Supporting information

Reactivity of Nitrogen Atoms from Zif-8 Structure Deposited over Ti$_3$C$_2$ MXene in the Electrochemical Nitrogen Reduction Reaction

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Experimental Section

Synthesis of Ti$_3$C$_2$ MXene

The Ti$_3$C$_2$ catalyst was synthesized by Ti$_3$AlC$_2$ MAX phase etching. The MAX phase synthesis was previously reported by the group[1]. In a typical synthesis procedure, 0.5 g of Ti$_3$AlC$_2$ MAX phase was slowly added into a plastic tube containing 10 mL of 0.8 g LiF dissolved in 9 mol.L^{-1} HCl. Therefore, the initial F/Al atomic ratio is 12. The reaction was performed for 72h at 60 °C under stirring.

The suspension obtained after the etching step is centrifuged 4 times at 6000 rpm for 6 min with ultrapure water to eliminate the excess of acid. At this point the supernatant must have pH $\geq$ 5. The sediment is redispersed in 5 mL of water following by vacuum-assisted filtration (PVDF membrane, 0.22 µm pore size), washed with ultrapure water and dried overnight under air at ambient temperature.

A final step is performed to eliminate Al impurities by dispersing the obtained MXenes in 350 mL of ultrapure water previously degassed with Ar and stirred during 4h under Ar atmosphere. Then, the suspension is filtered and dried overnight at ambient conditions. Finally, the obtained film is stored under Ar atmosphere to avoid possible oxidation by air.

Synthesis of Zif-8@Ti$_3$C$_2$ MXene

60 mg of Ti$_3$C$_2$ is added to 20 mL of methanol, followed by 15 min under ultrasound. Then, 219 mg of zinc acetate (1 mmol) is added into the beaker and dispersed using ultrasonication during 1h. In another beaker, 328 mg (4 mmol) of 2-methylimidazole is dissolved in 20 mL of methanol and both solutions are mixed. The mixture is stirred for 4h at room temperature to synthesize the Zif-8 structure. Finally, the solution is centrifuged 4 times with methanol at 9000 rpm for 10 min,

following by vacuum-assisted filtration (PVDF membrane, 0.22 μm pore size) and dried overnight under air at ambient temperature.

Characterization:

X-ray diffraction (XRD) of the samples was performed with a PANanalytical EMPYREAN powder diffractometer using CuKα radiation source ($K_{\alpha 1}$ = 1.5406 Å and $K_{\alpha 2}$ = 1.5444 Å). The diffractograms were collected between 3 and 70° with a 0.07° step and 420 s dwell time at each step. An ultra-fast X-Ray detector (X'Celerator) was used to collect the signals. The phase identification is based on the previous work[1].

The Raman spectroscopy was performed using a HORIBA Jobin Yvon LabRAM HR800 confocal Raman microscope with a CCD detector. The spectra were obtained at room temperature using an excitation wavelength of 532 nm. A limit of 1 mW of power was carefully delivered to the sample. The spectral resolution is 0.5 cm^{-1}.

The MXene morphology was evaluated by field emission gun scanning electron microscope (FEG-SEM) 7900F from JEOL. The microscope is equipped with an Energy Dispersive X-ray Spectrometer (EDS) from Brücker to analyze the presence of Zn and Ti from Zif-8 and MXene structures, respectively.

Electrochemical NRR measurements:

All electrochemical tests were performed at room temperature using a potentiostat Autolab (PGSTAT-302N). For the ink preparation, 7 mg of catalyst is dispersed in a mixture of Mili-Q H_2O (250 μL, 18.2 MΩ.cm), isopropanol (250 μL) and Nafion® (20 μL) by sonicating for 20 minutes to form a homogeneous ink.

The Linear Sweep Voltammetry tests (LSV) were performed in a standard three-electrode electrochemical cell coupled with a rotating disc electrode (5 mm) as working electrode. A saturated calomel and a glassy carbon plate were used as reference and counter electrodes, respectively. The catalyst ink was deposited onto the glassy carbon rotating electrode (7 µL, 0.5 mg.cm^{-2}). The measurements were conducted in a N_2 and Ar-saturated 0.1 M NaOH electrolyte (99.7 %, VWR) between 0.1 to -0.6 vs RHE at a scan rate of 10 mV.s^{-1} applying a rotating rate of 1600 rpm to the working electrode. The electrochemical double-layer capacitance (Cdl) has been measured through cyclic voltammograms (CVs) in non-faradaic potential regions and are extracted by the linearization of $\Delta J = j_A - j_C$ vs. scan rate (Figure S4).

