Dual modification of $TiNb_2O_7$ with nitrogen dopants and oxygen vacancies for selective aerobic oxidation of benzylamine to imine under green light

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1. Optimized calcination time for nitrogen doped $TiNb_2O_7$ sample in air

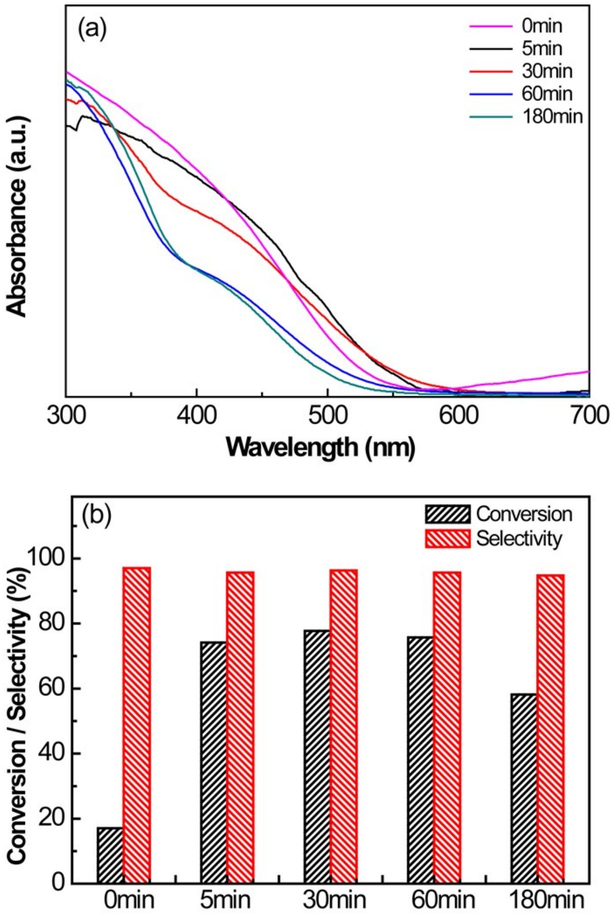


Fig. S1 (a) UV-Vis diffuse reflectance (UV-Vis-DR) spectra and (b) benzylamine conversion, imine selectivity (80 °C, 24 h, 100 mW/cm^2 green light) over the different nitrogen-doped samples. Firstly, $TiNb_2O_7$ sample was calcined at 700 °C for 3 h under NH_3 atmosphere and left to cool naturally to room temperature. Secondly, the obtained powders were put in tube furnace of 500 °C for different times including 0, 5, 30, 60, and 180 min (The sample was introduced to the 500 °C furnace and removed quickly after keeping for the designated time). The sample calcined in air for 5 min has good green light absorption ability and exhibits high activity. Therefore, the processing time of 5 min was chosen in this study.

