

Electronic Supplementary Information

MIL-101(Fe)@Nb₂C MXene for efficient electrocatalytic ammonia production: an experimental and theoretical study

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Preparation of Nb₂C

Typically, 1 g of Nb₂AlC fabricated by the NaCl-assisted method³⁶ was slowly added to 30 mL HF solution (40 wt%, volume percentage), followed by a continuous stirring for 24 h at room temperature. After that, the sample was centrifuged and washed repeatedly to pH > 6, and then vacuum-dried at 60 °C for 12 h.

Preparation of MIL-101(Fe)

In brief, 2 mmol FeCl₃·6H₂O and 1 mmol H₂BDC were dissolved into the mixture of 10 mL DMF under vigorous stirring, and subsequently heated at 120 °C for 20 h. After repeated centrifugation and washing with the DMF water and MeOH, the precipitation was freeze-dried to obtain MIL-101(Fe).

Synthesis of MIL-101(Fe)@Nb₂C MXene

The MIL-101(Fe) was loaded onto Nb₂C MXene via a simple self-assembly approach. For instance, 150 mg of Nb₂C MXene and 100 mg of **MIL-101(Fe)** were sequentially dispersed into 100 mL DI water under Ar bubbling. Then the MIL-101(Fe)@Nb₂C can be synthesized through centrifuging and freeze-drying above mixture followed by an annealing treatment at 400 °C for 30 min.

Catalyst characterization

XRD with a scanning rate of 5 degrees min⁻¹ was conducted to characterize the phase composition and crystal structure of S-NPC at accelerating voltage of 35 kV and tube current of 25 mA, respectively. XPS was used to determine the chemical composition and valence of the catalyst. The surface morphology of S-NPC was observed using SEM (Nova Nano SEM

450). Moreover, the nano-structural characteristic and elemental distribution of MIL(101)@Nb₂C MXene were analyzed by the TEM technique.

Electrochemical measurement

Electrocatalytic performance of S-NPC was evaluated using the CHI760E electrochemical workstation (Shanghai Chenhua) in a three-electrode system with glassy carbon (effective area 0.196 cm²), Ag/AgCl, and platinum wire as the working, reference, and auxiliary electrodes, respectively. The electrolyte was 0.1 M KOH aqueous solution, while the preparation process of work cathode was as follows. For example, 10 mg catalyst and 30 μ L Nafion were dispersed into 1 mL isopropanol under the ultrasonic condition to obtain a uniform slurry, and then 20 μ L slurry was dropped onto the glassy carbon electrode. Before the test, the ultrapure N₂ was successively bubbled into the electrolyte for 2 h to achieve its saturation.

Calculation of NH₃ yield and FE

The indophenol blue reaction was carried out to determine NH₃ yield. Specifically, a 2 mL electrolyte was firstly extracted from the electrocatalytic NRR system. Subsequently, 2 mL of 1 M sodium hydroxide solution containing 5 wt% (weight percentage) sodium salicylate and 5 wt% sodium potassium tartrate was added to the above electrolyte, followed by adding 1 mL of 6 wt% sodium hypochlorite solution and 0.2 mL of 1 wt % sodium nitroferricyanide solution. After quiescence for 1 h at room temperature, the absorption peak ($\lambda \approx 655$ nm) of generated NH₄⁺ was detected with a UV-vis spectrophotometer.

The NH₃ yield (*Yield*) was calculated by the following equation:

$$Yield = \frac{c \times V}{t \times A} \quad (1)$$

where c is the NH₄⁺ concentration, V is the electrolyte volume, t is the NRR time, and A is the effective area of electrode.

The FE value of NRR was calculated according to the following equation:

$$FE = \frac{3F \times c \times V}{17Q} \quad (2)$$

The FE value of NO_3^- -RR was calculated according to the following equation:

$$FE = \frac{8F \times c \times V}{17Q} \quad (3)$$

where F is the Faradic constant, and Q is the total quantity of electric charge.

