

Electronic Supplementary Information

The synthesis of 3D organic-inorganic hybrid heterojunctions of g-C₃N₄ nanoneedles@Ti₃C₂ MXene with superior photocatalytic H₂ evolution

Fang He,* Yuying Mao, Yan Hu, Jingyang Wu, Enqi Xie, Zhenxing Wang, and
Yuexiang Li*

*School of Chemistry and Chemical Engineering, Nanchang University, Nanchang,
330031, P.R. China*

AUTHOR INFORMATION

Corresponding Author

*E-mail: hefang1009@163.com (F. He); liyx@ncu.edu.cn (Y. Li)

Experimental Section

Materials.

Potassium chloride (KCl), sodium chloride (NaCl), lithium chloride (LiCl), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), melamine (MA, $\text{C}_3\text{H}_6\text{N}_6$), Ti_3AlC_2 (MAX) were obtained from Aladdin (China). Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and triethanolamine (TEOA) were acquired from Chemical Reagent Co. of Sinopharm. The chemicals practiced in the experiments were not further purified.

Synthesis.

Synthesis of pristine g- C_3N_4

Pristine g- C_3N_4 was obtained by thermal condensation of melamine at 550°C for 2 h and finely ground to powder.

Synthesis of Ti_3C_2 MXene sheets

Few layer Ti_3C_2 MXene sheets was prepared by molten salt etching of Ti_3AlC_2 . Detailedly, Ti_3AlC_2 (1 g), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3.0678 g), NaCl (0.6006 g) and KCl (0.7662 g) were quickly ground in the morta to form mixture and then transferred to the 25 ml crucible. The mixture was calcined at 700°C in N_2 atmosphere for 7 h, and then was washed to remove salts and dried with 2~3 L ultra-pure water. The Ti_3C_2 MXene needs to be soaked in 0.1 mol L^{-1} sodium persulfate (APS) solution for 12 h, then drained and washed, and dried at 60°C for 12 h before use.

Synthesis of MCS-x

A certain content of Ti_3C_2 MXene was first ultrasounded for 2 h to disperse evenly,

and 0.45 g of g-C₃N₄ was added and stirred for 4 h. And then washed with deionized water, dry at 60 °C to obtain Ti₃C₂ MXene/g-C₃N₄ mixed powder. Afterwards, the Ti₃C₂ MXene/g-C₃N₄ powder mixed with salts of LiCl and KCl to grind evenly. The mass of KCl was 2.25 times than that of the mixed Ti₃C₂ MXene/g-C₃N₄ powder, and the mass of LiCl was 2.75 times than that of the mixed Ti₃C₂ MXene/g-C₃N₄ powder. The evenly ground Ti₃C₂ MXene/g-C₃N₄ with LiCl/KCl powder was transferred to a 25 ml ceramic crucible and heated at 550 °C for 2 h under N₂ protection. After cooling to room temperature, the sample was soaked in hot water, drained and washed, and dried at 60 °C for 12 h. The obtained sample was named as MCS-x (x= 0, 8, 13, 18, 23 mg Ti₃C₂ MXene in 450 mg of g-C₃N₄), M stands for Ti₃C₂ MXene, C stands for g-C₃N₄, S stands for molten salt treatment.

Characterization.

The crystal structure and phase were identified by powder X-ray diffractometer (XD-2/3), X-ray photoelectron spectrometer (Thermo ESCALAB 250Xi). The morphology of the samples was studied by cold field emission scanning electron microscopy (Regulus 8100) and field emission transmission electron microscopy (Talos F200X). N₂ adsorption desorption isotherms were obtained on the equipment of Micromeritics ASAP 2460. Light absorption was measured by UV-vis spectrophotometer (UV-3310); Fluorescence spectrophotometer (F-7000) was used to measure fluorescence intensity. Carrier lifetime was measured by stable transient fluorescence spectrometer (FLS1000).

Electrochemical and Photochemical Measurements.

