

Supporting Information

Photoelectrochemical Properties of Well-Structured 1.3-nm-thick pn Junction Crystal.

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Materials

Titanium oxide (TiO_2 , 99.9%, Sigma Aldrich), potassium carbonate (K_2CO_3 , 99.5%, Katayama Chemical), lithium carbonate (Li_2CO_3 , 99.0%, Wako Pure Chemical Industries), molybdenum oxide (MoO_3 , 99.9%, Wako Pure Chemical Industries), tetrabutylammonium hydroxide ($(\text{C}_4\text{H}_9)_4\text{NOH}$, TBA, 40 %, Sigma Aldrich), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Wako Pure Chemical Industries), sodium dodecyl sulfate ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$, SDS, 50%, Wako Pure Chemical Industries), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMT, 99%, Wako Pure Chemical Industries), formamide (CH_3CONH_2 , FA, 98.5%, Wako Pure Chemical Industries) were used for synthesis of starting materials of TiO/NiOH nanosheets.

Sample Preparation

Single crystal of starting layered lithium potassium titanium oxide ($\text{K}_{0.8}\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$) was prepared using previously reported method.¹ TiO_2 (rutile form), K_2CO_3 , Li_2CO_3 , and MoO_3 were mixed in agate mortar in a molar ratio of 1.73, 1.67, 0.13, and 1.27. The mixture was placed in a Pt crucible and heated at 1473 K for 10 h. The layered crystals were rinsed with distilled water and dispersed in 0.5 M HCl under the ratio of K^+ , Li^+ : H^+ was 1 : 20. After 5 days stirring, the protonated titanium oxide monohydrate ($\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$) dispersion was washed and centrifuged with distilled water for several times until supernatants indicated pH 5-6. After drying in oven, the $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$ powder was placed into 0.025 M tetrabutylammonium hydroxide (TBA) solution adjusted the ratio of H : TBA to be 1 : 3, and delaminated into single layer $\text{Ti}_{0.87}\text{O}_2$ nanosheets.

Nickel hydroxide layered single crystals were synthesized by hydrothermal method.² 0.5 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.2 M SDS, 1 M HMT, and distilled water were mixed in the volumes of 4, 40, 12, and 44 mL (100 mL in total) in a Teflon vessel (200 cm^3) and heated at 393 K for 24 h. After the 50 mg dodecyl sulfate (DS) ion intercalated nickel hydroxide crystal was washed with distilled water and ethanol, the precipitate was put into water bath at 313 K for two weeks in 50 mL FA to promote delamination. The nanosheet dispersed solution was centrifuged at 4000 rpm for 30 min, the supernatant was collected, followed by 12000 rpm centrifugation for 30 min. The precipitates were dissolved into ethanol and this dispersion was used as a nickel hydroxide nanosheets solution. To attach a single layer of the nanosheets onto indium tin oxide (ITO) coated glass, silicon wafer, and glassy carbon plate, Langmuir-Blodgett (LB) method was employed. These substrates were contacted calmly on surface of the solutions when its surface pressures reached 8-10 mN/m, followed by annealing at 573 K for 1 h.

Titanium niobate nanosheet (TiNbO_5^-) was prepared by previously reported method.³

Characterization

Atomic force microscopy (AFM) measurements were performed using a Nanocute (Seiko Instruments Inc., SII). Field emission-scanning electron microscopic (FE-SEM) images were obtained using a SU8000 (Hitachi High-technologies Corporation) at an accelerating voltage 1-10 kV. 2θ and $2\theta/\varphi$ X-ray diffraction (XRD) patterns were measured using a SmartLab X-ray diffractometer (Rigaku Corporation) with 1.2 kW CuK α radiation. All electrochemical measurements were performed in 0.5 M Na₂SO₄ + 0.1 M CH₃OH aqueous solution in a quartz glass beaker using the nanosheet attached substrates, Pt wire, Ag/AgCl electrode as the working, counter, reference electrode, respectively. Those three electrodes were connected to IVIUM Compactstat (Ivium Technologies) and a 300 W Xe lamp (MAX-302, Asahi Spectra Co., Ltd.) was employed as a UV light source.