A series of was used to calibrate the concentration–absorbance curve, giving the following linear fitting curve: $y = 0.37127x + 0.00336$, $R^2 = 0.999$

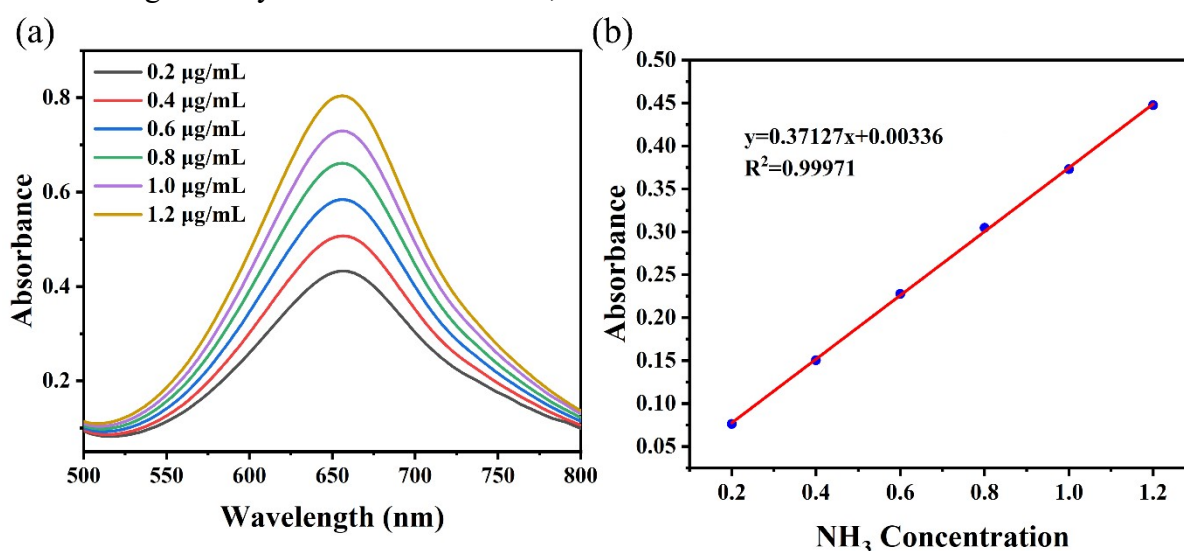


Figure S1 (a) UV-vis spectra for the known concentration of NH_4^+ solutions, and (b) the corresponding absorbance vs. concentration plot.

Calculation details

DFT calculations were performed using a Cambridge sequential total energy package (CASTEP). The projector augmented wave pseudopotentials and the generalized gradient approximation parameterized by Perdew–Burke–Ernzerhof (GGA-PBE) for exchange–correlation functional, and the core electrons were described by the projector-augmented wave (PAW) technology. DFT-D method was employed to calculate the van der Waals (vdW)

interactions, with an energy cut-off of 500 eV. The frontier molecular orbitals were studied by the Dmol³ module.

A series of standard N₂H₄ solutions was used to calibrate the concentration–absorbance curve, giving the following linear fitting curve: $y = 1.05682x + 0.04896$, $R^2 = 0.999$.

