

Electronic Supplementary Information

Ti₃C₂T_x MXene nanosheet-confined Pt nanoparticles efficiently catalyze dye-sensitized photocatalytic hydrogen evolution

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1. Experimental

1.1 Chemicals and materials

All chemicals were of analytical grade and used as received without further purification. Triethanolamine (TEOA) was purchased from Xilong Scientific (>99.8%). Erythrosin B (ErB) was received from Tianjin Guangfu Fine Chemical Research Institute. Ti_3AlC_2 powders were purchased from Beijing Dk Nano technology Co., Ltd. LiF was purchased from Aladdin Industrial Corporation. Graphene nanosheets (3 nm flakes) for R&D use was kindly provided by Uniregion Bio-Tech Company. g- C_3N_4 nanosheets were prepared by pyrolyzing urea at 823 K for 2 h according to our previous reports.¹ All solutions used throughout the experiments were prepared with ultrapure water (18.2 M Ω).

1.2 Preparation of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets ($\text{Ti}_3\text{C}_2\text{T}_x$ NSs)

$\text{Ti}_3\text{C}_2\text{T}_x$ NSs were synthesized according to a reported procedure.² 1 g of LiF was added into 20 mL of 6 M HCl and the solution was allowed to mix thoroughly at room temperature for a few minutes. After that, 1 g of Ti_3AlC_2 powder was slowly added to avoid initial overheating due to exothermic nature of the reaction. Then, the temperature was brought to 35 °C and the reaction allowed to proceed under continuous stirring for 24 h. The powder was repeatedly washed with DI water until almost neutral pH (≥ 6). The freshly produced powder was then bath sonicated in 100 mL of DI water for 30 min under continuous N_2 bubbling to minimize oxidation. Then, the resulted suspension solution was centrifuged at 3500 rpm for 1 h and the supernatant, a colloidal solution of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets, was collected and freezing-dried.

1.3 Characterization

X-ray diffraction (XRD) patterns were investigated with a Rigaku smartlab diffractometer with a nickel filtrated Cu $K\alpha$ radiation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a Tecnai-G2-F30 field emission transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on a Thermo Scientific Escalab-250Xi electron spectrometer using an Al $K\alpha$ X-ray source. Binding energies were referenced to the C 1s peak (set at 284.8 eV) of the sp^2 hybridized (C=C) carbon from the sample. UV-

vis absorption spectra were taken with a Thermo Scientific-Evolution 220 spectrophotometer. Photoluminescence spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer. The methylene blue (MB) adsorption method was also used to determine the specific surface area of $\text{Ti}_3\text{C}_2\text{T}_x$ NSs. Briefly, 10 mg of $\text{Ti}_3\text{C}_2\text{T}_x$ NSs was dispersed into an excessive amount of MB aqueous solution (0.1 mg mL^{-1} , 100 mL) in an airtight glass and the resulting mixture was stirred for 12 h at room temperature in the dark. After filtration, the concentration of the MB in the filtrate was measured at 665 nm using a spectrophotometer. The specific surface area of the $\text{Ti}_3\text{C}_2\text{T}_x$ NSs was determined based on the adsorbed MB ($2450 \text{ m}^2 \text{ g}^{-1}$).³

1.4 Photocatalytic H_2 evolution experiments

The photocatalytic H_2 evolution experiments were performed in a sealed Pyrex reactor with a top flat quartz window for light irradiation and a silicone rubber septum was fixed on its side for sampling produced H_2 in the headspace of reaction cell. In a typical procedure, ErB (0.2 mM), $\text{Ti}_3\text{C}_2\text{T}_x$ NSs (10 mg), and calculated amount (1.3, 2.6, 5.2, 10.5, and 21.4 μM , corresponding to Pt mass loadings of 0.25, 0.5, 1, 2, and 4 wt.% on $\text{Ti}_3\text{C}_2\text{T}_x$ NSs, respectively) of H_2PtCl_6 aqueous solution were added to the reaction cell containing 100 mL of 10 vol.% TEOA aqueous solution under vigorous stirring. The pH values of the reaction solution were adjusted by addition of hydrochloric acid or sodium hydroxide. Then, the reaction solution was thoroughly degassed by repeated evacuation- N_2 filling, and finally refilled with N_2 to reach ambient pressure. After that, the reaction solution was irradiated by a 520 nm LED lamp. During the reaction, the mixture solution was continuously stirred. The amount of H_2 produced was manually taken out by a gas-tight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with a gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column, and with N_2 as carrying gas.