Electrochemical Impedance Spectroscopy (EIS) was performed on the IVIUMSTAT electrochemical workstation. Working electrode was prepared below: 2 mg sample, 490 μL deionized water, 490 μL anhydrous ethanol, and 10 μL Nafion were added into a 10 ml quartz bottle. The samples were dispersed uniformly by ultrasound for 2 h. 10 μL ultrasonic homogeneous liquid was dropped onto the $1 \times 2 \text{ cm}^2$ area of the $1 \times 3 \text{ cm}^2$ FTO conductive glass. After drying at room temperature for 6 h. The dry FTO conductive glass using as a working electrode. The counter electrode is a platinum wire electrode, reference electrode is Ag/AgCl electrode. The electrolyte is 0.1 mol L^{-1} PBS solution. The test conditions: the extra voltage is 0 eV, and the frequency is 0.1 Hz \sim 100000 Hz.

Mott-schottky measurement was performed at the IVIUMSTAT electrochemical workstation. The preparation method of working electrode is the same as that of EIS. Platinum wire used as electrode, Hg/HgO electrode used as reference electrode. The electrolyte is 1 mol L^{-1} KOH solution. The frequency is 1000 Hz and the scanning speed is 10 mV/s.

Photocatalytic H₂ evolution Measurements.

The photocatalytic hydrogen evolution experiment was carried out in a closed quartz container, using 300W Xenon lamp (PLS-SXE300, $\lambda > 420 \text{ nm}$) as the light source with a light intensity of 160 mW cm^{-2} . In general, 50 mg photocatalyst was ultrasonic dispersed in 100 ml aqueous solution containing 10 vol% triethanolamine (TEOA) for 5 min with a platinum load of 3 wt%, and kept stirring continuously. The hydrogen

evolution performance was monitored by gas chromatograph (GC1690). UV LED light source irradiation machine (UVEC-4II) measured the apparent quantum efficiency at different wavelengths.

The apparent quantum efficiency (AQE) of MCS-13 was consistent with the photocatalytic hydrogen production reaction conditions. First, 50 mg of catalyst was treated with loading platinum by Xe lamp with same element. The flask was removed oxygen with N₂ blowing 30 min before radiation every time. The light source was measure by the monochromatic LED lamp (several monochromatic LED lamps were used). The effective area of the irradiation was about 0.80 cm².

The AQE can be calculated by the following equation:

$$\text{AQE [\%]} = \frac{2 \times \text{number of hydrogen molecules}}{\text{number of incident photons}} \times 100\%$$

Density function theory (DFT) calculations: The DFT calculations were implemented using the Vienna Ab initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) generalized gradient approach (GGA) was used to describe the exchange-correlation potential. The projector augmented wave (PAW) was used to complete the electron-ion interactions. The DFT calculations were carried out using a cut-off energy of 400 eV, and using a 1×1×1 k-point grid to sample the Brillouin zone. The force and energy convergence criteria of the self-consistent iteration were set as 0.05 eV Å⁻¹ and 10⁻⁴ eV, respectively. Van der Waals (vdW) interactions were describe by DFT-D3 method.

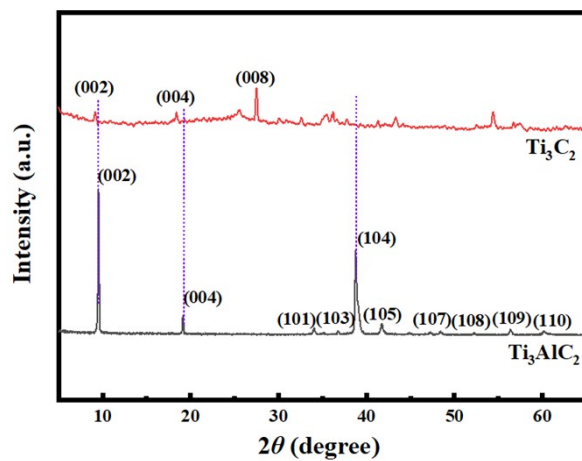


Fig. S1 XRD patterns of Ti_3AlC_2 and Ti_3C_2 MXene.

