Supporting information

Near-infrared driven N_2 fixation on ZnO-MXene (Ti_3C_2) heterostructures through pyroelectric catalysis

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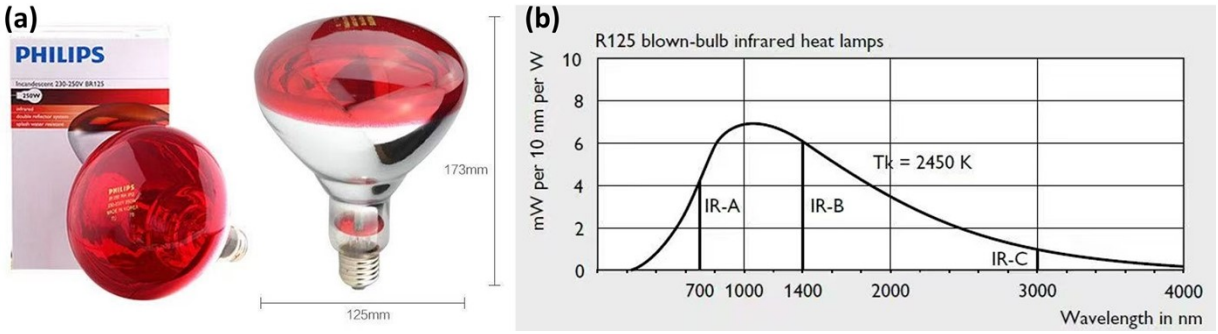

Figure S1. (a) a photograph and (b) the spectrum of the R125 blown-bulb infrared heat lamp.

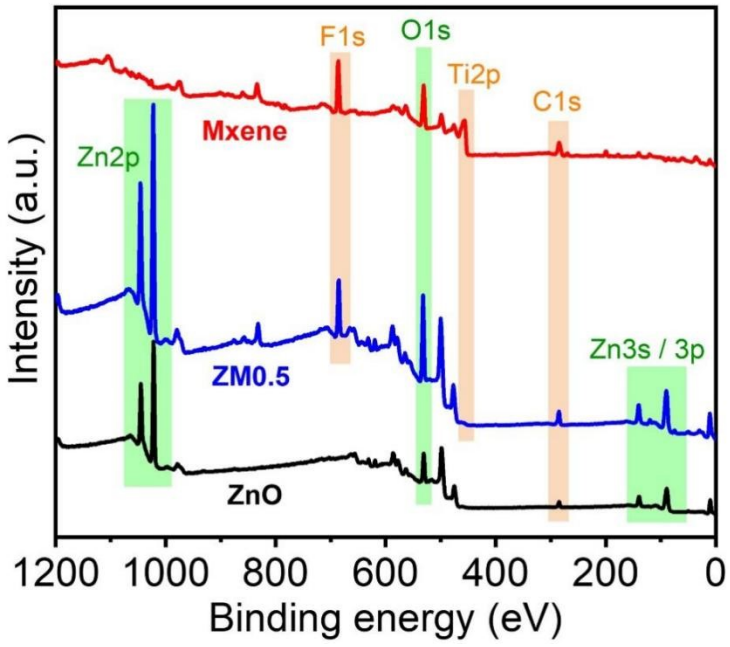

Figure S2. XPS survey spectra of ZnO, Mxene and ZM0.5.