The chronoamperometry analysis was performed to produce NH_3 for quantification and it was performed in the same three-electrode electrochemical cell. A saturated calomel and carbon glassy plate were used as reference and counter electrodes. For the working electrode, it was used a carbon paper (1 cm^2), where it was deposited 74.2 µL of catalyst ink (1 mg.cm^{-2}). Just before the entrance of the cell, two vials were connected containing $KMnO_4$ and H_2SO_4 solutions each one to eliminate any NH_3 or NO_x contamination in the high-purity gas. The same reaction was performed in an H-cell type obtaining similar results of NH_3 production, indicating that the NH_3 produced in the reaction is not oxidized in the anode.

The reaction was performed at different controlled potentials in N_2 and Ar-saturated 0.1 M NaOH and at open-circuit potential in N_2-saturated electrolyte for 2 h (N_2 and Ar purity of 99.9999 %). It was used 25 mL of electrolyte in the cell. The electrochemical cell was degassed for 1 h before the experiment with the gas bubbling into the electrolyte and the gas was constantly bubbled into the electrolyte during all the reaction. To rule out the quantification of NH_3 from air ambient, the

electrochemical cell was maintained isolated from air under gas circulation and no experiences with ammonia solution was performed in the same laboratory.

NH₃ quantification:

The amount of NH_3 produced during the reaction was determined by the Indophenol method. Typically, 1.5 mL of electrolyte was immediately taken after the reaction and added to a plastic tube. Then, 100 µL of phenol solution is added (0.5 mol L^{-1}) followed by 50 µL of $Na_2[Fe(CN)_5NO]$ (0.002 mol L^{-1}) and 100 µL of NaClO alkaline solution (0.7 mol L^{-1} dissolved in 1 mol L^{-1} NaOH). The solution is maintained in the dark for 2 h and the concentration is obtained by measuring the absorption peak at 655 nm by UV-VIS spectrometer (Thermo Helios Omega). The fresh 0.1 M NaOH electrolyte was also evaluated to create a background absorption peak and eliminate the influence of NH_3 in the air. The calibration curve was performed with different NH_4Cl concentrations in 0.1 M NaOH solution (Figure S8).

The NH_3 formation rate the faradaic efficiency were calculated as described below:

$$NH_3 \text{ rate of formation} = (C_{NH3} \times V) / (t \times m_{cat}) \tag{1}$$

$$\text{Faradaic efficiency} = (3 \times F \times C_{NH3} \times V) / (17 \times Q) \tag{2}$$

Where, C_{NH3} is the NH_3 concentration calculated (ppm), F is the Faraday constant (96487 C.mol^{-1}), t is the electrolysis time, m_{cat} is the mass of catalysts, V is the volume of electrolyte and Q is the amount of charge consumed during the reaction.

Hydrazine quantification:

The possible production of hydrazine was evaluated by the spectrophotometric Watt-Chrisp method[2]. Previously, a color reagent was prepared with a mixture of 100 mL ethanol, 2.0 g of