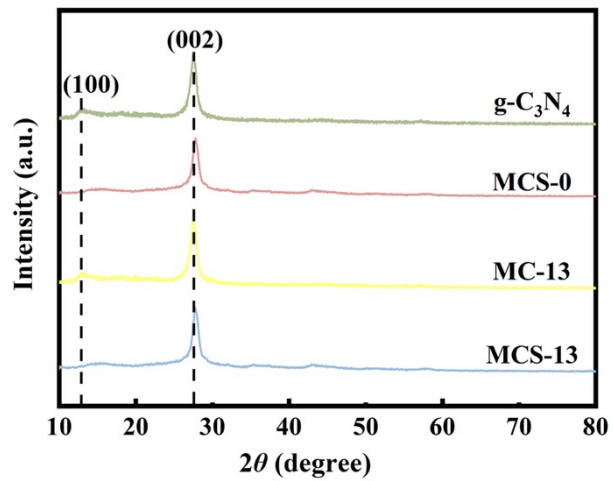


Fig. S2 XRD patterns of g-C₃N₄, MC-13, MCS-0 and MCS-13.

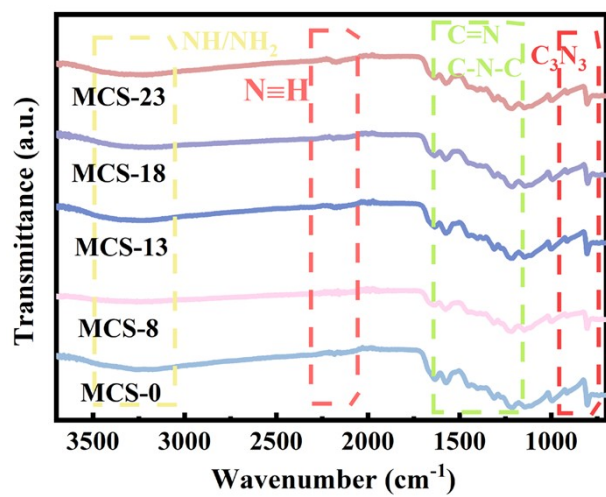


Fig. S3 FT-IR spectra for MCS-x composites with different content of Ti₃C₂ MXene.

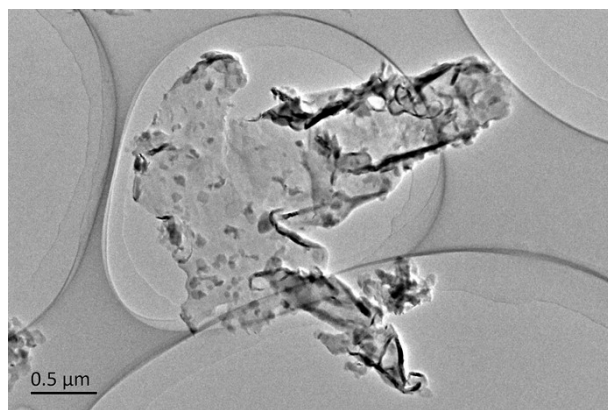


Fig. S4 TEM image of pristine g-C₃N₄.

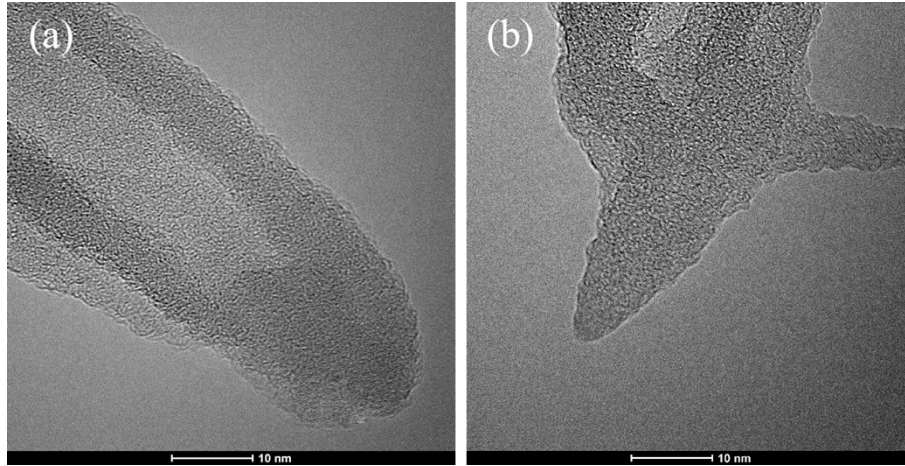


Fig. S5 High-resolution TEM images of g-C₃N₄ nanorods (a) and nanoneedles (b).

