Supporting Information

**Photoelectrochemical Water splitting with a SrTiO$_3$:Nb / SrTiO$_3$ n$^+$-n Homojunction Structure**

1. XRD

![XRD Diagram]

**Figure S1.** The XRD for samples deposited under 1, 10, and 20 mTorr.
2. EDX analysis

**Figure S2.** The map of SEM-EDX sampling for samples. Each spot represents a sampling position.

The EDS were collected on a JEOL 7600F analytical SEM with accelerating voltage of 10 kV. Spectra were quantified with Cu K emission line. The reference SrTiO$_3$ single crystal was reduced at 900°C for 5 hours to gain high conductivity and get rid of charging. The Sr/Ti ratio was calculated by the following equation:

$$\text{Sr/Ti ratio} = \frac{\text{TF}(\text{Sr/Ti}) - \text{Ref}(\text{Sr/Ti})}{\text{Ref}(\text{Sr/Ti})} \times 100\%$$

TF(Sr/Ti) represents the Sr/Ti ratio of the deposited thin film, and the Ref(Sr/Ti) represents the Sr/Ti ratio of the reference SrTiO$_3$ single crystal.
3. Angle Resolved XPS

**Figure S3.** The experimental and fitted Angle-resolved XPS spectra of Nb and Ti obtained under $\theta = 0$, 30, and 80 degrees.

AR-XPS was performed in a standard ultra-high vacuum (UHV) chamber, equipped with a hemispherical electron energy analyzer and an Al/Mg twin anode X-ray source. The XPS spectra were obtained using unmonochromatized Mg K$_\alpha$ (1253.6 eV) radiation. All atom-specific core level spectra were taken at analyzer pass energy of 50 eV, with a step size of 0.05 eV, and dwell time of 0.1. Each region was signal averaged for 30 scans. Analysis of the XPS spectra was performed using XPSPEAK version 4.1. The Ti 2p peak at 458.4 eV of SrTiO$_3$ was used to calibrate the energy scale to which all the measured binding energies were adjusted. A Shirley background was applied to the spectra which were then fit with an appropriate number of peaks. The fits were allowed to optimize without constraints as long as a reasonable FWHM (below 3 eV) and goodness of fit were obtained. In cases where a FWHM greater than 3 eV occurred, widths and/or known peak separations were fixed to one another, until an acceptable fit was achieved. The atomic sensitivity factors of 0.63 (O), 1.1 (Ti), 1.05 (Sr), and 2.4 (Nb) were used to correct for differences in photoemission cross sections to obtain relative surface atomic compositions. AR-XPS was performed at different tilting angles along the manipulator.
4. Mott-Schottky analysis

Figure S4. The equivalent circuit used to model the electrochemical impedance of the cell. Impedance data for P20-T1, P20-T2, and P20-T3 in the range of -0.33 to 1.36 V_RHE. Nyquist plot of the experimental and fitted data for P20-T1, P20-T2, and P20-T3 at 1.26 V_RHE. The fitted data was based on the equivalent circuit under frequency from $10^1$ to $10^3$ Hz.

The impedance of the electrochemical cell (Z) was measured under dark conditions at a series of electrode potentials, in the frequency (f) range $10^1$ to $10^3$ Hz. To extract the space-charge region capacitance from the experimental impedance, the electrochemical cell was modeled by the equivalent circuit shown in Figure S4. The two current components flow together through the electrolyte solution and the electrical
contact to the working electrode, which were represented by a series resistance $R_0$. The current passing through the cell contributes in parallel to the faradic process that is represented by the charge transfer resistance $R_1$ and nonfaradic interface charging that is represented by $C_{sc}$, the capacitance per unit area of the aqueous interface. The capacitance $C$ includes the space-charge region capacitance ($C_{sc}$) and the double-layer capacitance ($C_{dl}$) in series, $1/C = 1/C_{sc} + 1/C_{dl}$. The experimental data shown in Figure 5a is then fit using the EIS Spectrum Analyzer (ZVIEW), software for analysis of impedance spectrum.
5. Electrical conductivity analysis

**Figure S5.** Device geometry for measuring the electrical conductivity of a STO/Nb:STO sample.

The conductivity of each sample is measured using an electrical probe station (Signatone). Ohmic contacts to the hematite film are established by depositing a film of 5 nm titanium and 50 nm gold over the sample, through a shadow mask that contains an array of circular holes (1.25 mm in diameter). Electrical resistance between two nearest neighbor contacts is thus given by a standard two-probe I-CV measurement. Multiple contact pairs are randomly selected and tested to give the mean resistance. Resistivity and conductivity for each sample are then calculated from the electrical flow channel geometry. For an $n$-type semiconductor, the free electron density can be roughly estimated by the following equation, $n_e \approx \frac{1}{e \mu_e \rho}$, where $\mu_e$ is electron mobility, $e$ the elementary charge, and $\rho$ the resistivity.
6. IPCE analysis

**Figure S6.** IPCE as a function of excitation wavelength potential, for P01-T2, P10-T2, P01-T3, P10-T3. The horizontal white lines indicate the thermodynamic potential for oxygen evolution (1.23 V_{RHE}).
7. Elemental Analysis of the PLD target

Figure S7. Elemental analysis provided by vendor of the STO target.