The monochromatic apparent quantum yield (AQY) of the H_2 evolution were measured under conditions similar to those in the above photocatalytic reaction. The photon flux of incident light was determined using a ray virtual radiation actinometer (Apogee MQ-500, a silicon ray detector, light spectrum, 389-692 nm; measurement range, 0–4000 $\mu\text{mol m}^{-2}\cdot\text{s}^{-1}$). The AQY was calculated from the ratio of the number of reacted electrons during H_2

evolution to the number of incident photons.

2. Additional data

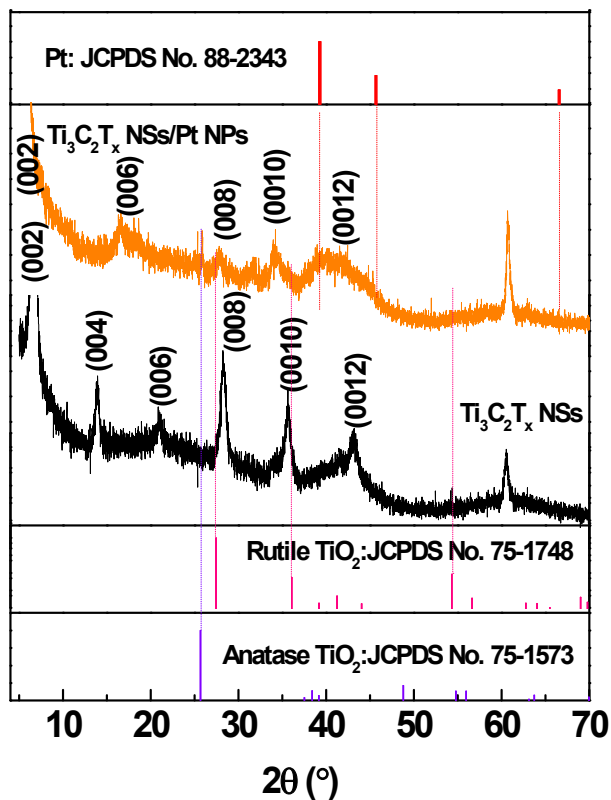


Fig. S1 Enlarged PXRD patterns of Ti₃C₂T_x NSs and Ti₃C₂T_x NSs/Pt NPs along with the standard PXRD patterns of anatase TiO₂, rutile TiO₂, and Pt.

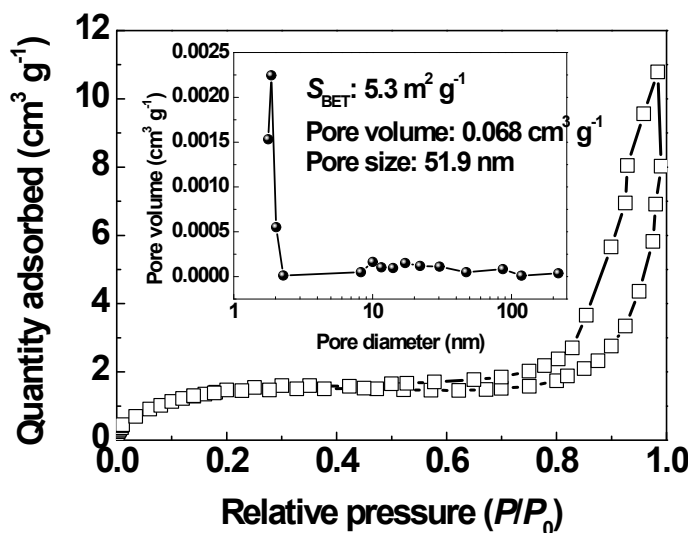


Fig. S2 N₂ adsorption-desorption isotherm and pore size distribution (inset) of Ti₃C₂T_x NSs.