The possible mechanism of the morphology transition from g-C₃N₄ nanorods to nanoneedles is as follows: Pristine g-C₃N₄ shows layered structure. When treated pristine layered sheet g-C₃N₄ with molten salt (LiCl-KCl), the g-C₃N₄ would be covered by the melted alkali metal salts with cubic structures acting as templates to facilitate the morphology from layered sheets to transfer nanorods; furthermore, the high-temperature molten salt (LiCl-KCl) fluid promote mass transfer and the reconstruction. As a result, after removing the mixed salts, the freestanding g-C₃N₄ nanorods are obtained.

Whereas, after the introduction of Ti₃C₂ MXene sheets into layered g-C₃N₄ by ultrasonic dispersion and stirring to form Ti₃C₂ MXene/g-C₃N₄ heterojunction. Further treating Ti₃C₂ MXene/g-C₃N₄ with molten salt (LiCl-KCl), the melted alkali metal salts with cubic structure will first act as templates to facilitate the morphology of g-C₃N₄ from layered sheets to transfer nanorods; and the presence of Ti₃C₂ MXene sheets acting as supporting materials to guide the formation of ordered standing g-C₃N₄ nanorods. Moreover, the high-temperature molten salt (LiCl-KCl) fluid will further lead the standing g-C₃N₄ nanorods to from nanoneedles due to the effect of the gravity.

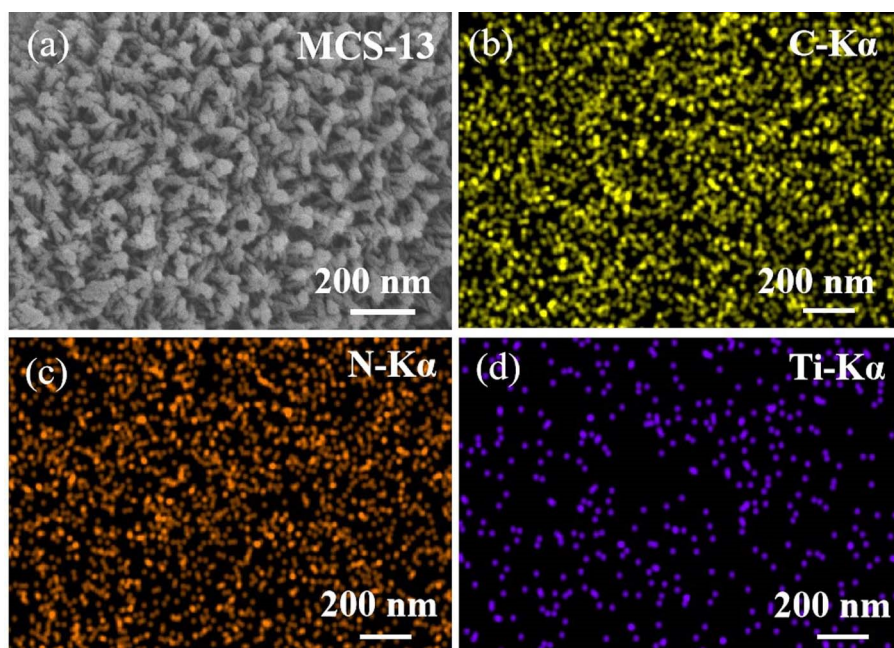


Fig. S6 (a) SEM image of MCS-13 with the corresponding element mapping (b-d) for C, N, and Ti.