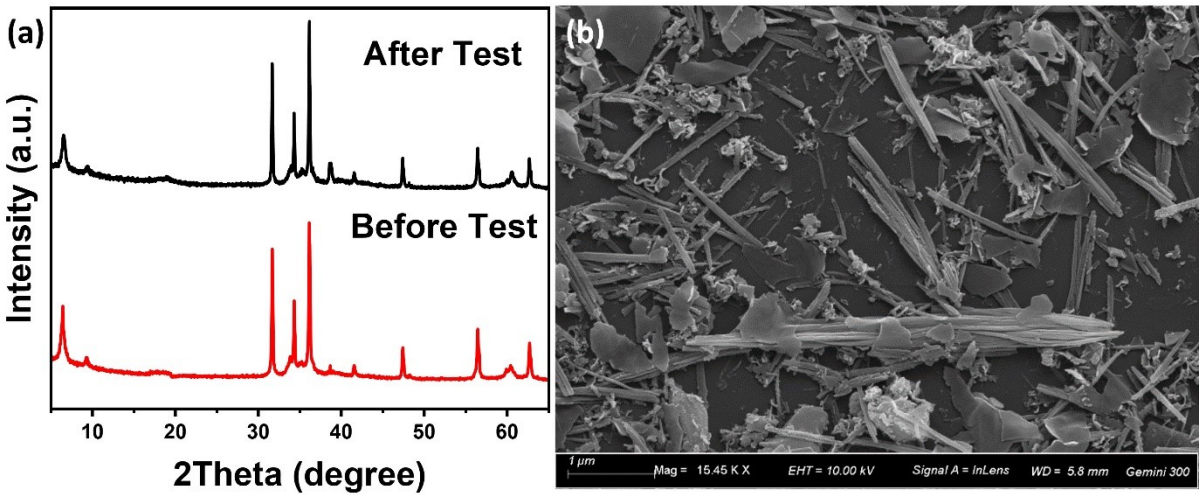

Figure S3. (a) XRD patterns of ZM0.5 before and after the catalytic tests. (b) SEM image of ZM0.5 after the catalytic tests.

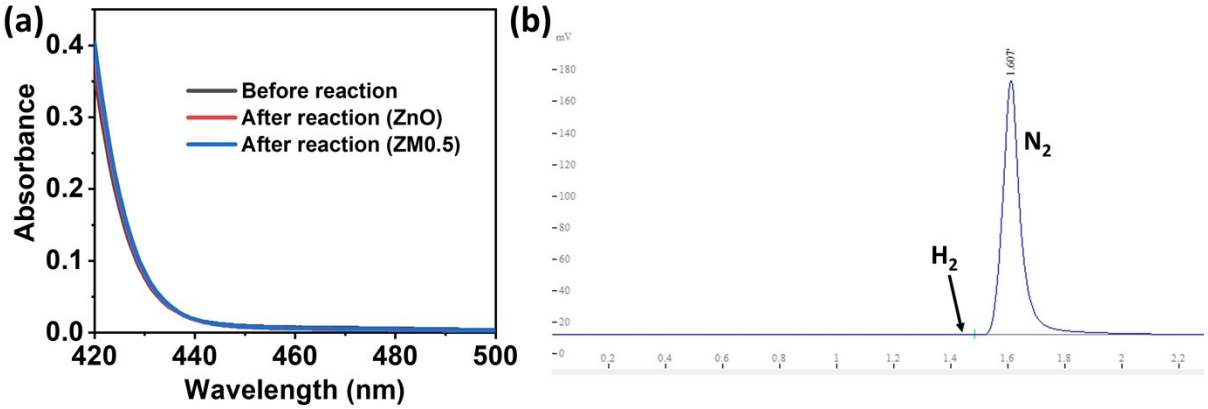

Figure S4. Presents the detection results for the reaction products from ZM0.5 after 5 hours. Panel (a) shows the UV-Vis absorption spectra recorded to detect the N_2H_4 product using the p-$C_9H_{11}NO$ indicator. Panel (b) illustrates the detection of the H_2 product using gas chromatography equipped with a thermal conductivity detector (TCD). In both cases, no product was detected.

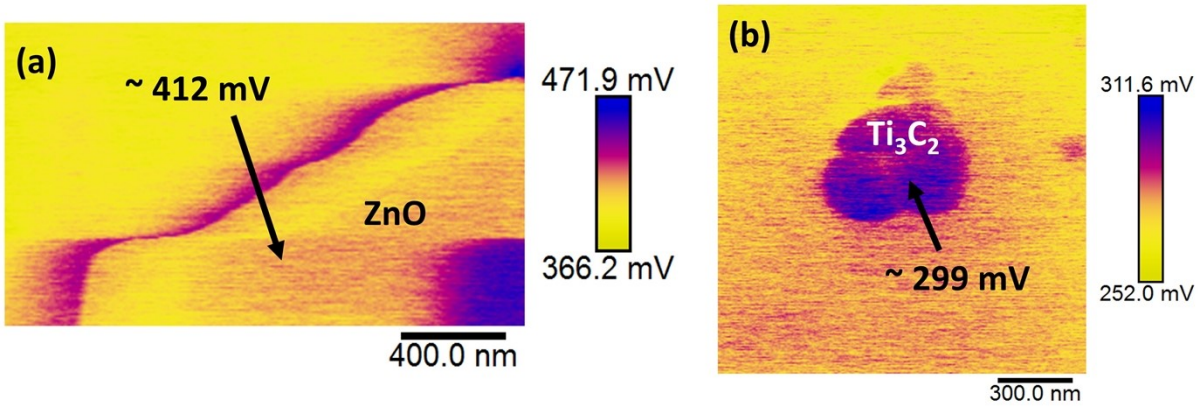

Figure S5. KPFM images of (a) ZnO and (b) Ti_3C_2 MXene and the corresponding potentials on their surface (V_{CPD}). The work functions difference were calculated as follow: $e \cdot V_{CPD} = E_{tip} - E_{sample}$. The work function of the tip (E_{tip}) was - 4.6 eV. So the work functions of ZnO and Ti_3C_2 were calculated to be 4.19 eV and 4.31 eV, respectively.