2. Optimized calcination time for N-$TiNb_2O_7$ in ethanol

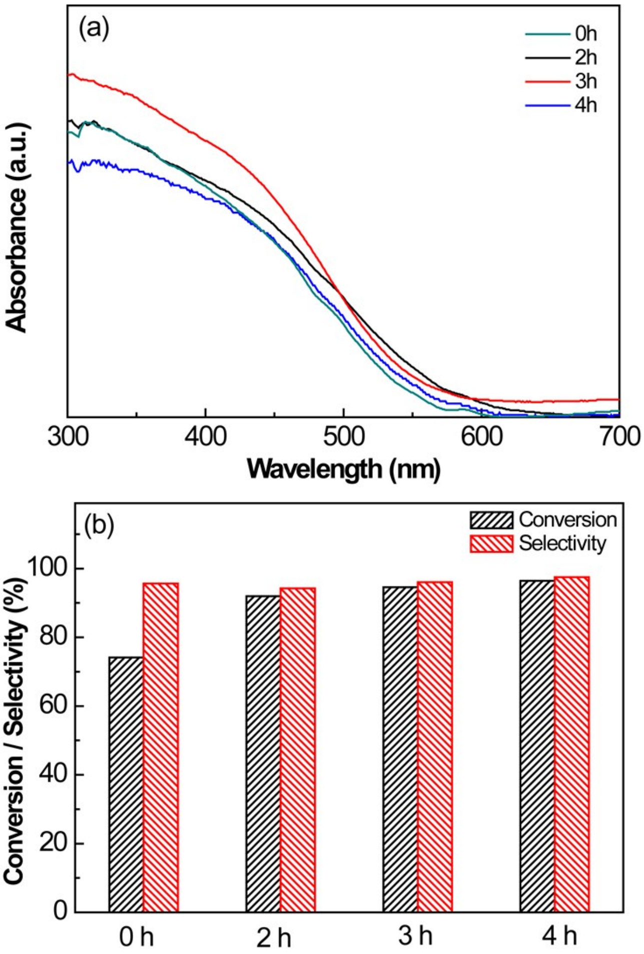


Fig. S2 (a) UV-Vis-DR spectra (b) Benzylamine conversion, imine selectivity (80 °C, 24 h, 100 mW/cm^2 green light) over ethanol treated N-$TiNb_2O_7$ photocatalysts. N-$TiNb_2O_7$ was treated with ethanol at 200 °C in argon gas for different times (0, 2, 3, and 4 h). It indicates that the ethanol treatment on N-$TiNb_2O_7$ is an effective method to improve the photocatalytic activity for selective oxidation of benzylamine. The sample treated in ethanol for 3 h (designated as V_o-N-$TiNb_2O_7$) exhibited the highest conversion rate and was chosen for the mechanism study.