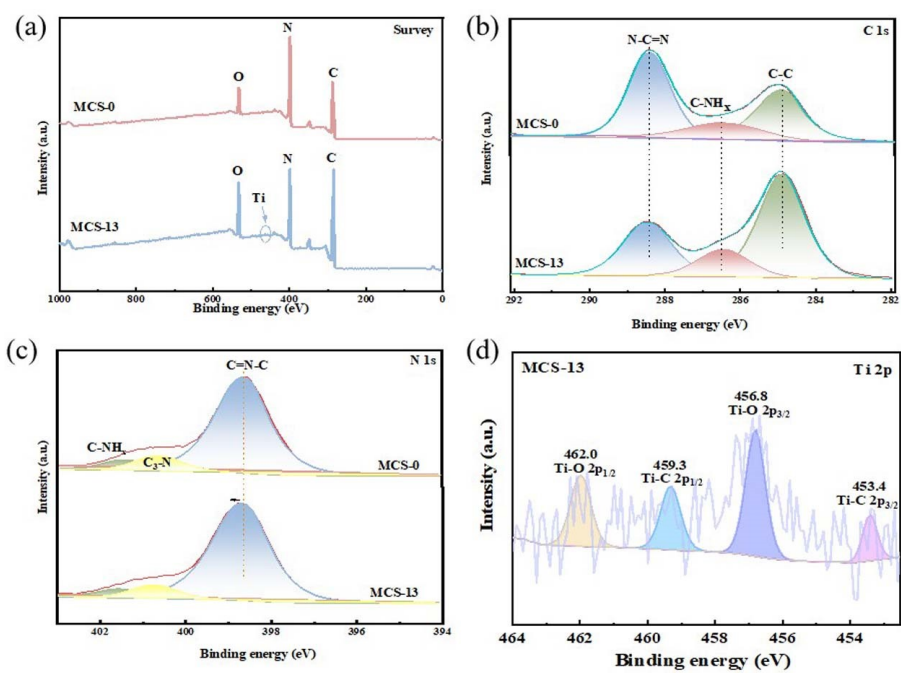


Fig. S7 (a) XPS survey spectra, (b) C 1s and (c) N 1s XPS spectra for MCS-0 and MCS-13, (d) Ti 2p XPS spectra for MCS-13.

Table S1 Elemental composition in MCS-0 and MCS-13 estimated from XPS spectra.

Sample	C(%)	N(%)	C/N
MCS-0	54.7	45.2	1.21
MCS-13	74.6	25.4	2.94

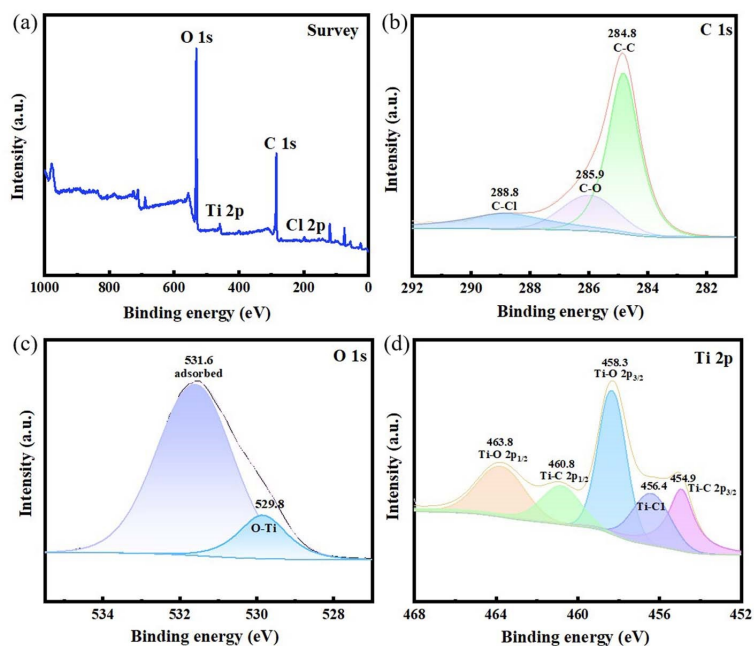


Fig. S8 XPS survey spectrum (a), C 1s (b), O 1s (c) and (c) Ti 2p XPS spectra for Ti_3C_2 MXene.