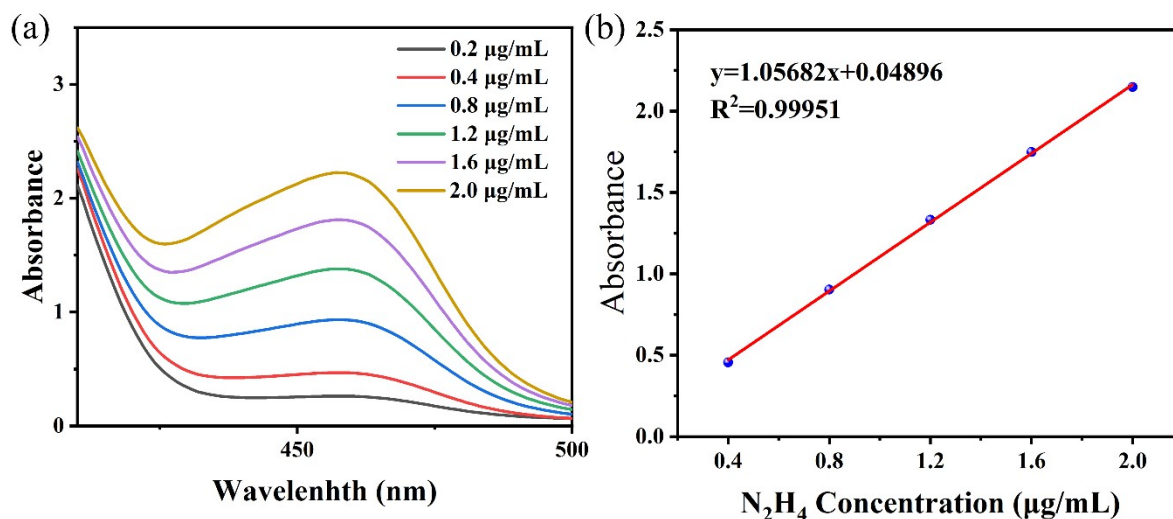


Figure S2 (a) UV-vis spectra for the known concentration of N₂H₄ solutions, and (b) the corresponding absorbance vs. concentration plot.

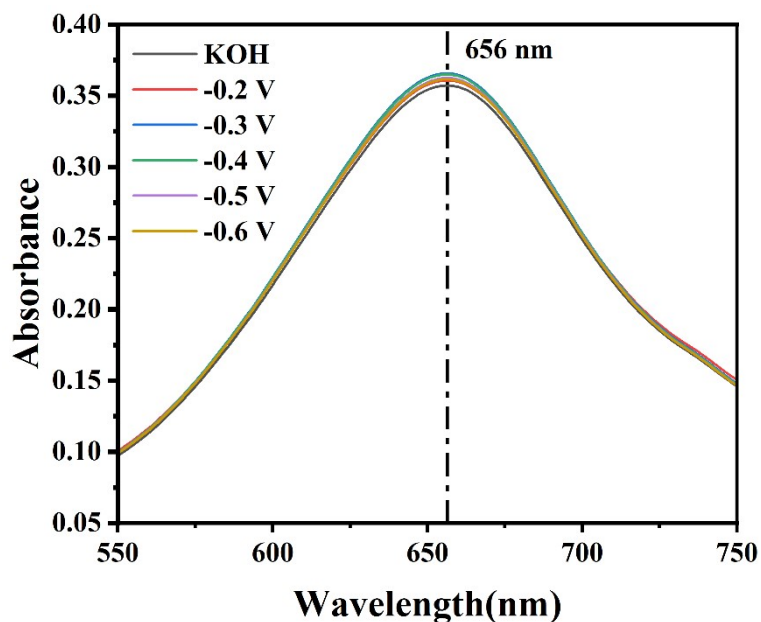


Figure S3 UV-vis spectra for NH₃ in the NRR electrolyte at different potentials.