3. Output spectra of colored LED light sources

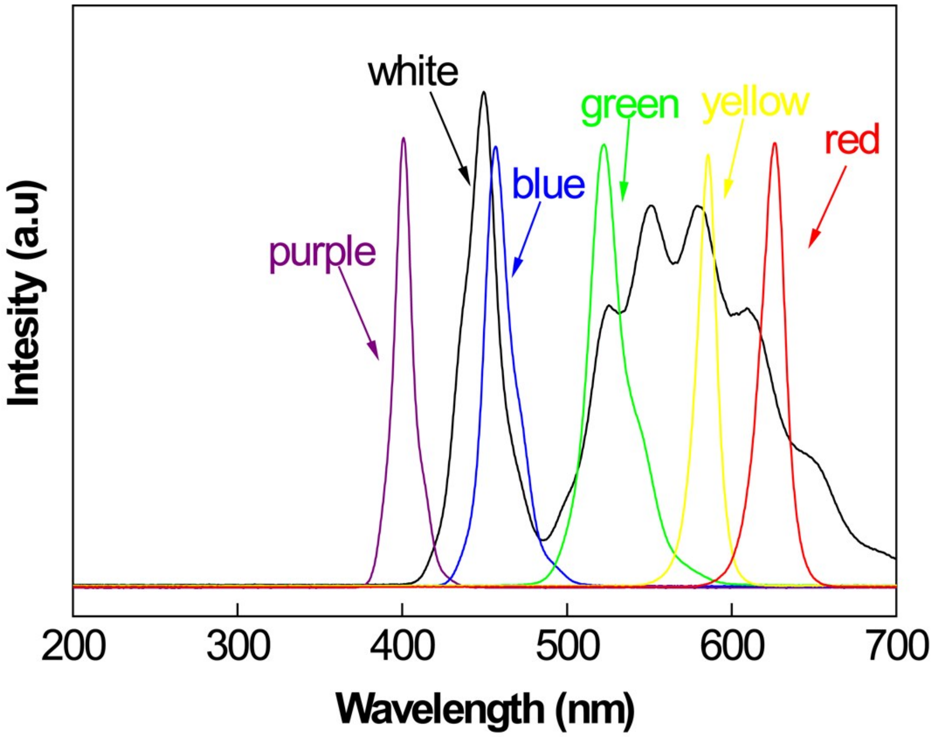


Fig. S3 Output spectra of colored LED light sources used in this study

4. N_2 adsorption–desorption isotherms of $TiNb_2O_7$ and modified samples

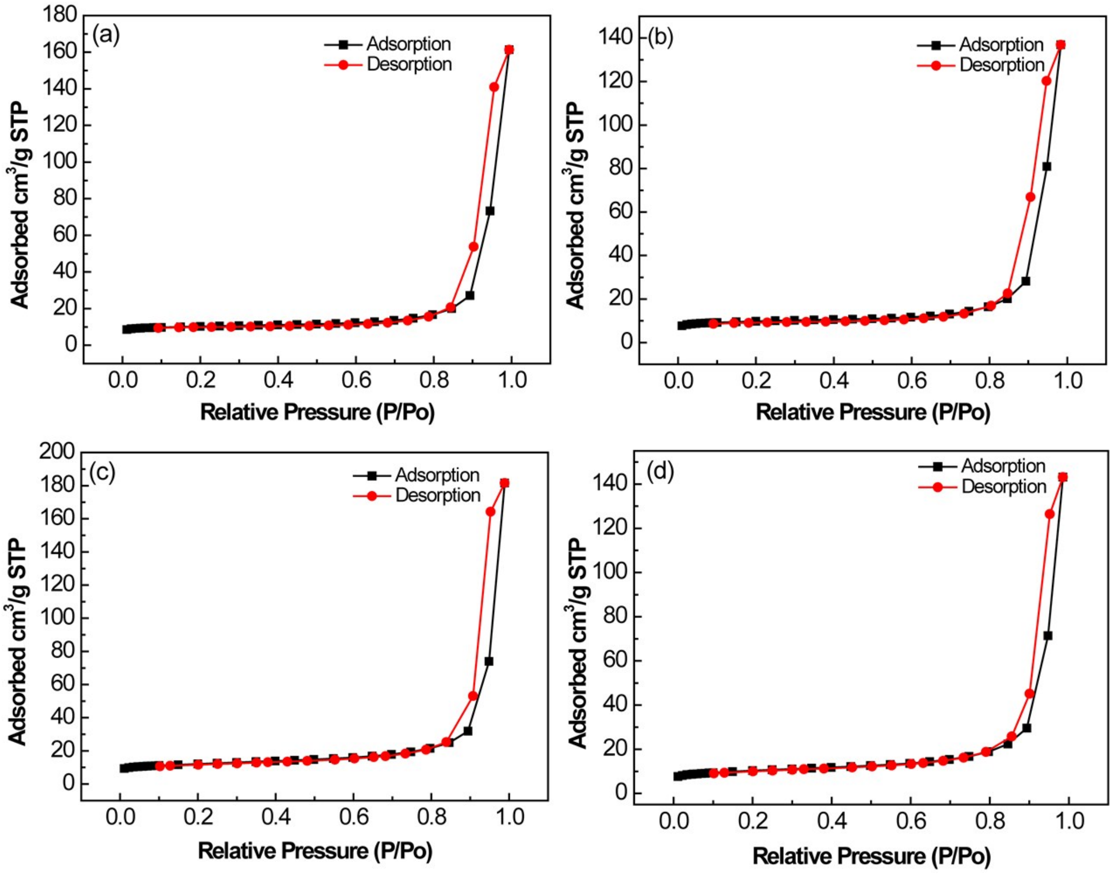


Fig. S4 N_2 adsorption–desorption isotherms of (a) $TiNb_2O_7$, (b) V_o-$TiNb_2O_7$, (c) N-$TiNb_2O_7$, and (d) V_o-N-$TiNb_2O_7$.

5. XRD patterns and XPS spectra of $TiNb_2O_7$-6h

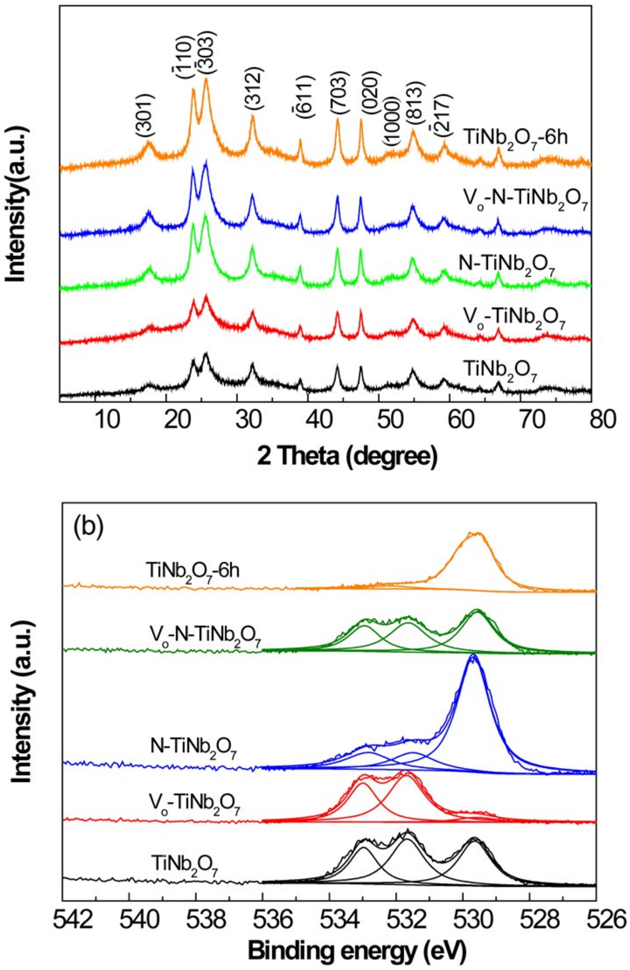


Fig. S5 (a) XRD patterns and (b) O1s XPS spectra of $TiNb_2O_7$ and modified samples. The $TiNb_2O_7$-6h sample was prepared by calcination of the dried precipitate from the hydrothermal reaction in air for 6 h.