A theory of open-circuit voltage and surface recombination rate

In the case of a pn junction, its short-circuit current, open-circuit voltage (onset potential), and surface carrier recombination velocity can be expressed as:⁴

$$I_{SC} = \frac{2eDN}{L \exp(d/L)S} \dots [1], \quad V_{OC} = \frac{nk_B T}{e} \ln \left(\frac{I_{SC}}{I_0} + 1 \right) \dots [2]$$

where I_{SC} is the short-circuit current, V_{OC} is the open-circuit voltage, k_B is the Boltzmann constant, T is the absolute temperature, n is the ideality factor, e is the elementary charge, D and L are respectively the diffusion coefficient and the diffusion length of the minor carrier, N is the density of absorbed photons, d is the thickness of the outermost n- or p-type layer, I_0 is the saturation current, and S is the surface recombination velocity. In these equations, D and L are assumed to stay constant after the formation of the pn junction because of the ultrathin thickness of the nanosheet.

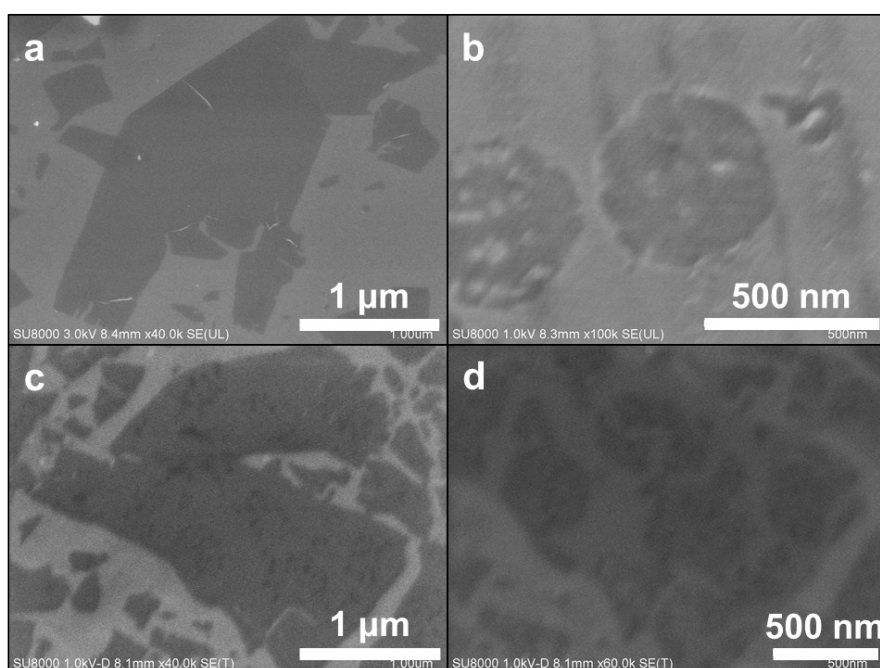


Figure S1 FE-SEM images of (a) TiO/Si, (b) NiOH/Si and (c-d) TiO/NiOH/Si. Image (d) is a magnified view of (c). Only top detector was used to observe surface potential at image (c) and (d). The darker contrast in image (d) indicated the TiO/NiOH pn junction region.