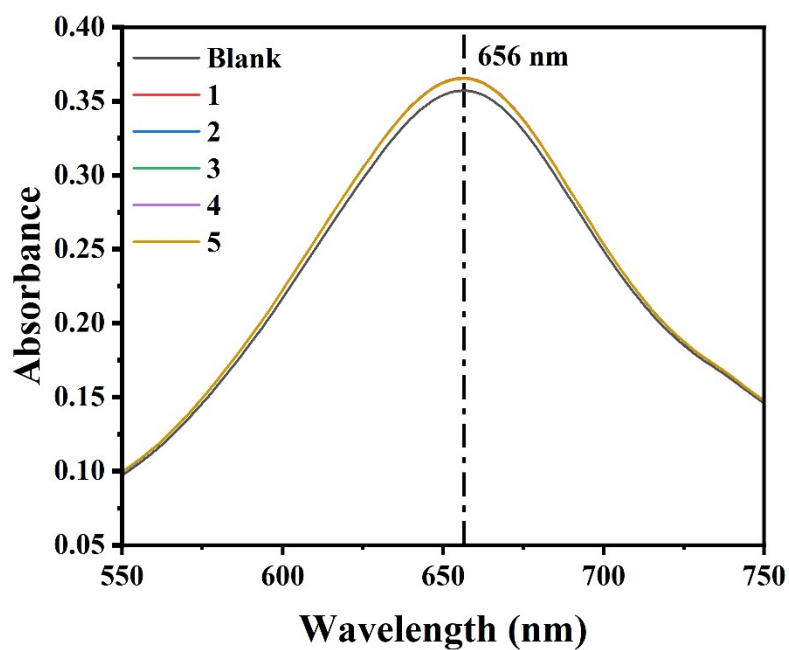


Figure S4 UV-vis spectra for NH_4^+ in the NRR electrolyte after cycling test.

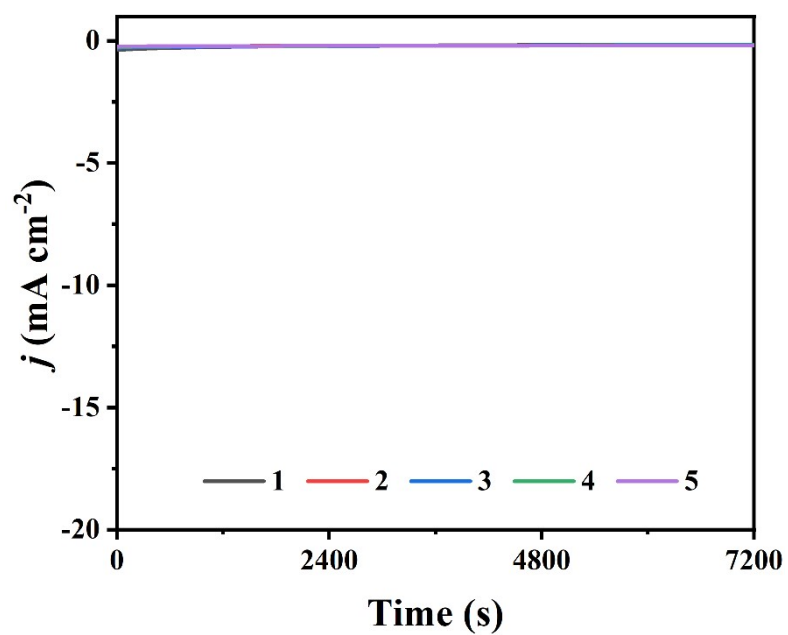


Figure S5 Chronoamperometry curves of MIL-101(Fe)@ Nb_2C MXene after four cycles in 0.1 M KOH solution at -0.3 V vs. RHE.

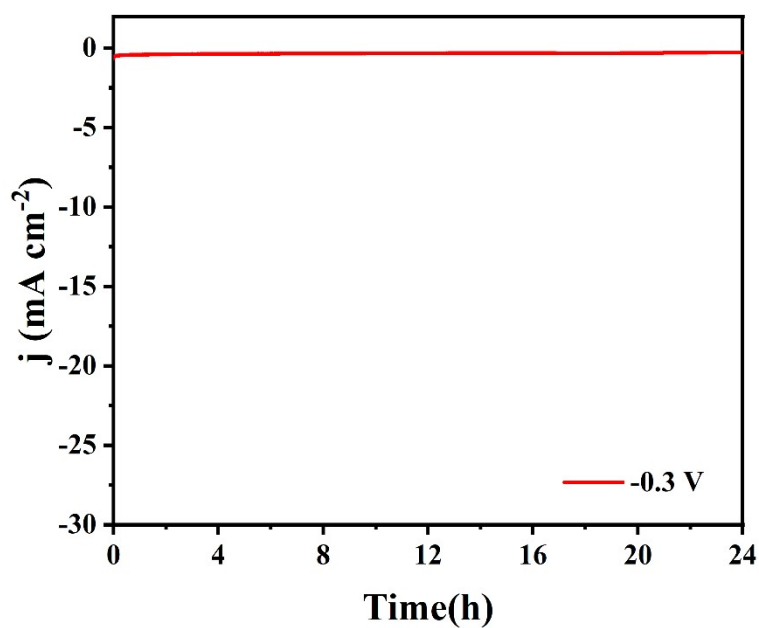


Figure S6 chronoamperometry plot of MIL-101(Fe)@Nb₂C at -0.3 V vs. RHE.