para(dimethylamino)benzaldehyde and 12 mL of HCl (37 wt%). Typically, 2 mL of electrolyte was immediately taken and reacted with 2 mL of color reagent during 30 min. After that, the absorbance is measured at 458 nm.
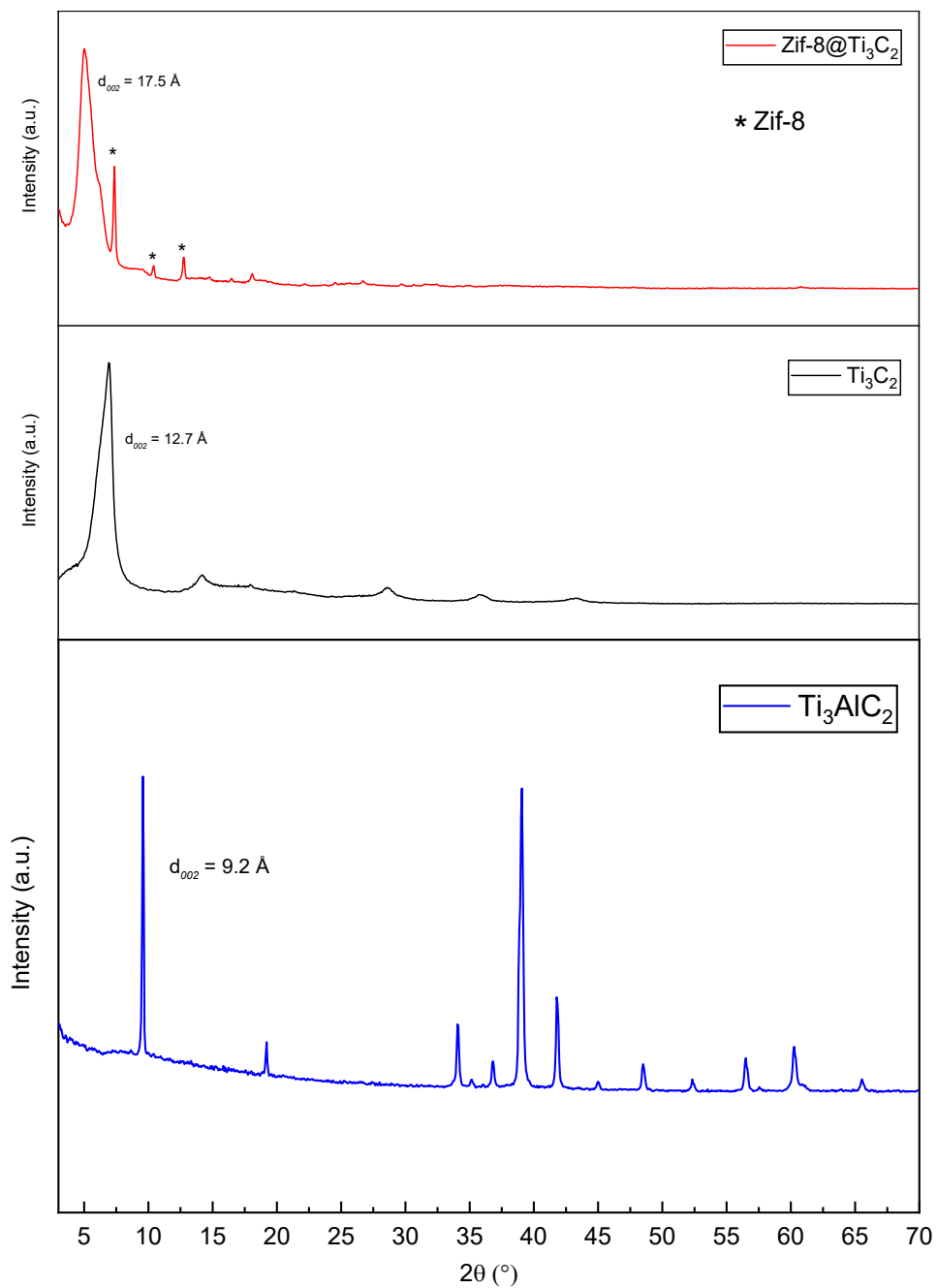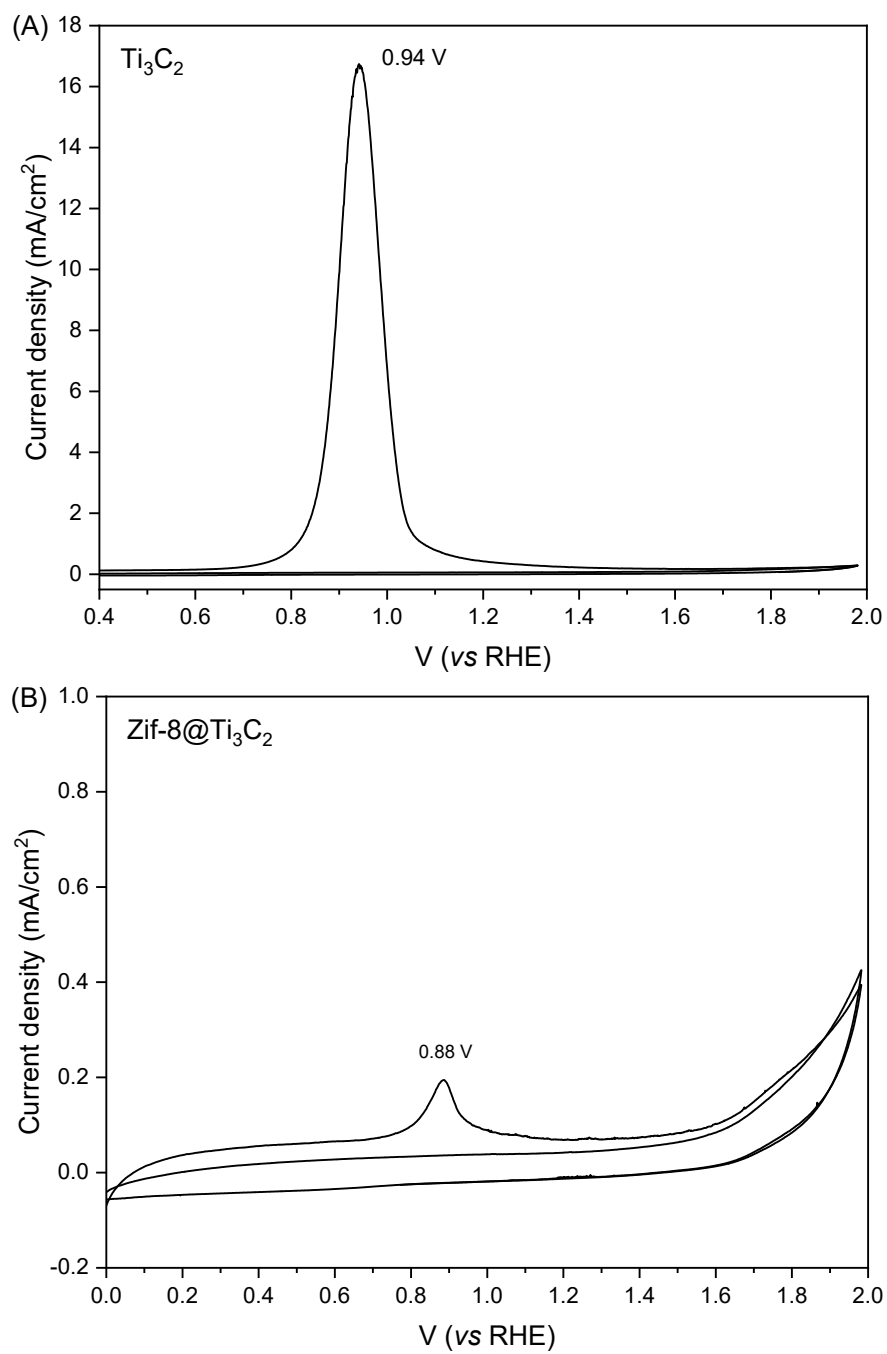