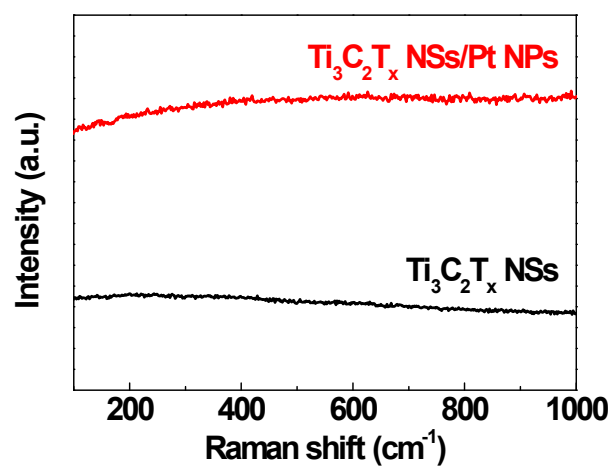


Fig. S3 Raman spectra of Ti₃C₂T_x NSs and Ti₃C₂T_x NSs/Pt NPs

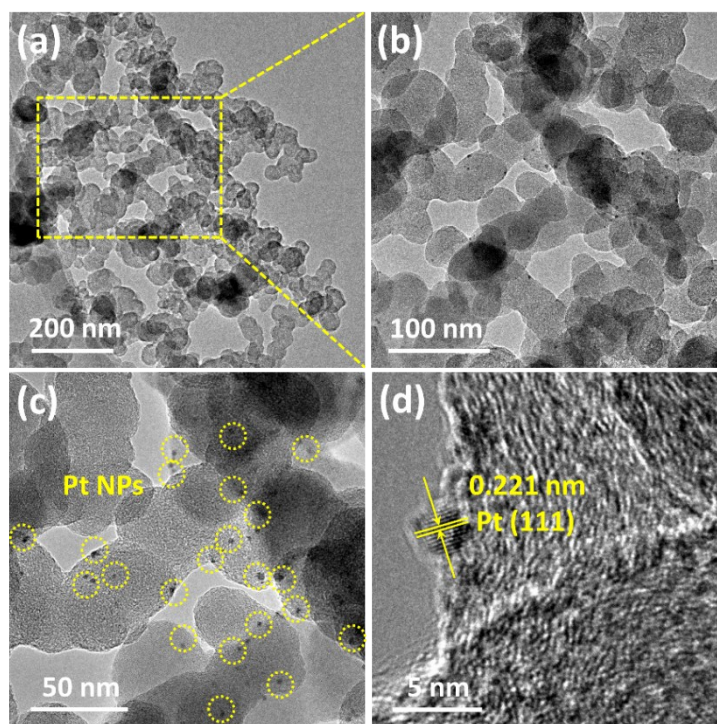


Fig. S4 TEM and HRTEM images of in situ grown free Pt NPs adsorbed on carbon black (Super P).

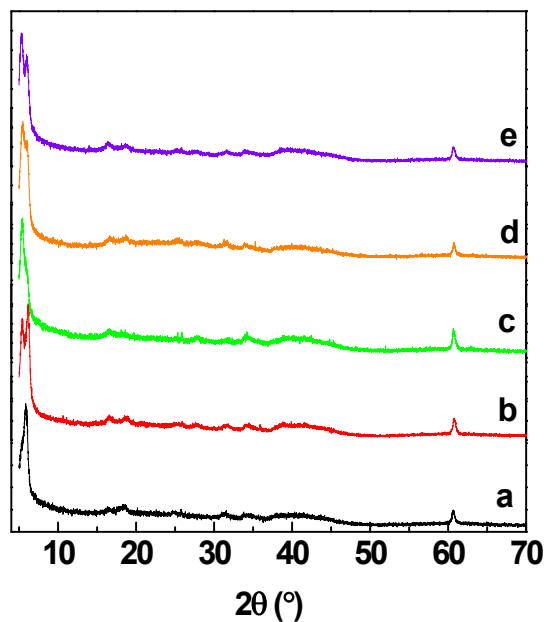


Fig. S5 XRD patterns of $\text{Ti}_3\text{C}_2\text{T}_x$ NSs/Pt NPs prepared by adding different concentrations of Pt precursor: (a) $1.3 \mu\text{M}$, (b) $2.6 \mu\text{M}$, (c) $5.2 \mu\text{M}$, (d) $10.5 \mu\text{M}$, and (e) $21.4 \mu\text{M}$.

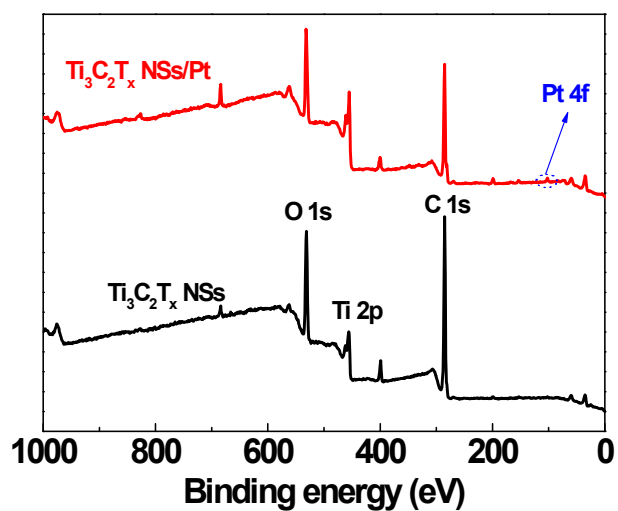


Fig. S6 XPS survey spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ NSs and $\text{Ti}_3\text{C}_2\text{T}_x$ NSs/Pt NPs prepared at a Pt concentration of $5.2 \mu\text{M}$.