6. PL spectra of $TiNb_2O_7$ and V_o-N-$TiNb_2O_7$

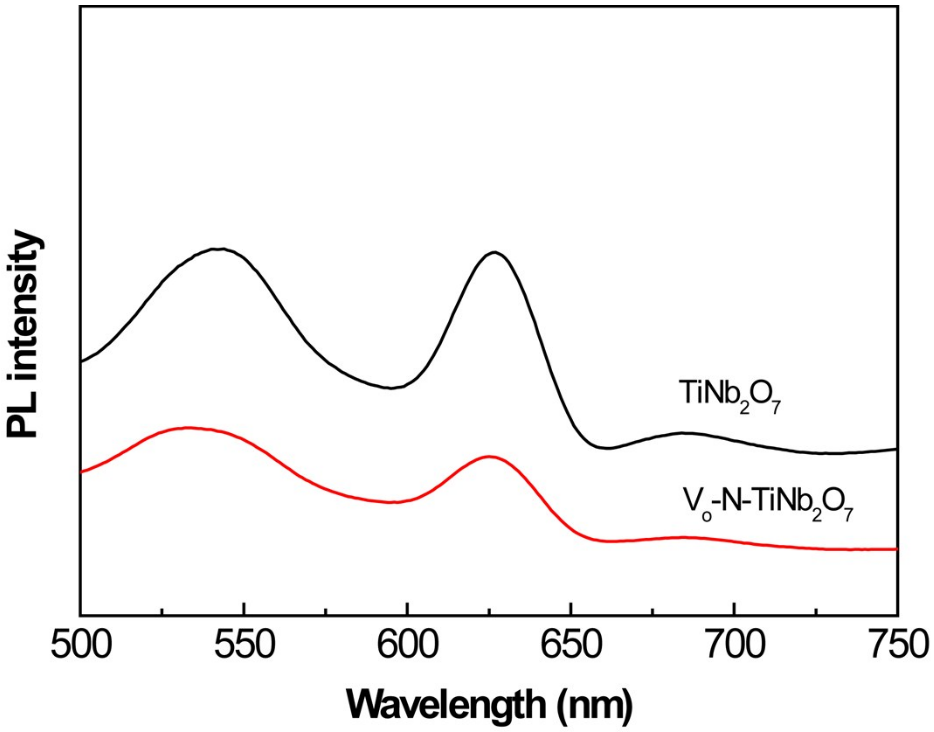


Fig. S6 Photoluminescence (PL) spectra of $TiNb_2O_7$ and V_o-N-$TiNb_2O_7$.

