Supporting Information

New Insights into Electronic Structure and Photoelectrochemical Property of Nitrogen-doped HNb_3O_8 Behaviors via A Combined In-situ Experimental with DFT Investigation

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1. Characterization

XRD patterns of the samples were recorded by using X-ray diffractometer (XRD, D/max-2200, Rigaku, Japan) with Cu K_a radiation. Morphological characteristics of the samples were examined by using scanning electron microscopy (SEM, Quanta F250) and transmission electron microscopy (TEM, JEM-2100). UV-Vis spectra of the samples were obtained by using spectrometer (Jasco V-570), aided with an integrating sphere. Chemical compositions of the samples were also analyzed by using energy dispersive spectrometer (EDS, Apollo XL-SDD) and X-ray photoelectron spectroscopy (XPS, Axis Ultra Kratos ,UK), which was recorded by using monochromatic Al K_α radiation at 10^{-9} Torr (150 W, 15 KV, 1486.6 eV). Mott-Schottky data was obtained in 0.5 M Na_2SO_4 aqueous solution by using an electrochemical analyzer (CHI600E, Shanghai China) at frequencies of 1500 and 1000 Hz. Electrochemical impedance spectroscopy (EIS) was conducted in 0.5 M Na_2SO_4 aqueous solution by using the electrochemical analyzer with a amplitude perturbation (5 mV) at frequencies over 0.1 Hz – 0.1 MHz.

2. The conversion of the obtained potentials (vs. SCE)

The measured potentials vs. the SCE were converted to the reversible hydrogen electrode (RHE) scale via the Nernst equation: [1-2]

$$E_{RHE} = E_{SCE} + E^0_{SCE\,vs\,NHE} + 0.059 \times pH \ , \tag{1}$$

where E_{RHE} is the converted potential vs. RHE, E_{SCE} is the experimental potential measured against SCE reference electrode, $E^0_{SCE\,vs\,NHE}$ is 0.2412 V at 25 ^oC.

3. Mott-Schottky Plots for Donor Density (N_d) Calculations

At 1 kHz, donor densities (N_d) of the HNb_3O_8 and N-HNb_3O_8 film electrodes were calculated according to the slope of the Mott-Schottky plots, given by:

$$N = \frac{2}{e\varepsilon\varepsilon_0(slope)}, \tag{2}$$

where e is the electron charge (1.602×10^{-19} C), ε is the dielectric constant of the semiconductor (ε= 9.5 was used according to KNb_3O_8, which has the same structure and type as HNb_3O_8 and N-HNb_3O_8) and ε_0 is the permittivity of free space (8.85×10^{-14} F cm^{-1}). The N_d values of the HNb_3O_8 and N-HNb_3O_8 film electrodes are $\sim 3.71\times10^{21}$ and $\sim 6.46\times10^{21}$ cm^{-3}, respectively.

4. DFT Calculations

All computational models were fully optimized by using the first-principle code, Vienna ab initio simulation package (VASP) [3-4]. The band structure and projected density of states (PDOS) of KNb_3O_8 and HNb_3O_8 are shown in Figure S6. The HNb_3O_8 has a smaller band gap and the delocalized energy contributed by the protons, which is consistent of literature data[5]. The optimized crystal structure, band structure and PDOS of $H_8Nb_{24}O_{63}N$-1(1.56%) and $H_8Nb_{24}O_{63}N$-2 (1.56%) are shown in Figure S7. It is worthwhile mentioning that the contribution related to the nitrogen doping is negligible because of the sufficiently low nitrogen concentration and the little change in band gap as compared with that of HNb_3O_8. The doping models, $H_4Nb_{12}O_{28}N_4$-1 and $H_4Nb_{12}O_{28}N_4$-2, are built based on elemental composition analysis of XPS (15.4%). The optimized crystal structure, band structure and PDOS of $H_4Nb_{12}O_{28}N_4$-2 are shown in Figure S8. Although the doped systems exhibit features similar to conductors, it cannot be concluded that they are not semiconductors, because PBE usually underestimates the band gaps. More accurate calculations, including by using hybrid functional and spin-orbital coupling (SOC), will be conducted as our future works.

