Supporting Information

In-situ synthesis of N-doped TiO_2 onto Ti_3C_2 MXene with enhanced photocatalytic activity in selective reduction of nitrate to N_2

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S1. Experimental section

S1.1. Materials

The Ti_3AlC_2 powder was supplied by Beijing Forsman Technology Co., Ltd. Potassium nitrate (KNO_3), ammonium chloride (NH_4Cl), 49 % HF aqueous solution, and formic acid aqueous solution were purchased from Sinopharm Chemical Reagent Co., Ltd (China). The deionized (DI) water used in this work was obtained from the instrument of SW AC-520, Japan.

S1.2. Characterizations

The morphologies and microstructures of the as-synthesized samples were characterized by scanning electron microscopy (SEM, Hitachi S4800 and JSM-6510LV) and transmission electron microscopy (TEM, FET Tecnai G2 F20). X-ray diffraction (XRD) characterization was obtained from an X-ray diffractometer (D8 ADVANCE, Bruker). Fourier transform infrared (FTIR, Nicolet Nexus 670) spectra were carried out to unveil the chemical composition and bonding information. X-ray photoelectron spectroscopy (XPS, Escalab 250xi, Thermo Scientific) was conducted to confirm the surface chemical composition and states of prepared samples. Raman spectroscopy was performed on a Raman spectrometer (DXR532, USA) with 532 nm laser excitation. UV-vis diffuse reflectance spectra (UV-vis DRS) were collected by UV-vis spectrophotometer (UV2550, Shimadzu).

Transient photocurrent responses, electrochemical impedance spectroscopy, and Mott-Schottky plots were performed by an electrochemical workstation (CHI760e

Instruments). The platinum-wire electrode, Ag/AgCl electrode, and as-fabricated samples were acted as the counter electrode, reference electrode, and working electrodes, respectively. In the process of electrochemical measurements, the slurry of the as-prepared sample was covered onto the conductive glasses of indium tin oxide (ITO). During the experiments of Transient photocurrent responses and electrochemical impedance spectroscopy, the 300 W Xenon lamp was served as the light source. The Mott-Schottky plots were carried out at different frequencies of 1000, 1500, and 2000 Hz.

S2. Supplementary Figures

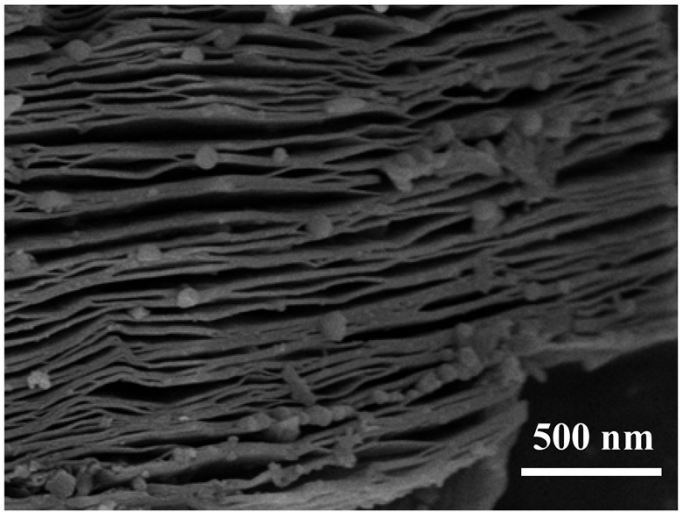

Fig. S1. SEM image of Ti_3C_2.

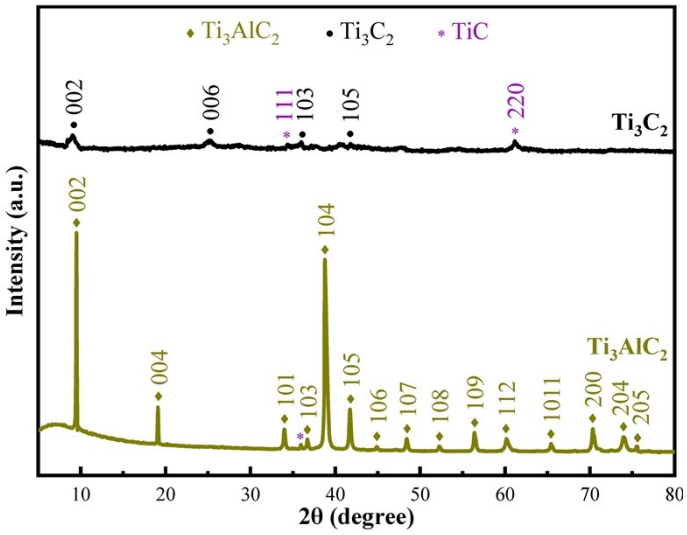

Fig. S2. XRD patterns of Ti_3AlC_2 and Ti_3C_2.

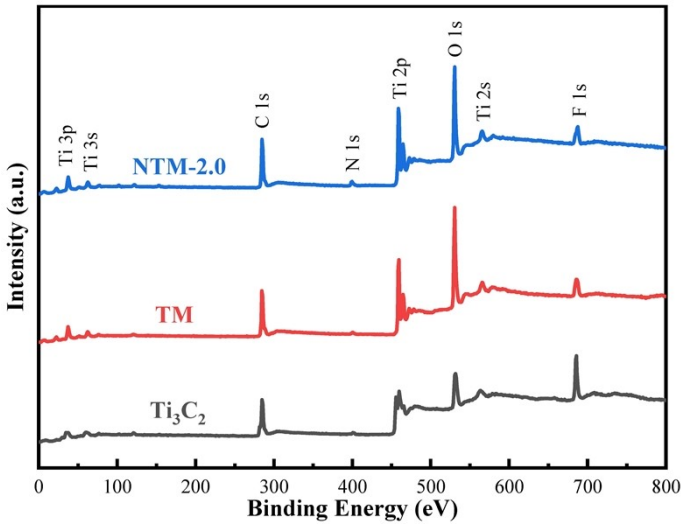

Fig. S3. XPS survey spectra of Ti_3C_2, TM, and NTM-2.0 samples.