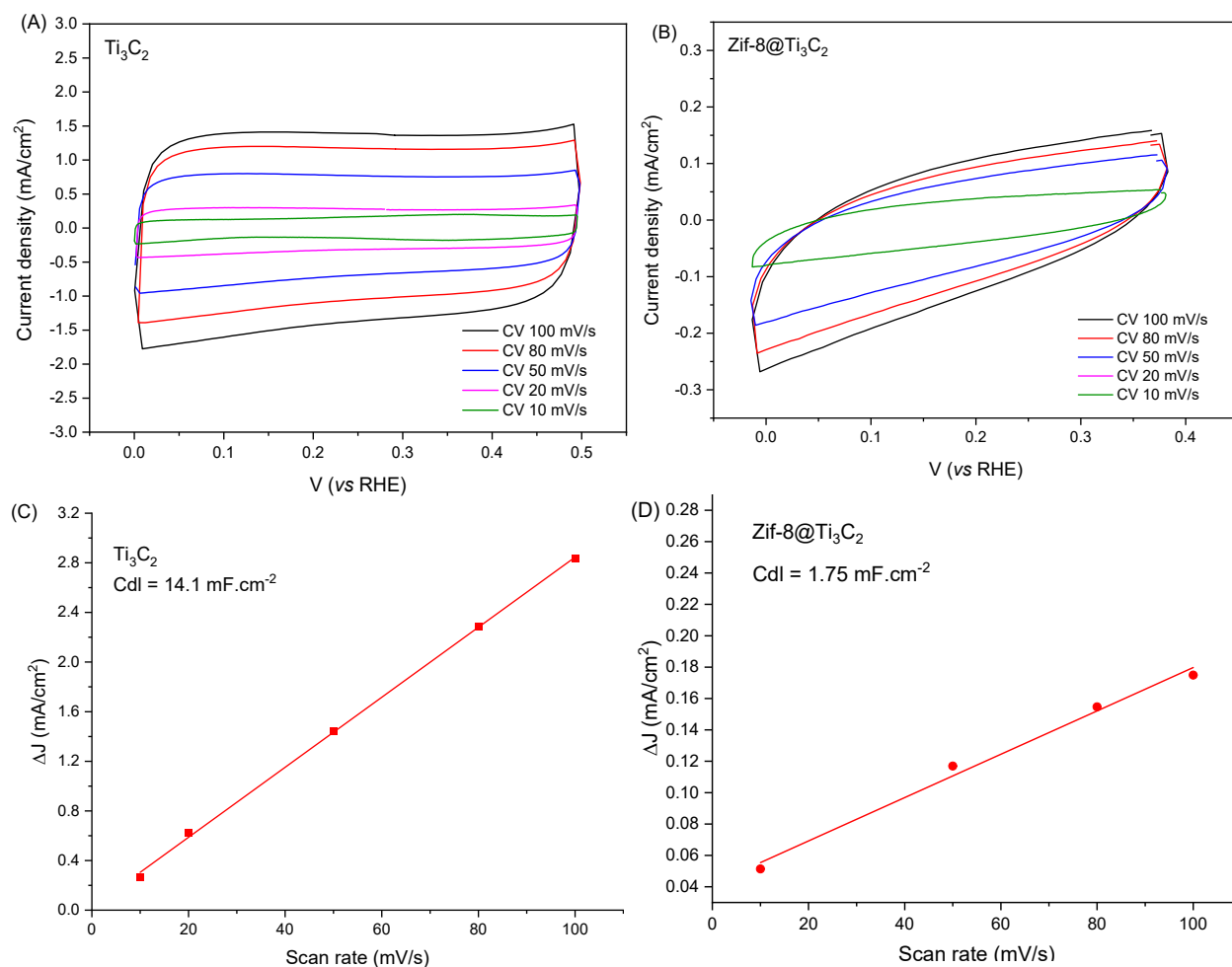**Figure S1.** XRD results of the MAX phase and MXene-based catalysts.