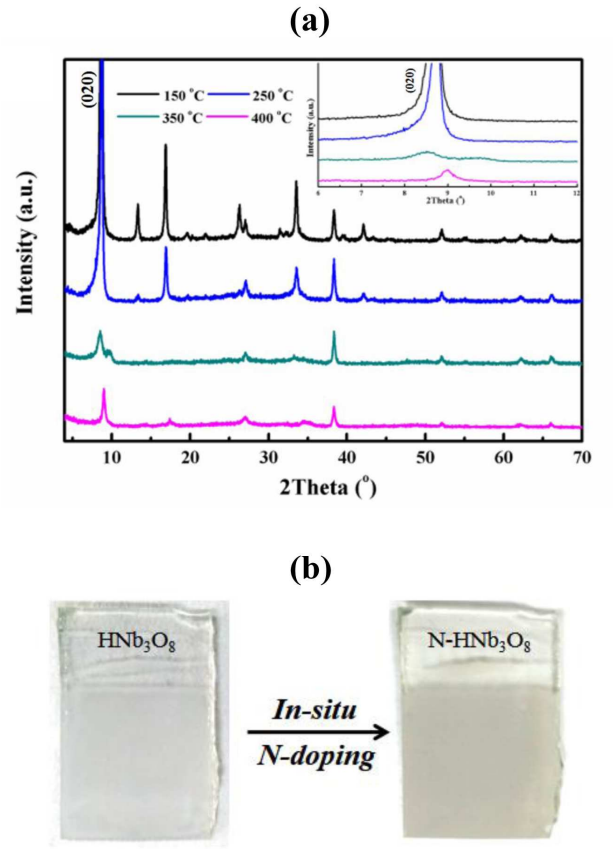

Figure S1 (a) XRD patterns of the urea-HNb_3O_8 film after being annealed at different temperatures. (b) The same sample before and after in-situ nitrogen doping.

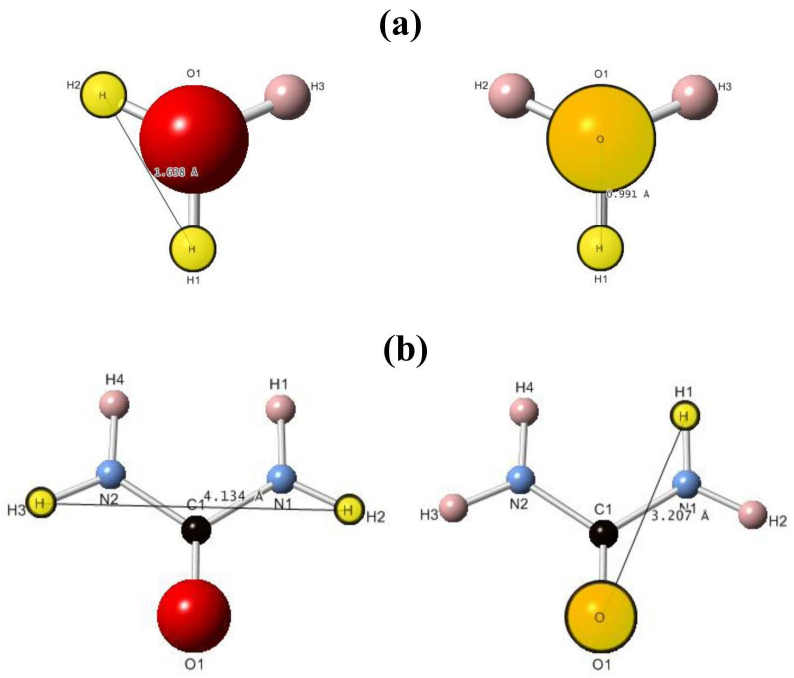

Figure S2 (a)Triangular cone H_3O^+ (1.638 and 0.991 Å, PubChem CID: 123332)

(b) Planar urea molecule (4.134 and 3.207 Å, PubChem CID: 1176)