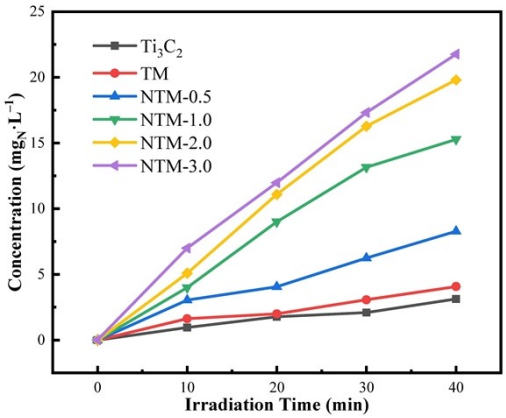

Fig. S4. Concentration of NH_4^+-N over different photocatalysts under the FA concentration of 35 mmol·L^{-1}.

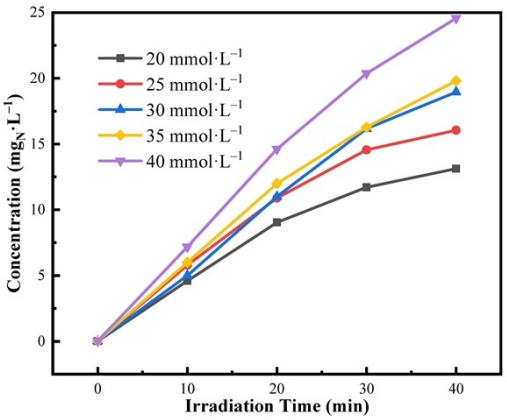

Fig. S5. Concentration of NH_4^+-N under different FA concentrations over NTM-2.0 photocatalyst.

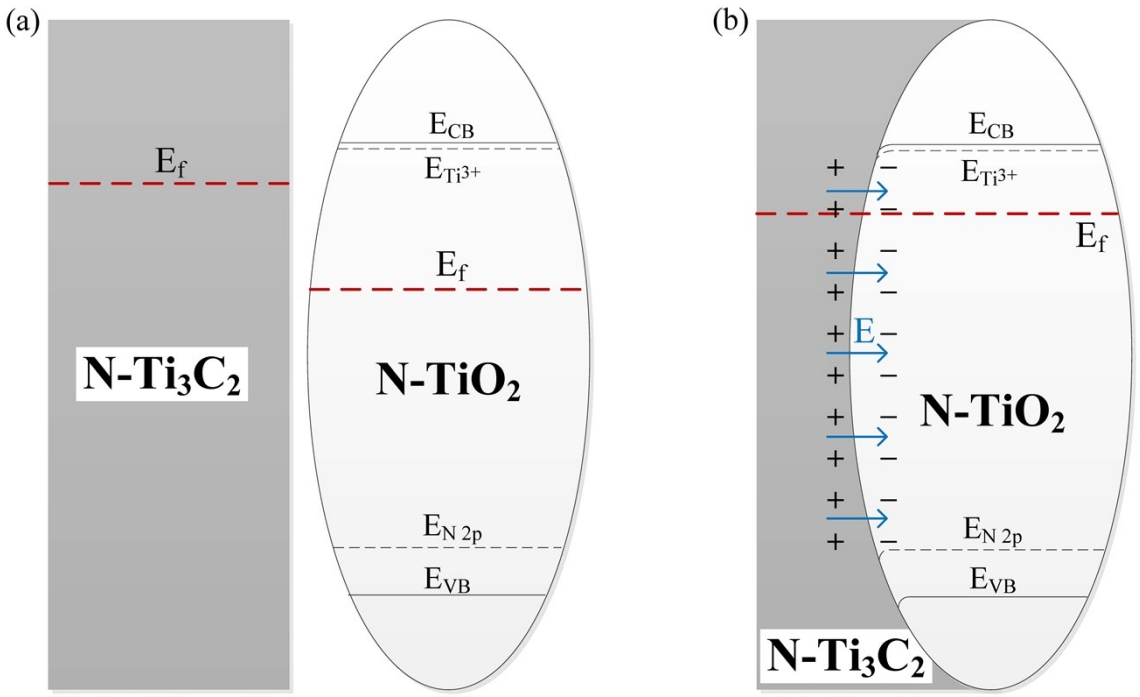

Fig. S6. Fermi levels of (a) N-Ti_3C_2, N-TiO_2, and (b) N-TiO_2/Ti_3C_2.

Example for calculation of N_2 selectivity:

Taking photocatalytic nitrate reduction over NTM-2.0 under the FA concentration of 35 $mmol \cdot L^{-1}$ as an example, the N_2 selectivity was calculated. The initial concentration of NO_3^- was 101.3 $mg_N \cdot L^{-1}$. Under illumination for 40 min, the concentration of NO_3^-, NO_2^-, and NH_4^+ were 0, 2.07, and 19.8 $mg_N \cdot L^{-1}$, respectively. The N_2 selectivity was calculated as Equation S1.

$$S_{N_2} = \frac{101.3 - 0 - 2.07 - 19.8}{101.3 - 0} \times 100\% = 78.4\% \quad \text{(S1)}$$