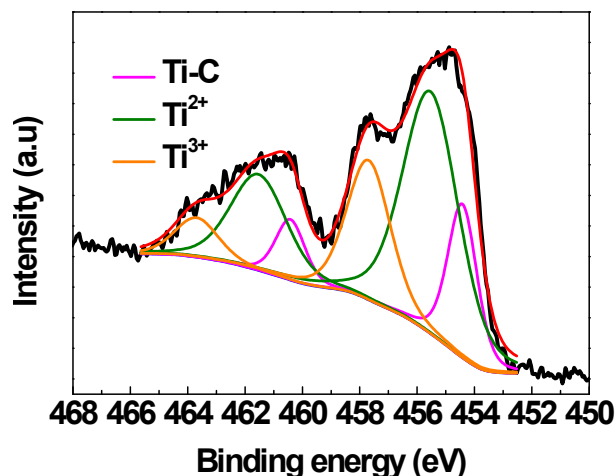


Fig. S7 XPS spectrum of Ti 2p for $\text{Ti}_3\text{C}_2\text{T}_x$ NSs.

Table S1 The fitting results of XPS spectra of Ti 2p and Pt 4f core levels for $\text{Ti}_3\text{C}_2\text{T}_x$ NSs and $\text{Ti}_3\text{C}_2\text{T}_x$ NSs/Pt NPs.

Sample	Ti-C	Ti ²⁺	Ti ³⁺	Pt	
	2p3/2 (eV) (%)	2p3/2 (eV) (%)	2p3/2 (eV) (%)	Pt ⁰ 4f7/2 (eV) (%)	Pt ^{δ+} 4f7/2 (eV) (%)
$\text{Ti}_3\text{C}_2\text{T}_x$ NSs	454.42 (19.1%)	455.53 (57.3%)	457.69 (23.6%)	/	/
$\text{Ti}_3\text{C}_2\text{T}_x$ NSs/Pt NPs	453.99 (29.1%)	455.21 (54.1%)	457.73 (16.8%)	70.32 (66.1%)	71.39 (33.9%)
$\text{Ti}_3\text{C}_2\text{T}_x$ NSs/Pt NPs after HER stability test	453.84 (34.6%)	455.10 (40.1%)	457.39 (25.3%)	70.67 (100%)	0

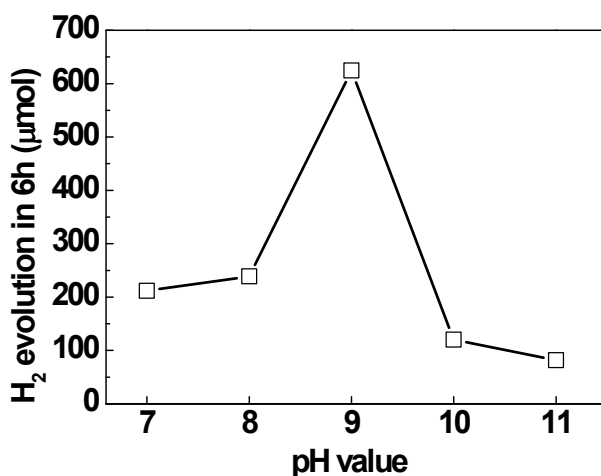


Fig. S8 Effect of the pH value on the H_2 evolution activity of $\text{Ti}_3\text{C}_2\text{T}_x$ NSs/Pt NPs catalyst in ErB-TEOA system. Reaction conditions: $\text{Ti}_3\text{C}_2\text{T}_x$ NSs, 10 mg; Pt, 5.2 μM ; ErB, 0.2 mM; 100 mL TEOA solution; light source, 520 nm LED lamp.