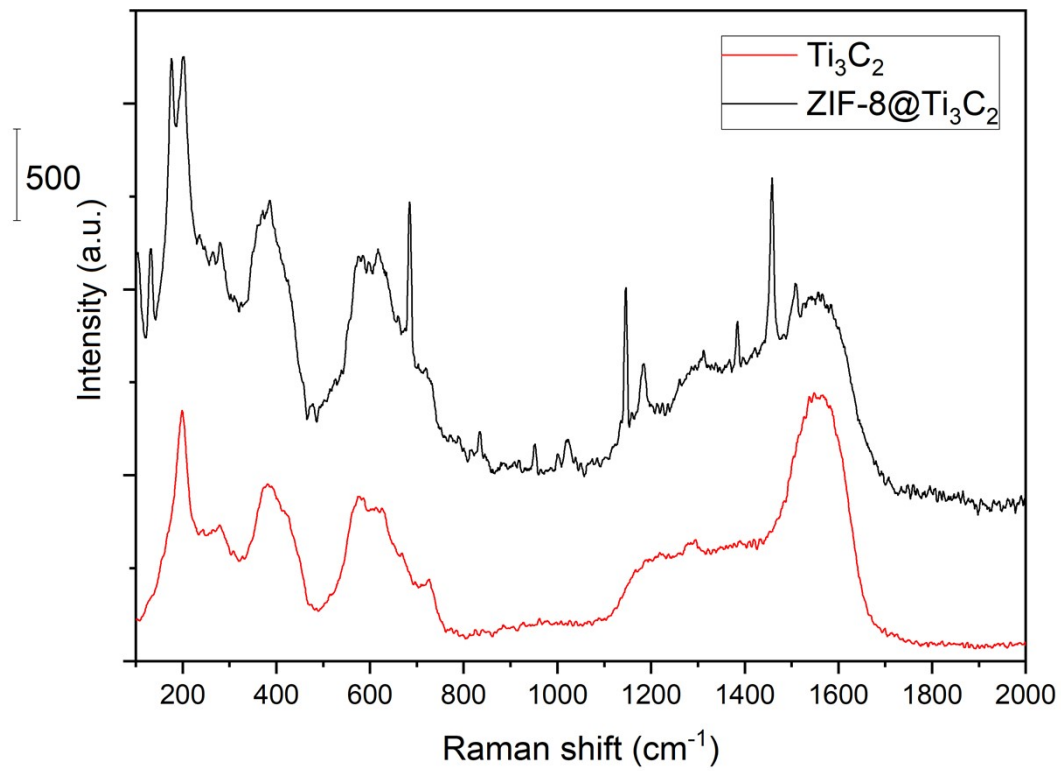
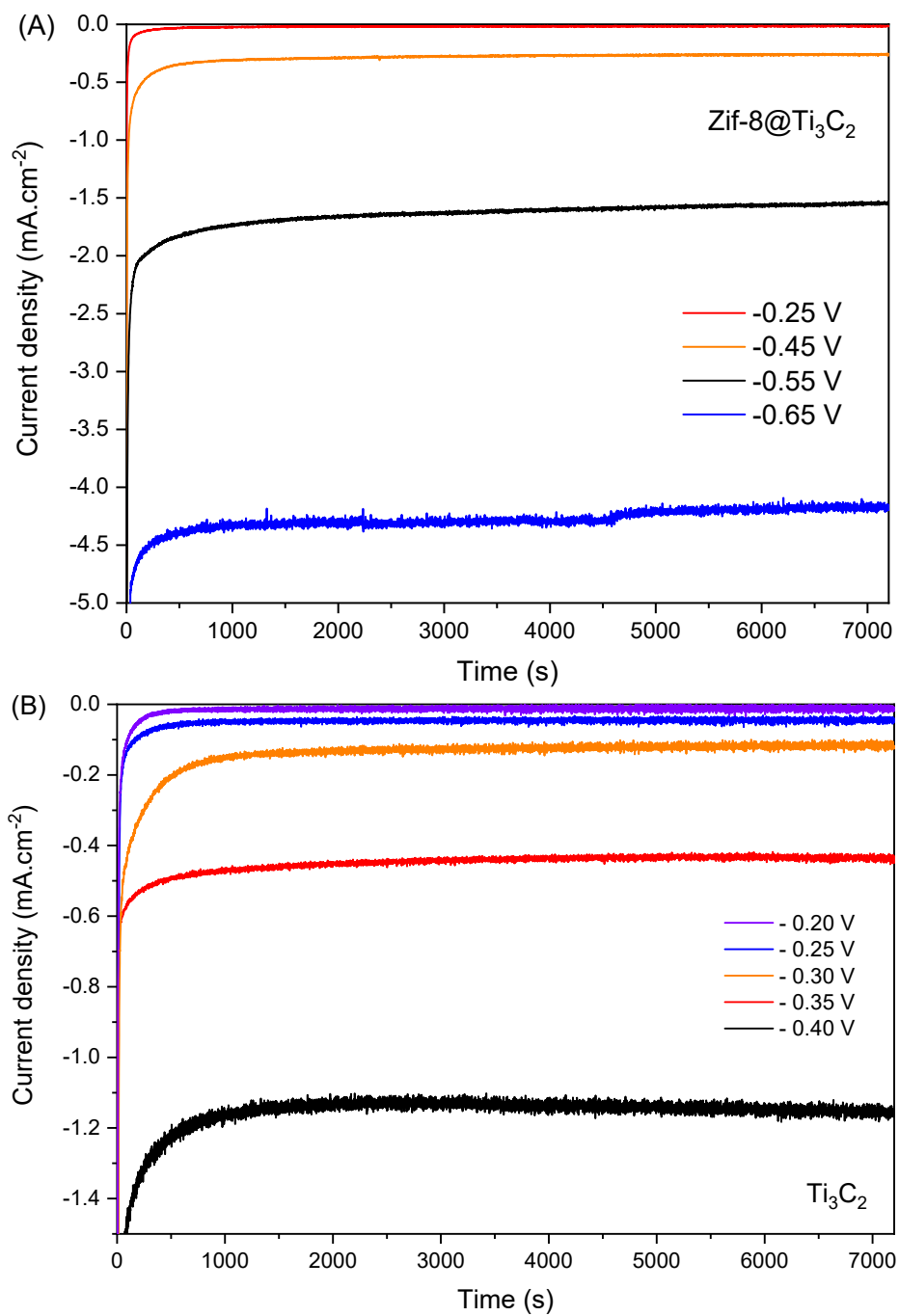**Figure S2.** Raman spectra of Ti_3C_2 and $Zif-8@Ti_3C_2$ materials.