7. Recyclability and stability of V_o-N-$TiNb_2O_7$

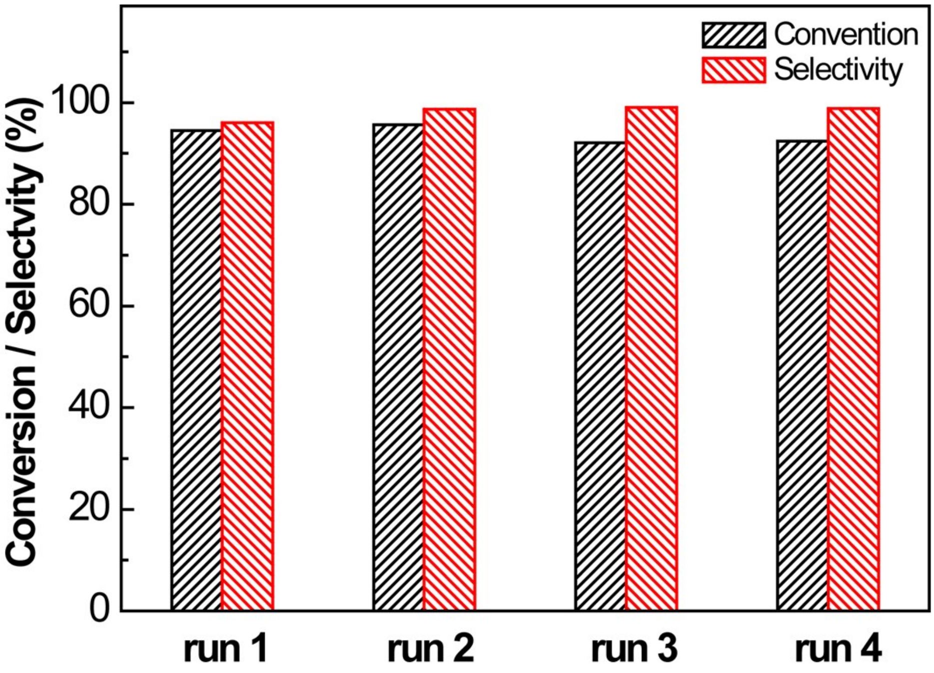
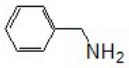
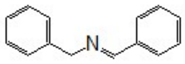
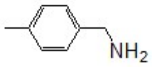
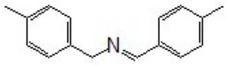
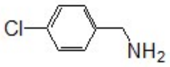
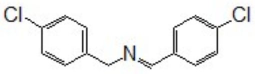
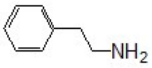
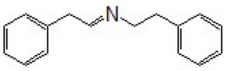
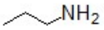
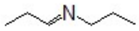


Fig. S7 Recyclability and stability of V_o-N-$TiNb_2O_7$ in the benzylamine oxidation reaction (80 °C, 24 h, 100 mW/cm^2 green light). The catalyst was used for four successive cycles.

8. Selective oxidation of different amines over V_o-N-$TiNb_2O_7$

Table S1 The activity for the selective oxidation of different amines over V_o-N-$TiNb_2O_7$

Entry	Substrate	Product	Conversion(%)	Selectivity(%)
1			68.1	96.4
2			37.9	94.5
3			40.7	95.9
4			8.5	91.5
5			13.8	80

Reaction conditions: 20 mg catalyst, 0.08 mmol reactant, 2 ml acetonitrile, 1 atm O_2, 80 °C, 12 h, green light (intensity at 100 mW/cm^2).

9. UV-Vis-DR spectra of V_o-N-$TiNb_2O_7$ before and after benzylamine adsorption

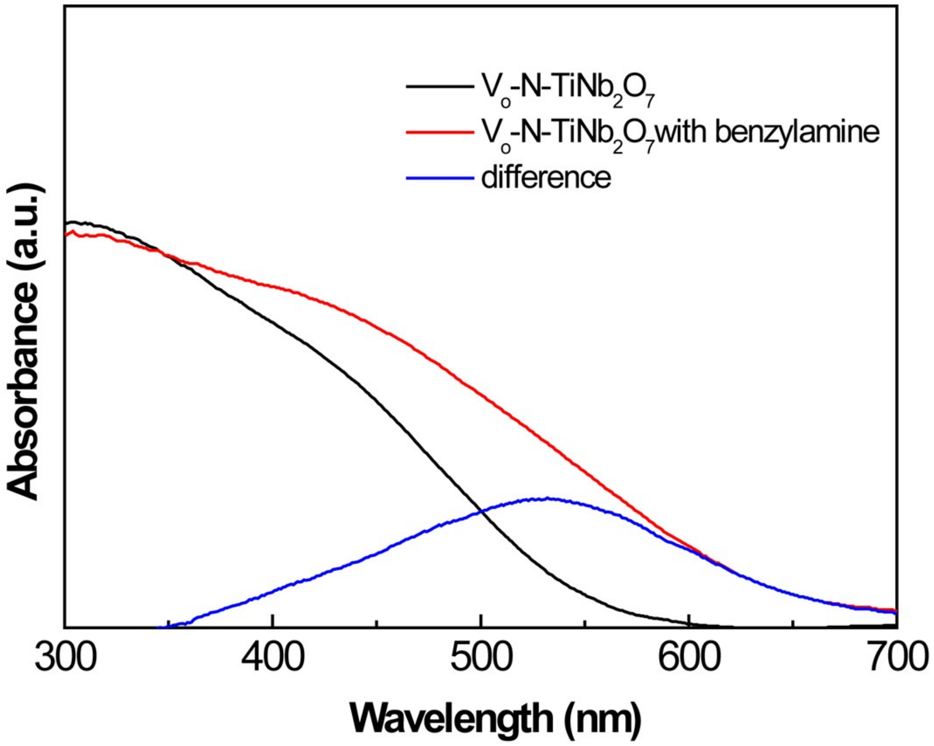


Fig. S8 UV-Vis-DR spectra of V_o-N-$TiNb_2O_7$ before and after benzylamine adsorption.