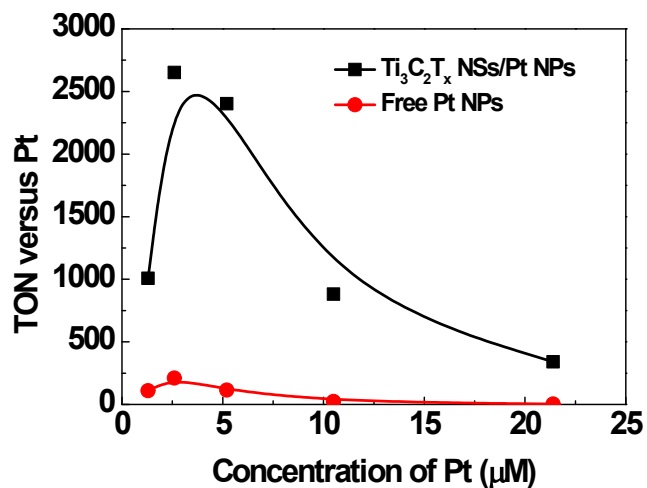


Fig. S9 TONs of H₂ evolution activity based on Pt used for Ti₃C₂T_x NSs/Pt NPs and free Pt NPs in ErB-TEOA system. Reaction conditions: Ti₃C₂T_x NSs, 10 mg; ErB, 0.2 mM; 100 mL TEOA solution, pH 9; light source, 520 nm LED lamp.

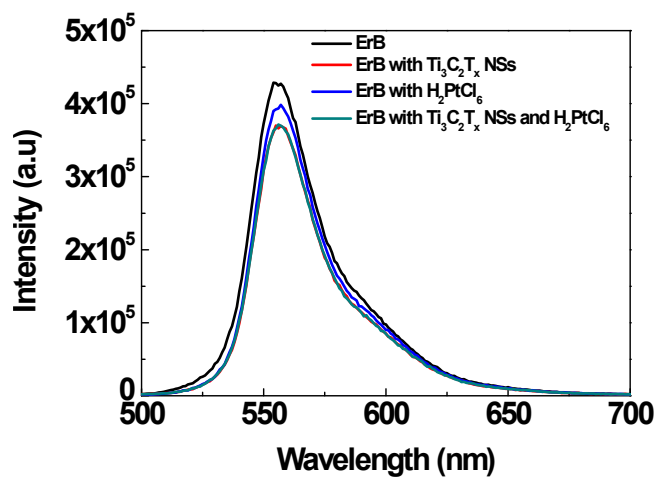


Fig. S10 PL spectra of ErB solution in the presence of Ti₃C₂T_x NSs, H₂PtCl₆, or both Ti₃C₂T_x NSs and H₂PtCl₆. Excitation wavelength: 480 nm.

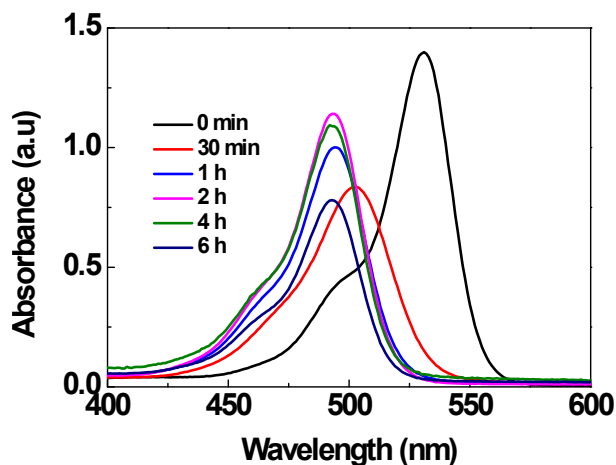


Fig. S11 Time-dependent UV-vis absorption spectra of the photocatalytic reaction systems. Reaction conditions: Ti₃C₂T_x NSs, 10 mg; ErB, 0.2 mM; 100 mL TEOA solution, pH 9; light source, 520 nm LED lamp. The in situ formed Ti₃C₂T_x NSs/Pt NPs catalyst was removed by centrifugation and the remaining solution was diluted by 10 times.