Figure S3. Cyclic voltammograms of Ti_3C_2 and Zif-8@Ti_3C_2 at high potential.

Figure S4. Cyclic voltammogram curves obtained in 0.1 M NaOH of (A) Ti_3C_2 and (B) Zif-8@Ti_3C_2 catalysts at different scan rates; Evolution of Δj vs. scan rate for Cdl estimation of (C) Ti_3C_2 and (D) Zif-8@Ti_3C_2 catalysts.

Figure S5. Chronoamperometry curves for electrolysis at different cathode potentials for Zif-8@Ti$_3$C$_2$ (A) and for Ti$_3$C$_2$ (B) catalysts.
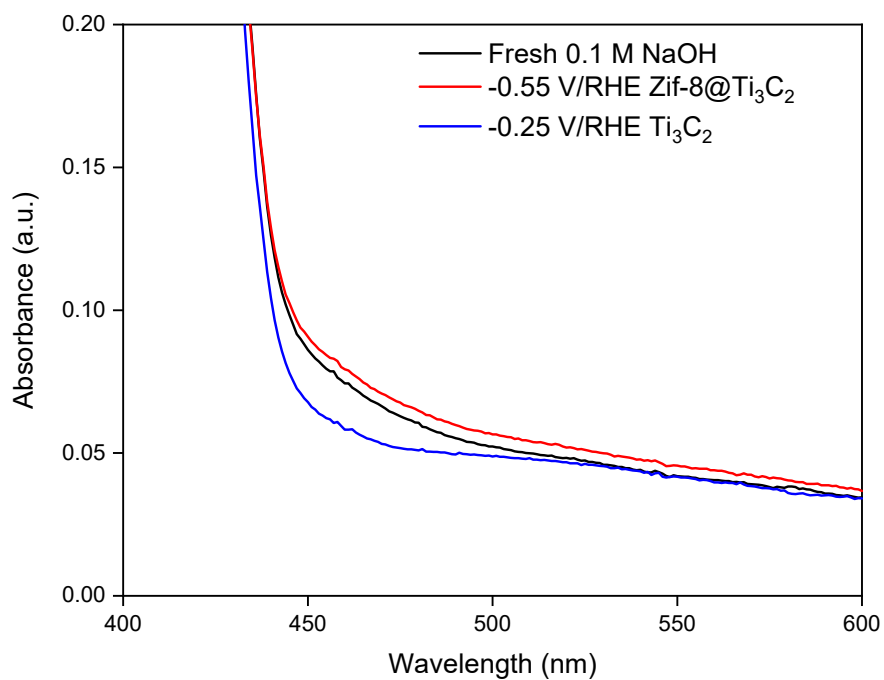
Figure S6. (A) Determination of hydrazine by UV-VIS analysis of electrolyte after 2 h of reaction at optimized potentials for Zif-8@Ti$_3$C$_2$ and Ti$_3$C$_2$ electrocatalysts in comparison to fresh 0.1 M NaOH.
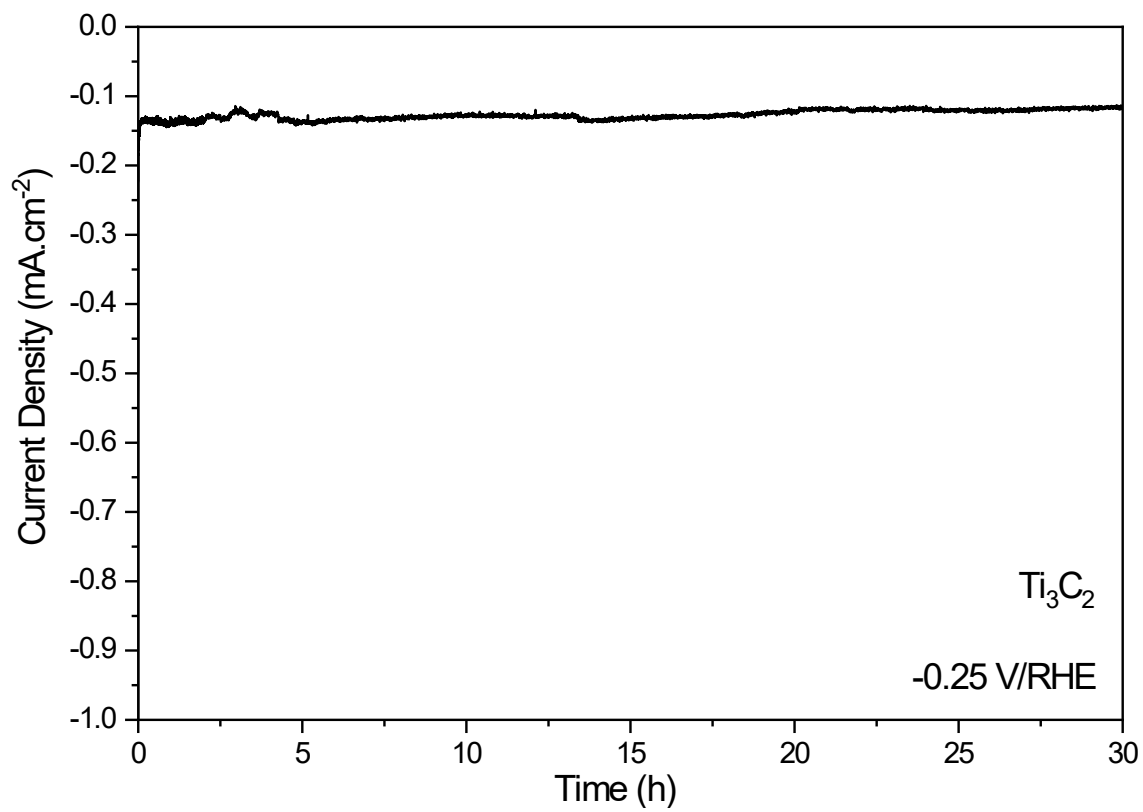
Figure S7. Chronoamperometric analysis of Ti_3C_2 at -0.25V vs RHE during 30h.