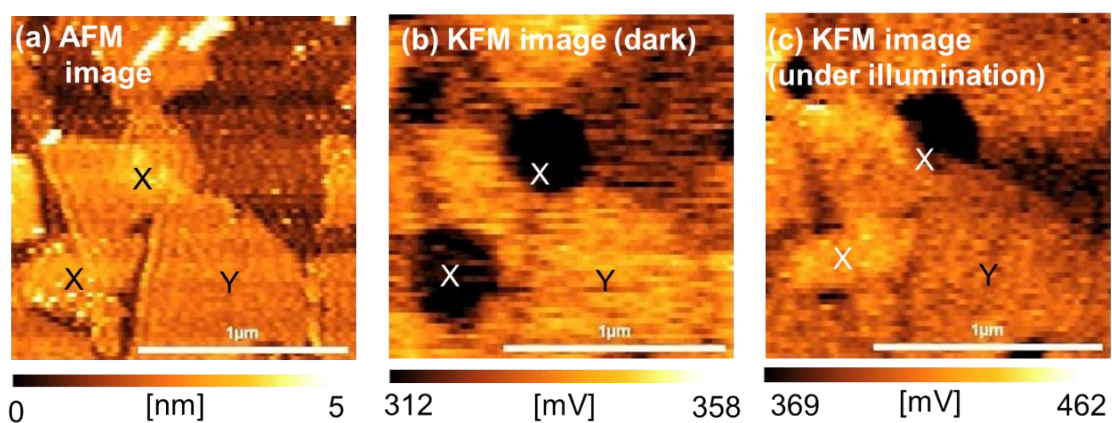


Figure S2 (a) AFM image of TiO/NiOH pn-junction surface and KFM images (b) under dark condition, and (c) under UV-light illumination. X marks a point on the pn junction part and Y marks a point on non-junction part. The surface potential at X was more negative than that at Y under dark condition. Although the surface potential at non-junction part Y showed no change under UV light irradiation, only pn junction part X got more positive.

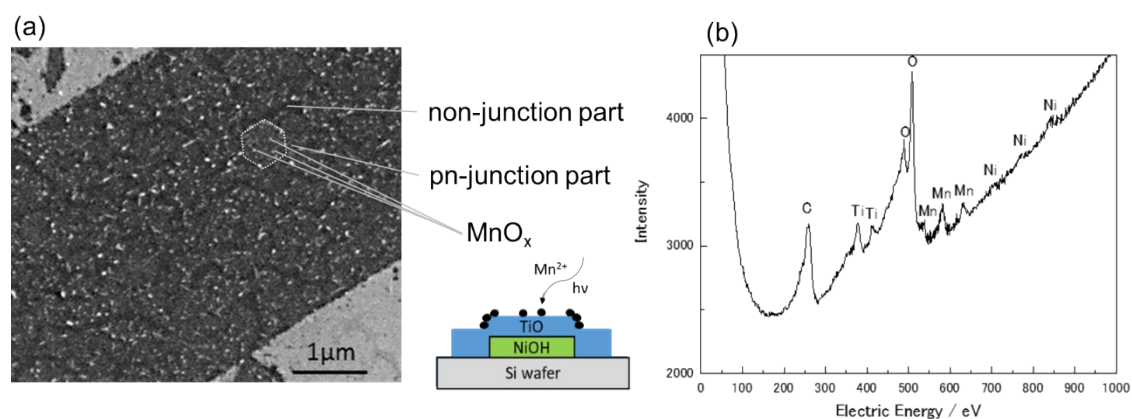


Figure S3 (a) FE-SEM image of TiO/NiOH pn-junction surface after photodeposition reaction@300nm in 0.1 MnSO₄ aqueous solution, (b) Auger spectra of deposition part on TiO/NiOH pn junction surface.