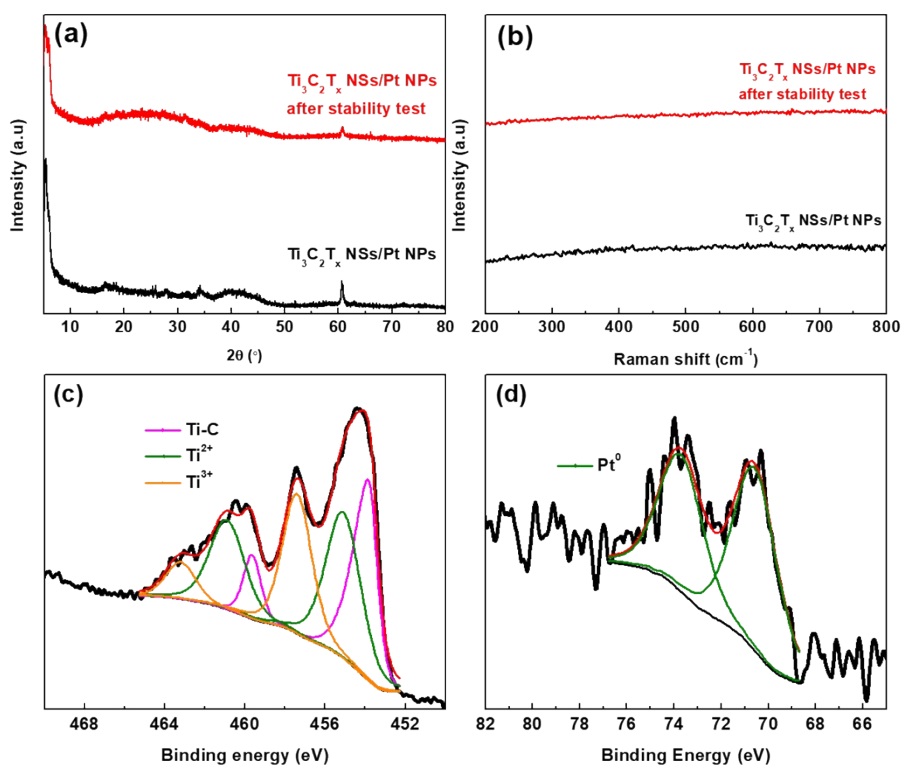


Fig. S12 (a) XRD patterns and (b) Raman spectra of Ti₃C₂T_x NSs/Pt NPs catalyst before and after stability test. XPS spectra of (c) Ti 2p and (d) Pt 4f of the Ti₃C₂T_x NSs/Pt NPs catalyst after stability test.

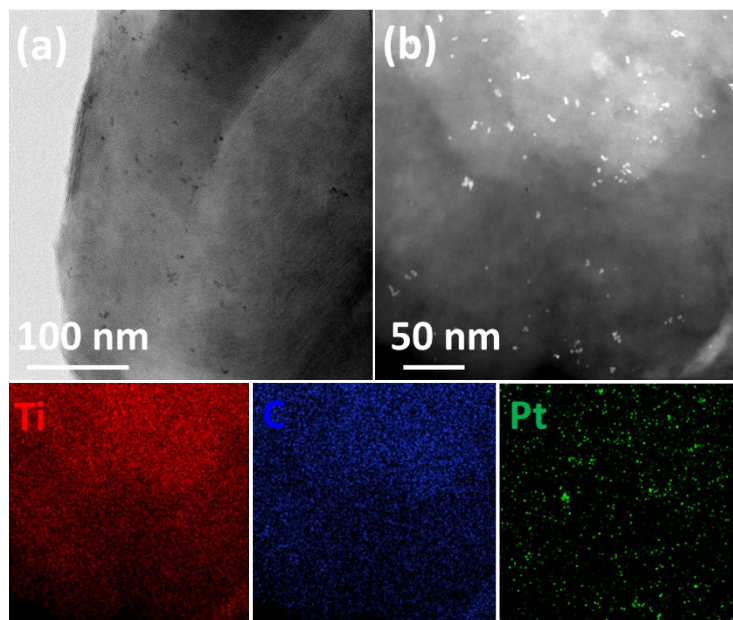


Fig. S13 (a) TEM and (b) HAADF-STEM images and corresponding element mappings of the $\text{Ti}_3\text{C}_2\text{T}_x$ NSs/Pt NPs catalyst after stability test.

References

1. Y. Xue, Y. G. Lei, X. Y. Liu, Y. N. Li, W. A. Deng, F. Wang and S. X. Min, *New J. Chem.*, 2018, **42**, 14083.
2. A. Lipatov, M. Alhabeab, M. R. Lukatskaya, A. Boson, Y. Gogotsi and A. Sinitskii, *Adv. Electron. Mater.*, 2016, **2**, 1600255.
3. X. Y. Liu, S. X. Min, Y. Xue, L. Tian, Y. G. Lei and F. Wang, *New J. Chem.*, 2019, **43**, 4152.