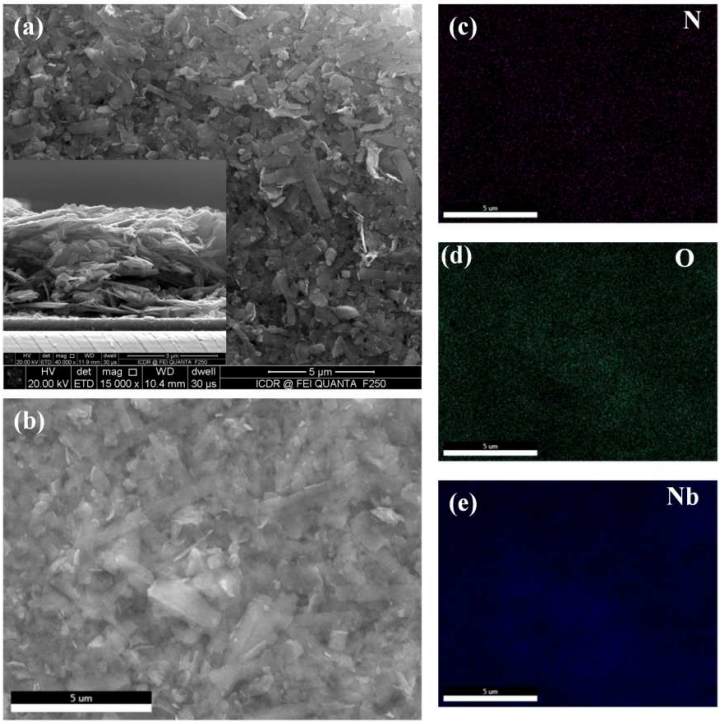

Figure S3 (a) SEM image of the HNb_3O_8 film with the inset showing a cross-sectional SEM image. (b) SEM image of the N-HNb_3O_8 film, together with the element mappings [(c) N, (d) O and (e) Nb elements].

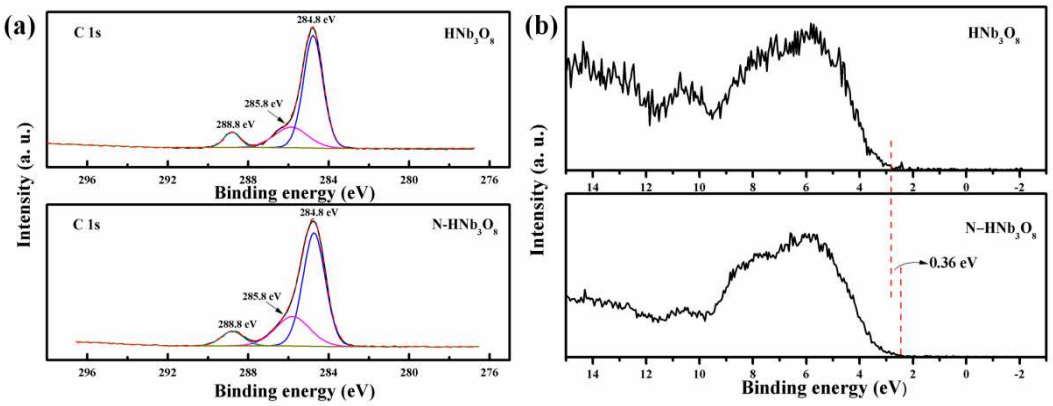

Figure S4 (a) XPS spectra of C 1s of the HNb_3O_8 and N-HNb_3O_8 samples. (b)Valance band spectra of the HNb_3O_8 and N-HNb_3O_8 samples.