There are C, O, Ti and Cl elements in the XPS survey spectrum of Ti_3C_2 MXene. The C 1s spectrum of Ti_3C_2 MXene presents three characteristic peaks at 284.8, 285.9 and 288.8 eV, which are attributed to the C-C, C-O and C-Cl, respectively [1]. There are two characteristic peaks at 529.8 and 531.6 eV in the O 1s spectrum of Ti_3C_2 MXene, corresponding to the O-Ti and adsorbed O, respectively [2]. The Ti 2p spectrum of Ti_3C_2 MXene are deconvoluted into five peaks, in which 454.9 and 460.8 eV can be assigned to Ti-C, 458.3 and 463.8 eV is related to Ti-O, and 456.4 eV belongs to Ti-Cl [3].

Reference:

- [1] S. Cao, B. Shen, T. Tong, J. Fu, J. Yu, *Adv. Funct. Mater.*, 2018, **28**, 1800136.
- [2] Y. Yang, Z. Zeng, G. Zeng, et.al, *Appl. Catal. B*, 2019, **258**, 117956.
- [3] M. Li, J. Lu, K. Luo, et.al, *J. Am. Chem. Soc.*, 2019, **141**, 4730–4737.

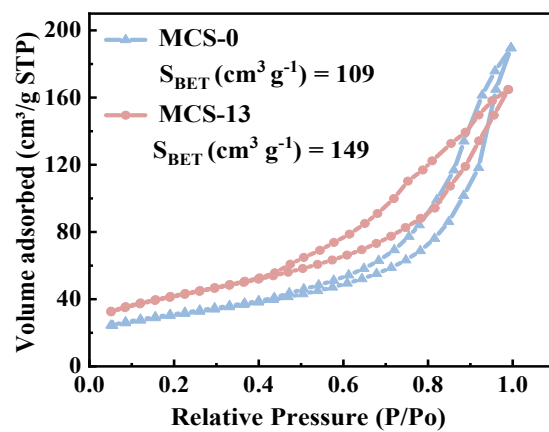


Fig. S9 The N₂ adsorption-desorption isotherms of MCS-0 and MCS-13.

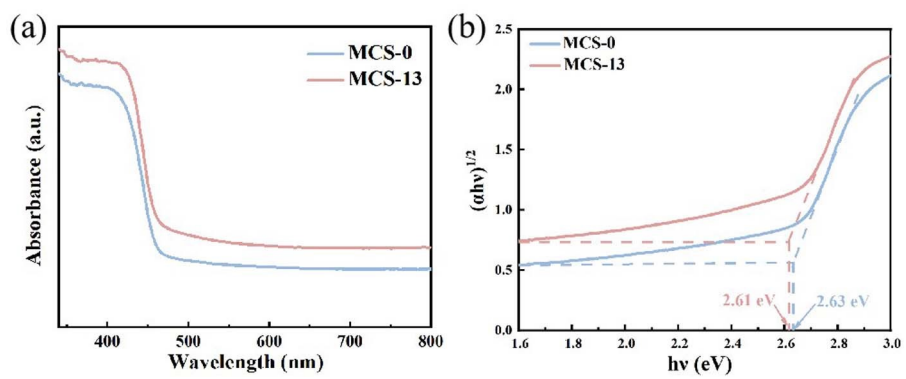


Fig. S10 The UV-vis absorption spectra (a) with the corresponding band gaps (b) for MCS-0 and MCS-13.

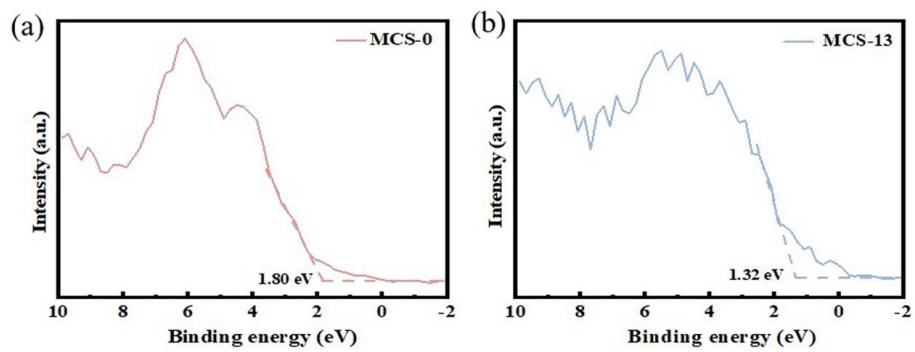


Fig. S11 VB XPS spectra of (a) MCS-0 and (b) MCS-13.