10. TPV spectra of V_o-N-$TiNb_2O_7$ before and after benzylamine adsorption

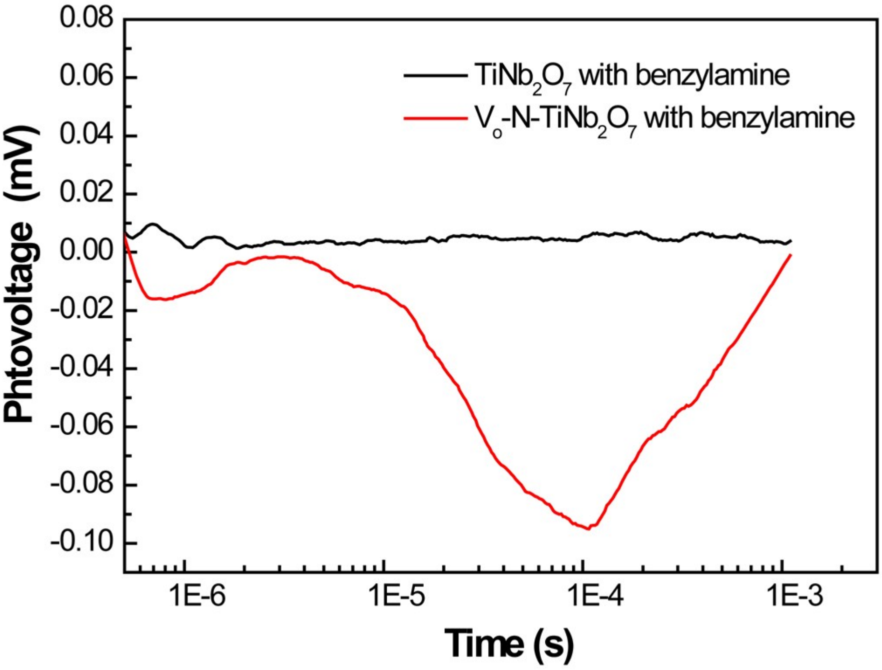


Fig. S9 Transient photovoltage (TPV) spectra of $TiNb_2O_7$ befor and after benzylamine adsorption.

11. Calculation of VB position for $TiNb_2O_7$

For $TiNb_2O_7$, the valence band edge and conduction band edge could be theoretically speculated using the equation related to Mulliken electronegativity,

$$E_{VB} = X - E^{e} + 0.5E_{g};\ E_{CB} = E_{VB} - E_{g}$$

where E_{CB} and E_g are the bottom position of CB and the band gap energy of the semiconductor, respectively, and X is the geometric mean of the Mulliken electronegativity of the constituent atoms in the semiconductor. The Mulliken electronegativity of an atom is the arithmetic mean of the atomic electron affinity and the first ionization energy. The Mulliken electronegativity for Ti, Nb and O atoms (X_{Ti}, X_{Nb}, and X_{O}) are 3.45 eV, 3.82 eV, and 7.54 eV (vs. NHE), respectively). Therefore, $X_{TiNb2O7} = (X_{Ti}\, X_{Nb}^{2}\, X_{O}^{7})^{1/10}$ = 6.08 eV (vs. NHE).[2,3] E^{e} is the energy of free electrons on the hydrogen scale (4.5 eV).[1] Therefore, the corresponding valence band positon and conduction band position is -7.64 eV and -4.54 eV (vs. vacuum energy level), respectively. According to the VB spectra in Fig. 5a, it shows that the valence band of $TiNb_2O_7$ is 0.21 eV more positive than V_o-N-$TiNb_2O_7$, therefore, the valence band of V_o-N-$TiNb_2O_7$ is -7.43 eV (vs. vacuum energy level).

1. H. Shi, G. Chen, C. Zhang and Z. Zou, *ACS Catal.*, 2014, **4**, 3637-3643.
2. Y. Qu, W. Zhou, Z. Ren, G. Wang, B. Jiang and H. Fu, *ChemCatChem*, 2014, **6**, 2258-2262.
3. G. Wang, Y. Huang, A. Kuang, H. Yuan, Y. Li and H. Chen, *Inorg. Chem.*, 2016, **55**, 9620-9631.