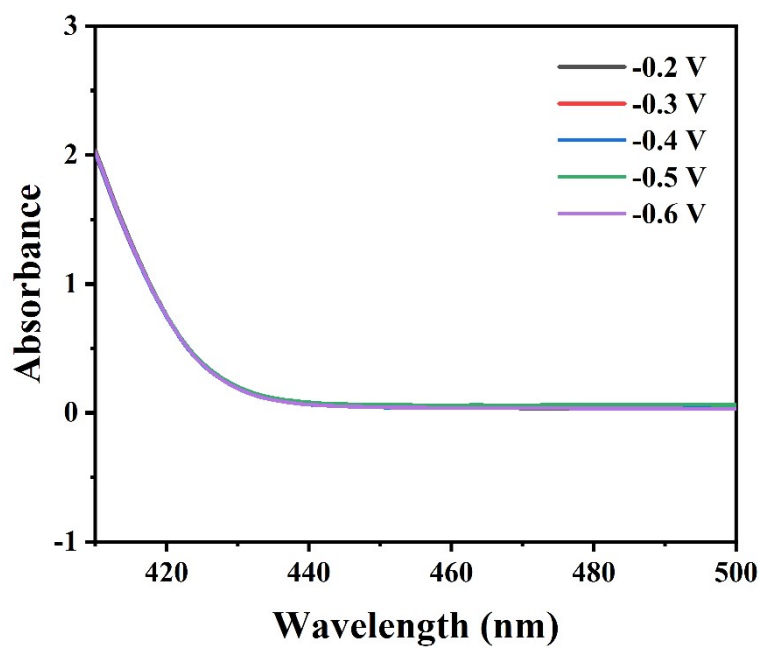


Figure S7 UV-vis spectra for N₂H₄ in the NRR electrolyte at different potentials.

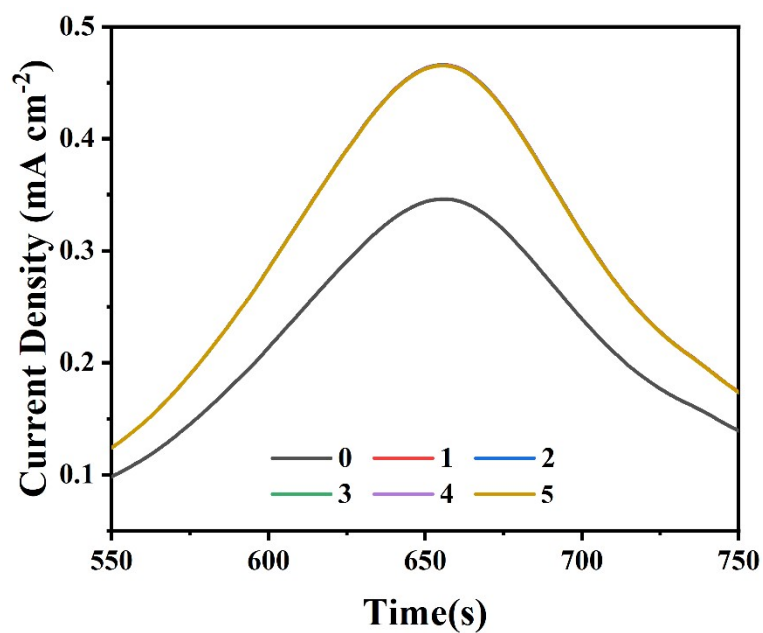


Figure S8 UV-vis spectra for NH_4^+ in the NO_3RR electrolyte after cycling test.