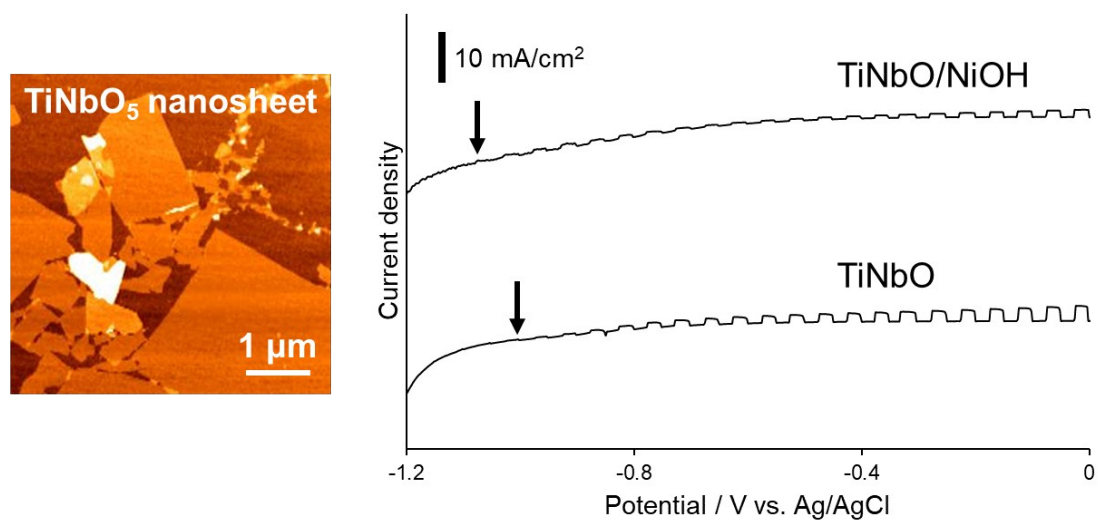


Figure S4 AFM image of TiNbO₅ (TiNbO) nanosheet and current-potential (I-E) curves in 0.5 M Na₂SO₄ + 0.1 M CH₃OH under chopped UV light irradiation (300 W Xe lamp) for TiNbO, and TiNbO/NiOH. on ITO coated quartz plate. Black arrows show the onset potentials of photooxidation current.

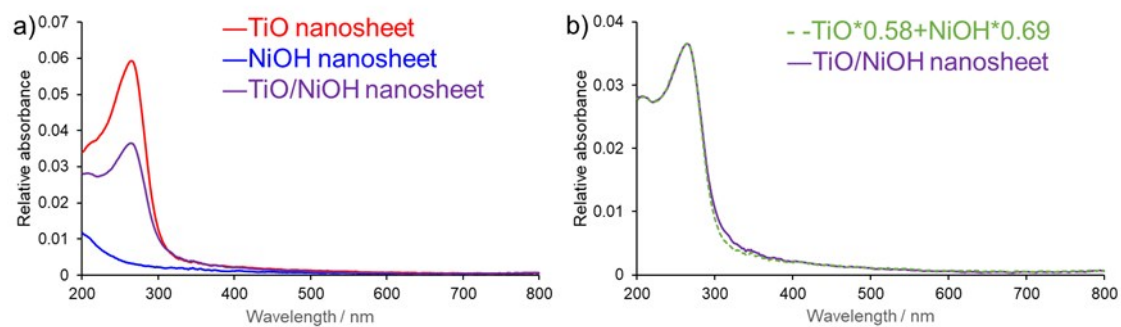


Figure S5 UV-Vis spectrum of a) TiO, NiOH, TiO/NiOH on quartz glass plate. b) algebraic sum of TiO, NiOH, and original TiO/NiOH.

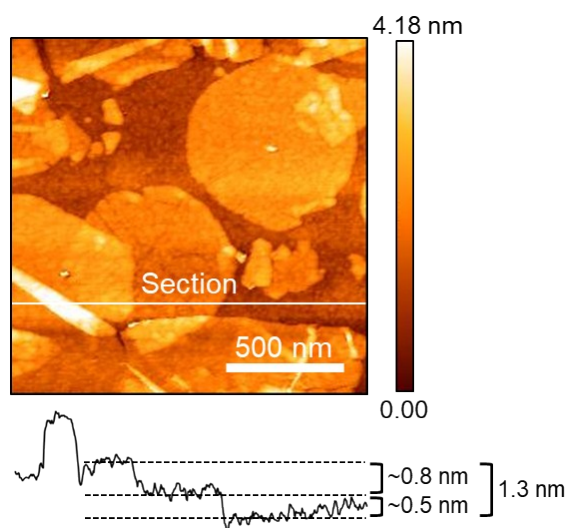


Figure S6 Another AFM image of TiO/NiOH on Si wafer. The whole thickness of TiO/NiOH bilayer is 1.3 nm.

References

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