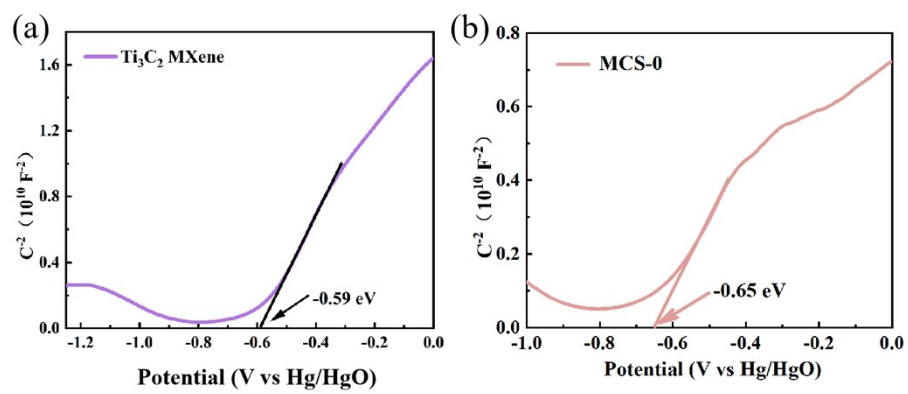


Fig. S12 Mott-Schottky plots of (a) Ti_3C_2 MXene and (b) MCS-0.

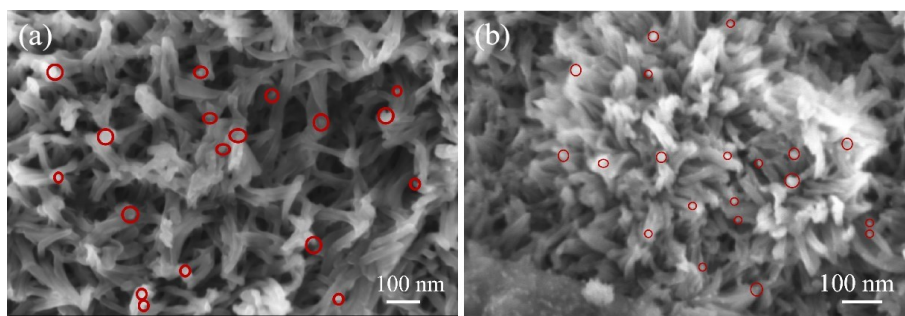


Fig. S13 SEM images of Pt nanoparticles deposited by in situ photoreduction method for (a) MCS-0 and (b) MCS-13.

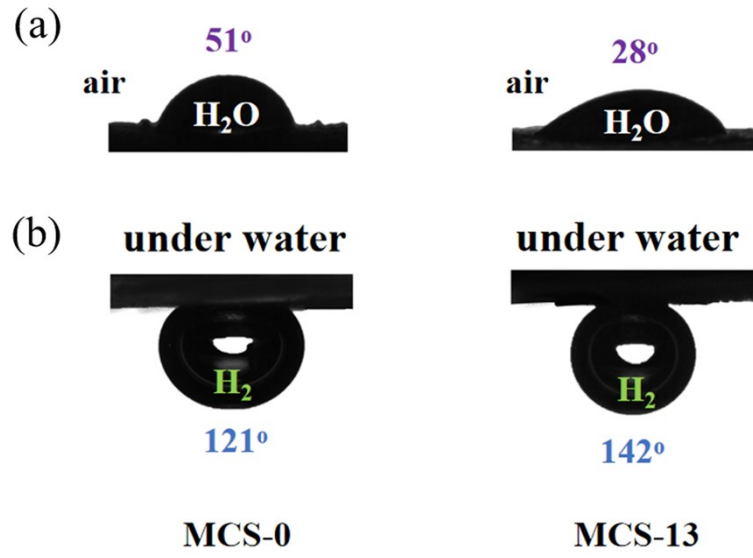


Fig. S14 (a) Water contact angles in air, and (b) H₂ bubble contact angles under water of MCS-0 and MCS-13.