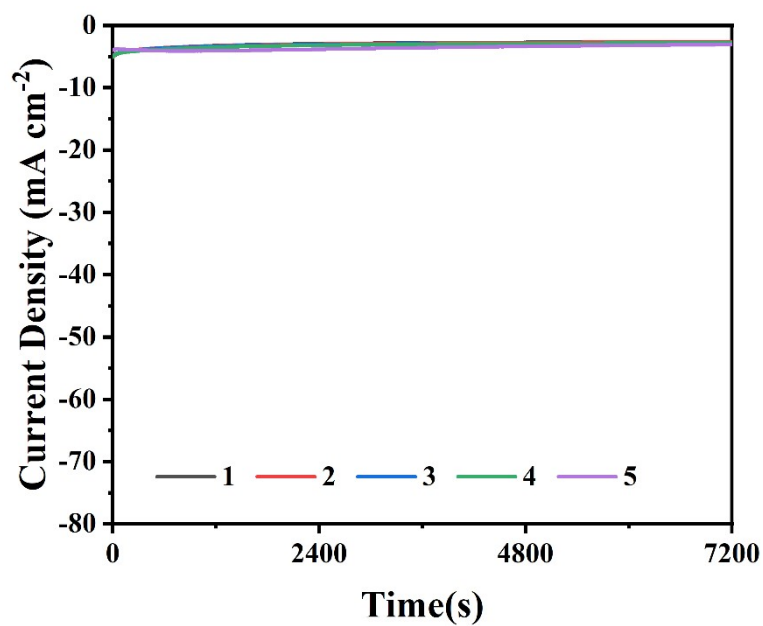


Figure S9 Chronoamperometry curves of MIL-101(Fe)@ Nb_2C MXene in the NO_3RR after four cycles in 0.1 M KOH solution at -0.3 V vs. RHE.

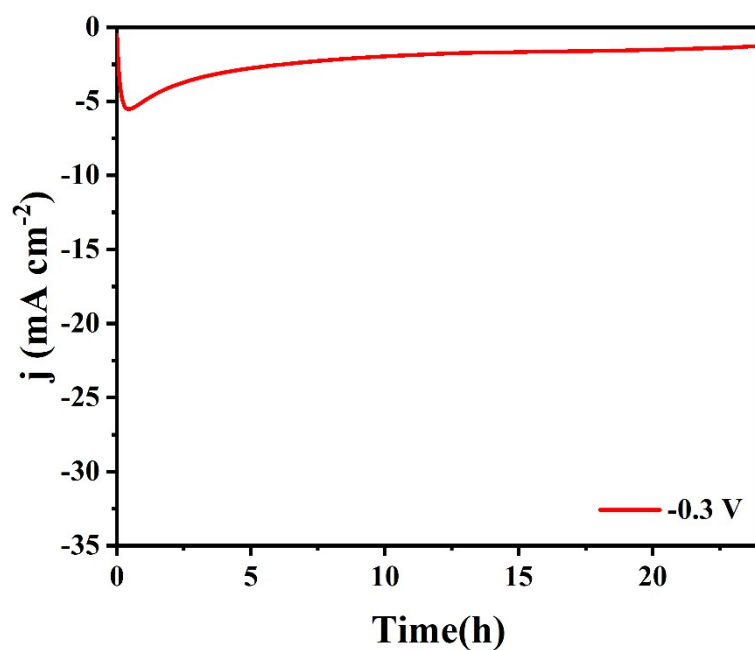


Figure S10 chronoamperometry plot of MIL-101(Fe)@Nb₂C at -0.3 V vs. RHE in the NO₃RR.