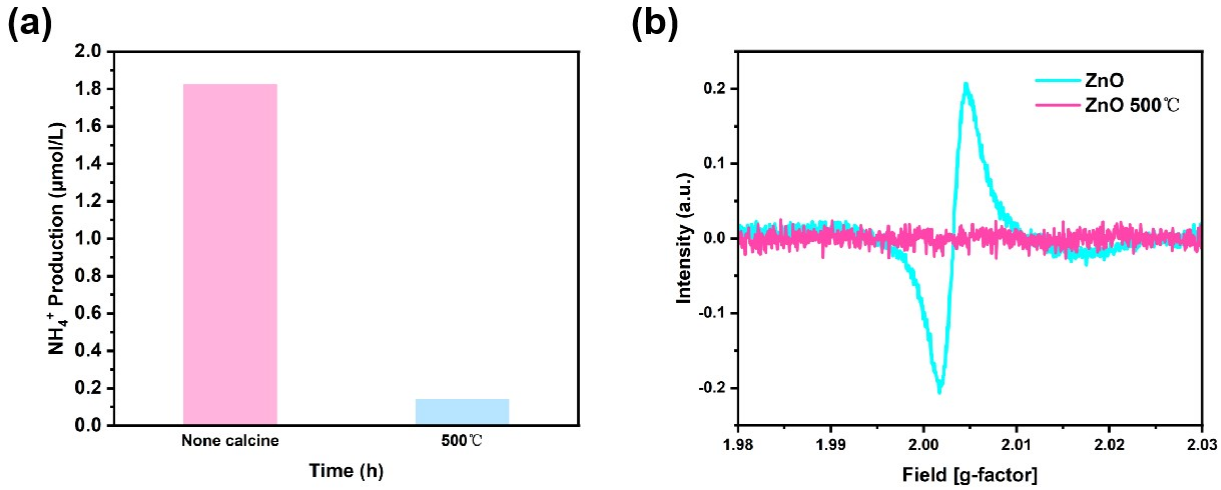

Figure S6. (a) NH_4^+ production of the pristine ZnO and the pre-calcined ZnO to fill its oxygen vacancies; (b) ESR spectroscopy of ZnO before and after a calcination treatment in air. The ESR signal at approximately g=2.004 represents the oxygen vacancy defects on ZnO.

The above experiment confirmed the essential role of the oxygen vacancies on ZnO for the N_2 fixation reaction. The calcination treatment at 500 °C in air was to refill the oxygen vacancies. It resulted in a dramatic decline of the ammonia production, meaning that the oxygen vacancies on the pristine ZnO contributed to the N_2 fixation reaction.

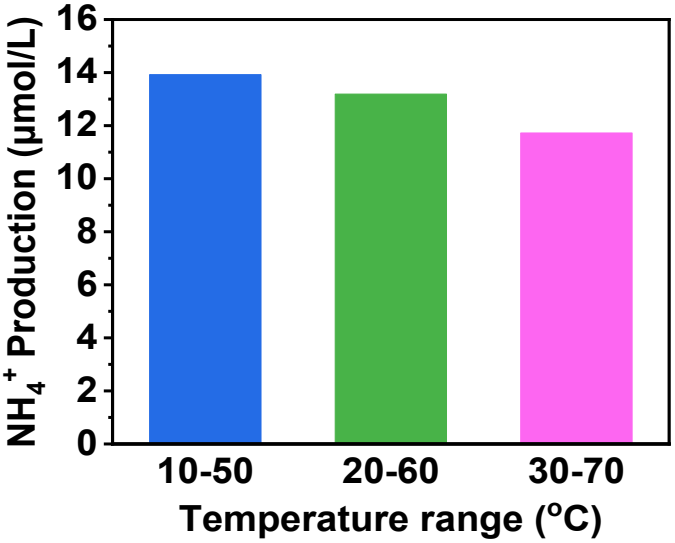

Figure S7. ammonia production under different ranges of temperature fluctuation.

Figure S7 shows the N_2 fixation activity of ZM0.5 at three different temperature ranges. Even with the same fluctuation width (i.e., 40 °C), the fluctuation at higher temperature (i.e., closer to the T_C of ZnO) does not favor the generation of pyro electrons and holes, thus the catalytic reaction.