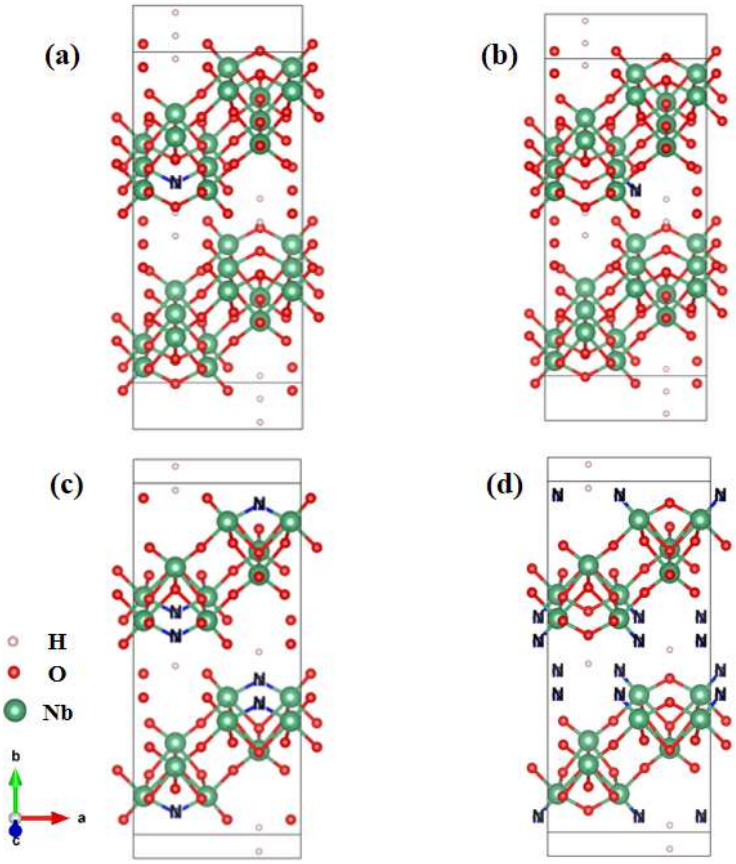

Figure S5 Models: (a) $H_8Nb_{24}O_{63}N$-1(1.56%), (b) $H_8Nb_{24}O_{63}N$-2(1.56%), (c) $H_4Nb_{12}O_{28}N_4$-1(12.5%) and (d) $H_4Nb_{12}O_{28}N_4$-2(12.5%)

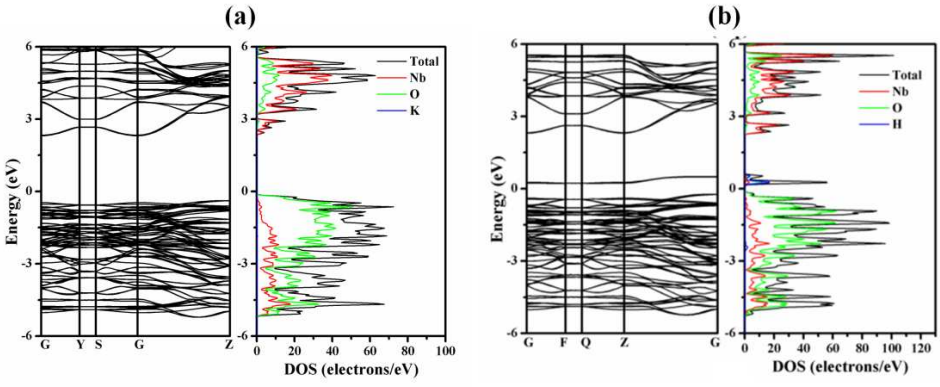

Figure S6 Energy band and PDOS data of the optimized (a) KNb_3O_8 and (b) HNb_3O_8