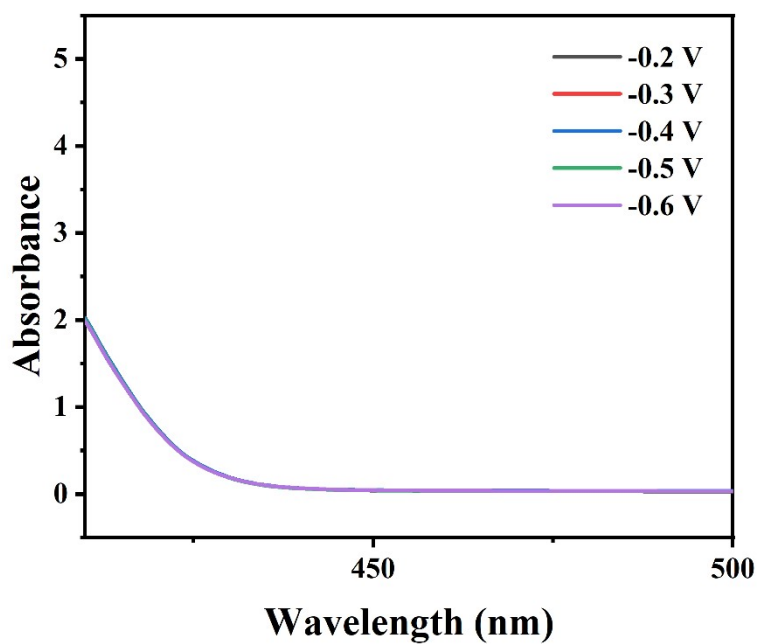


Figure S11 UV-vis spectra for N₂H₄ in the NO₃RR electrolyte at different potentials.

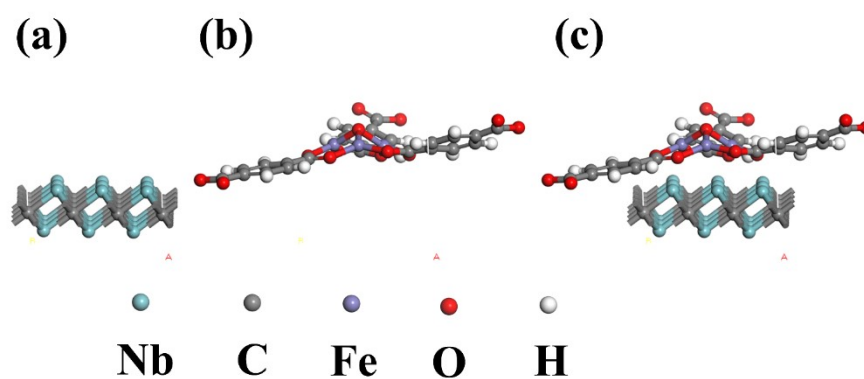


Figure S12 Theoretical structures of catalysts, (a) Nb_2C ; (b) MIL-101(Fe); (c) MIL-101(Fe)- Nb_2C

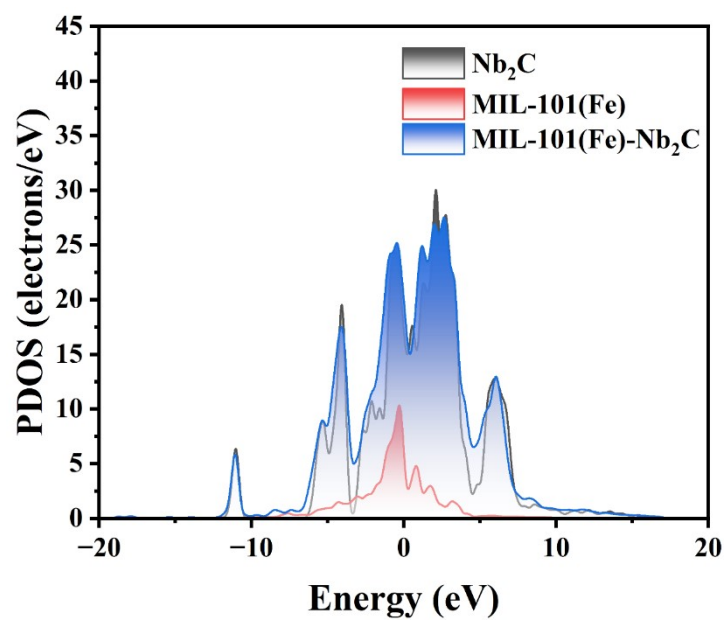


Figure S13 d-PDOS of Nb_2C , MIL-101(Fe), and MIL-101(Fe)- Nb_2C