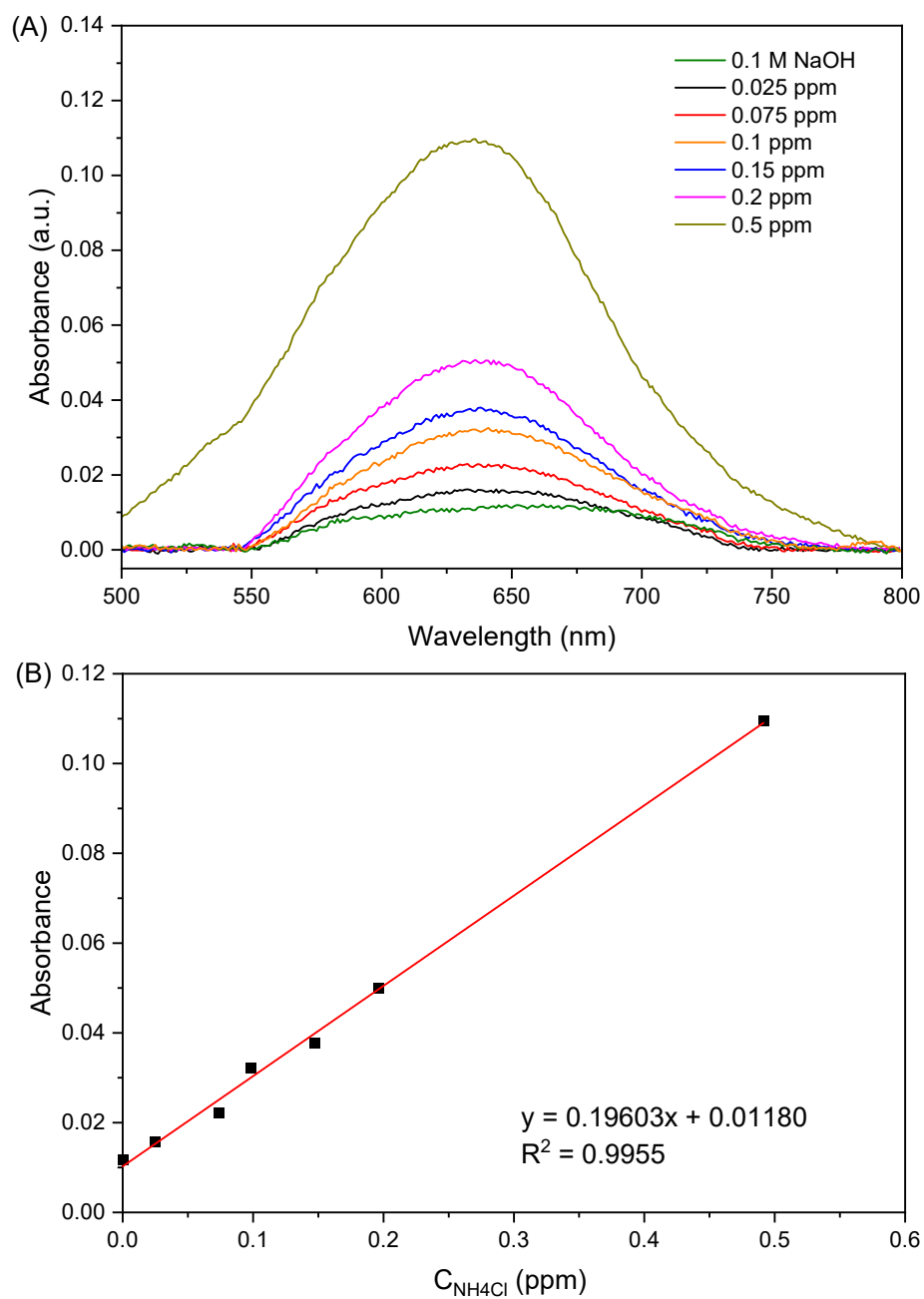
Figure S8. (A) UV-VIS spectra of standard samples at different concentrations of NH_4Cl. (B) Linear fitting for the absorbance vs. NH_4Cl concentration.

References

(1) Benchakar, M.; Loupias, L.; Garnero, C.; Bilyk, T.; Morais, C.; Canaff, C.; Guignard, N.; Morisset, S.; Pazniak, H.; Hurand, S.; Chartier, P.; Pacaud, J.; Mauchamp, V.; Barsoum, M. W.; Habrioux, A.; Célérier, S. One MAX Phase, Different MXenes: A Guideline to Understand the Crucial Role of Etching Conditions on Ti3C2Tx Surface Chemistry. *Appl. Surf. Sci.* **2020**, *530*, 147209. https://doi.org/10.1016/j.apsusc.2020.147209.

(2) Watt, G. W.; Chrisp, J. D. Spectrophotometric Method for Determination of Hydrazine. *Anal. Chem.* **1952**, *24* (12), 2006–2008. https://doi.org/10.1021/ac60072a044.