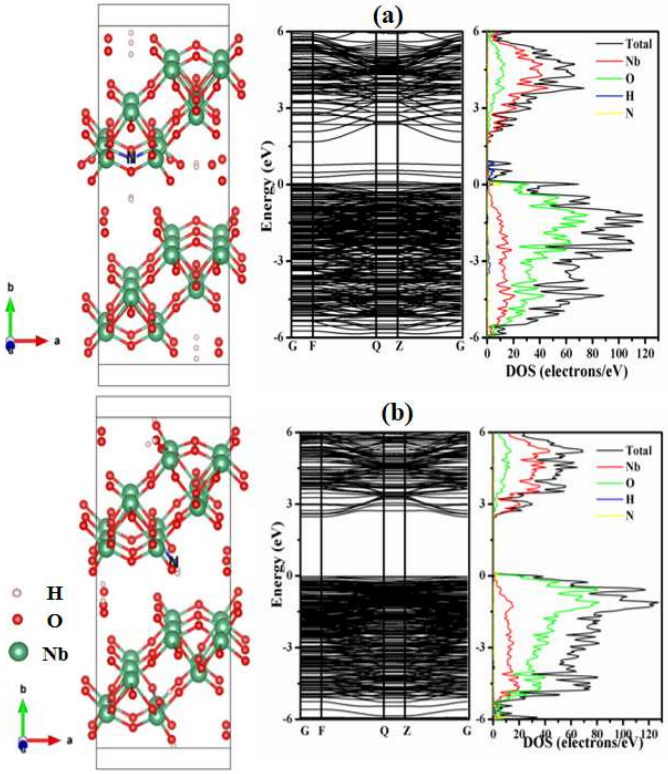

Figure S7 (a) Crystal structure, energy band and PDOS data of optimized $H_8Nb_{24}O_{63}N$-1.

(b) Crystal structure, energy band and PDOS data of optimized $H_8Nb_{24}O_{63}N$-2.

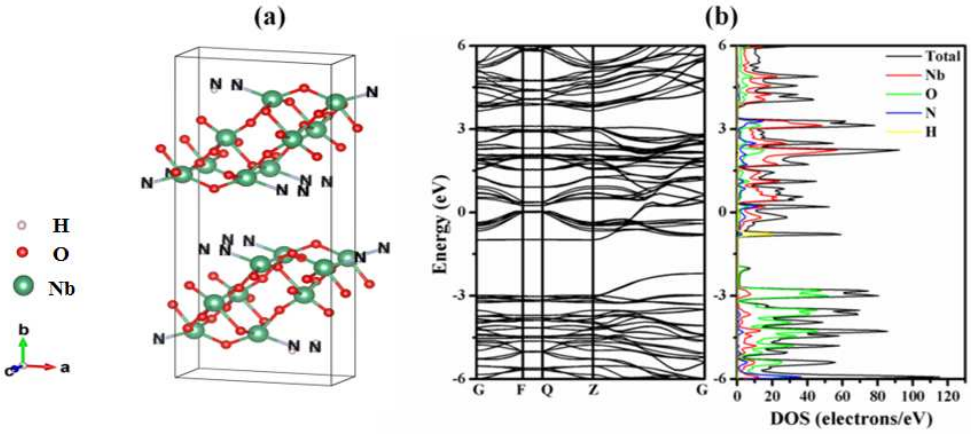

Figure S8 (a) Optimized crystal structure, (b) energy band and PDOS data of $H_4Nb_{12}O_{28}N_4$-2.

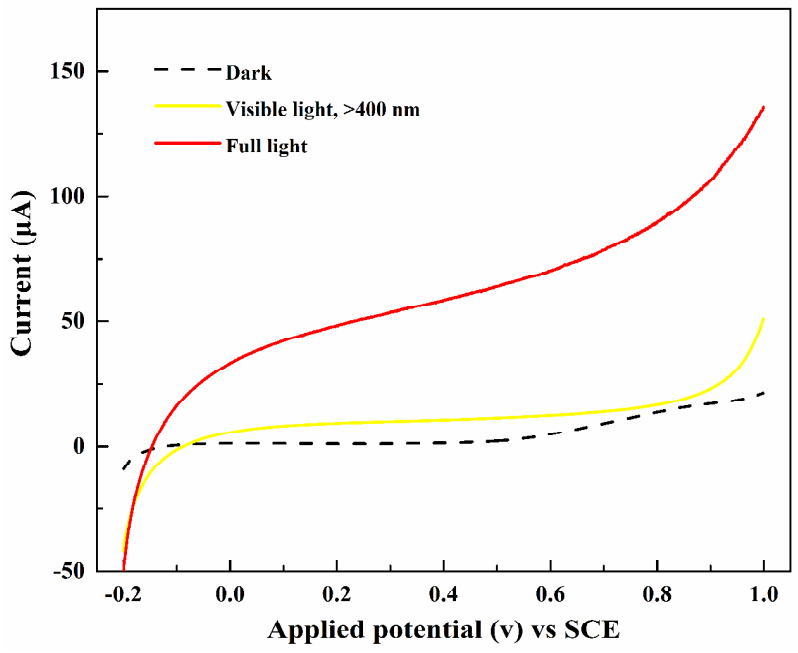

Figure S9 Linear sweep voltammetry (LSV) curves of the Co-Pi loaded N-HNb_3O_8 electrode in 0.5 M Na_2SO_4 aqueous solution under dark, visible light (>400 nm) and full light irradiation

