table 1

Photocatalytic oxygen evolution rate for pristine LiNbO$_2$. Measurements were performed upon 0.1 g powders in 200 mL AgNO$_3$ aqueous solution (0.005 M).

| Light condition       | $\text{O}_2$ evolution rate ($\mu$mol/h) |
|-----------------------|-----------------------------------------|
| Full spectrum         | 2.51                                    |
| Visible light         | 0.81                                    |

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