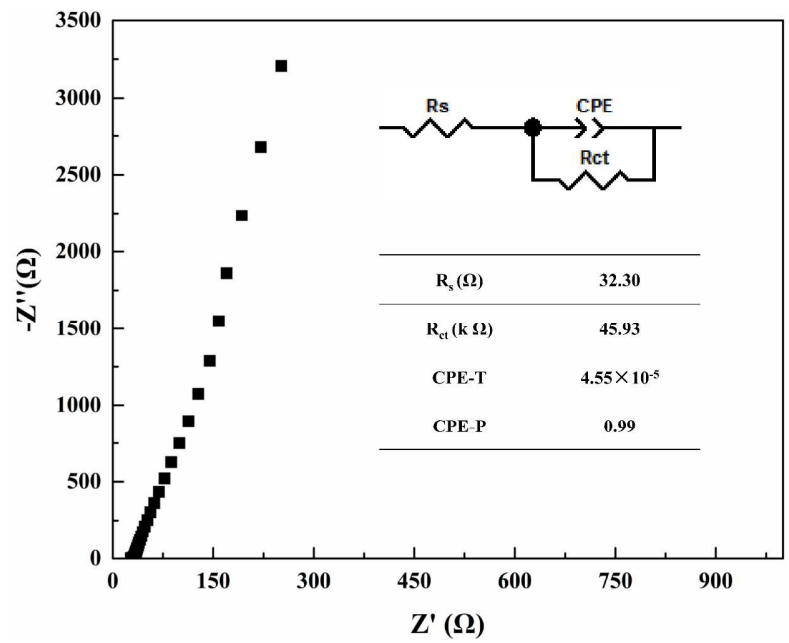

Figure S10 EIS of the Co-Pi loaded N-HNb_3O_8 electrode at 0.288 V vs SCE. The inset is the equivalent circuit diagram and data.

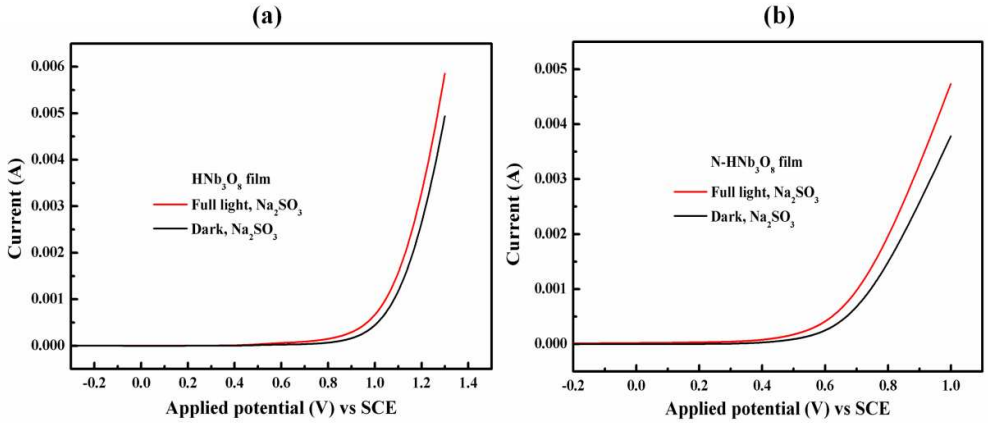

Figure S11 Linear sweep voltammetry (LSV) of (a) HNb_3O_8 and (b) N-HNb_3O_8 electrodes in 0.5 M Na_2SO_3 and Na_2SO_4 aqueous solution under dark and light conditions.

References

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