Supplementary Information

Titanium-based Photo-Fenton Bifunctional Catalyst of mp-MXene/TiO_{2-x} nanodots for Dramatic Enhancement of the Catalytic Efficiency in Advanced Oxidation Processes

Experimental Section

1 Chemicals

MAX (Ti_3AlC_2, Carbon-Ukraine LTD.), Hydrofluoric Acid (HF, 40%, Sinopnarm Chemical Reagent Co., LTD), Hydrogen Peroxide Solution (H_2O_2, 30%, Aladdin Bio-Chem Technology Co., LTD), Ethanol(95%, Aladdin Bio-Chem Technology Co., LTD), Potassium Chloride (KCl, 99%, Alfa Aesar chemical Co. LTD), tetrabutyl titanate($C_{16}H_{36}O_4Ti$, ≥99.0%, Alfa Aesar chemical Co. LTD)

2 Synthetic method

2.1 Preparation of mp-MXene/TiO_{2-x} NDs

Multilayer MXene (ml-MXene) was prepared by selectively etching of Al element from 2 g MAX (Ti_3AlC_2) using 40% HF as reported in Gogotsi's work.[s1] Afterwards, 50 mg ml-MXene was dispersed in 5 ml deionized water by magnetic stirring at room temperature for 10 min. Then 1 ml 30% H_2O_2 was added, stayed in still for 10 min, the supernatant was collected by centrifugation at 8000 rpm to get the mp-MXene/TiO_{2-x} NDs.

2.2 Preparation of TiO_2-Ti_3C_2

TiO_2-Ti_3C_2 was prepared according to Wang et. al's method.[s2] To be specific, 150 mg the as-prepared ml-MXene was dispersed in 200 ml ethanol and stirred for 1 hour before 0.5 ml, 0.4 mM KCl solution was added. Afterwards, 1ml tetrabutyl titanate was added followed by vigorous stir for 6 hours. The precipitate was separated by centrifugation and rinsed thoroughly with ethanol and water before redispersing in 60 ml ethanol for solvothermal treatment at 180 ℃ for 1 hour to get the target product of TiO_2-Ti_3C_2.

[s1] O. Mashtalir, M. R. Lukatskaya, M. Q. Zhao, M. W. Barsoum, Y. Gogotsi, *Adv. Mater.* **2015,** 27, 3501-6

[s2] F. Wang, C. Yang, M. Duan, Y. Tang, J. Zhu, *Biosens. Bioelectron.* **2015,** 74, 1022-1028.

3 Characterizations

Powder X-ray diffraction（XRD）data was acquired using a Bruker D8 Advance with filtered Cu-K_α radiation (40 kV and 40 mA, λ=0.154 nm); Field-emission scanning electron microscopy (FE-SEM) analysis was performed on Hitachi S-4800; Transmission electron microscopy (TEM) images were obtained on a JEOL-JEM-2100F electron microscope with an acceleration voltage of 200 kV and a Bruker EDS System; Chemical compositions and oxidation states of the sample were analyzed using X-ray photoelectron spectroscopy (XPS) with monochromated Al K_α radiation ($h\nu$ = 1486.6eV). Binding energies were calibrated using C 1s peak of C-C bond set at 284.8eV. The fitting and analysis of the spectra was performed in XPS PEAK version 4.1; N_2 adsorption-desorption isotherms were measured on Micromeritics ASAP 2460 device at 77K. Before detection, the sample was degassed at 373K; The content of Ti element in the sample was measured by Inductively Coupled Plasma

Mass Spectrometry (ICP-MS, Thermo ScientificTMiCAPTM Q ICP-MS); The zeta potential and hydrodynamic diameter of the sample were obtained using Zetasizer Nano ZS90; Fourier transform infrared spectrum (FTIR) was carried out on Bruker TENSOR 27 (4000-400cm^{-1}); The pollutant degradation experiments were conducted on multi-channel photocatalysis instrument (Shanghai Deyangyibang Instruments CO., LTD, DY-D type) and the results were monitored via UV-Vis spectrum measured by Varioskan LUX microplate reader (VarioskanTM LUX, Thermo Fisher Scientific, US); The EPR spectra were recorded on a Bruker A300 EPR spectrometer at 77 K with an X-band frequency of 9.852 GHz, sweep width of 200.00 Gauss, and center field of 3580.00 Gauss. Raman analysis was performed on Renishaw-inVia with an excitation wavelength of 532nm. The mineralization efficiency was measured by a total organic carbon analyzer (TOC-L-CPH Shimadzu, Japan).

4 Degradation of dye molecules under light and dark conditions

5 ml of the as-prepared mp-MXene/TiO2-x NDs solution with different titanium concentrations were separately dropped into quartz tubes containing15ml Rhodamine B (RhB) to make the [Ti] equal to 150 ppm, 30 ppm, 10 ppm(considering that there are Ti species in both MXene skeleton and TiO_{2-x} dots and all these Ti species could contribute to the photo-Fenton reaction, the dosage of the synthesized product and the comparison samples of commercial P25 and TiO_2-Ti_3C_2 were determined according to the concentration of the titanium element ([Ti])), respectively, while the concentration of RhB kept the same of 30 mg/L. Correspondingly, P25 suspension of 0.25 g/L, 0.05 g/L and 16.7 mg/L in RhB (30 mg/L) were prepared for comparison.

The tubes holding above suspension were kept in darkness for 2 hours before adding different amount of H_2O_2 to initiate the pseudo-Fenton reactions. The photocatalytic reactions were irradiated with 500W Xe lamp with a cooling system (also mentioned as “simulated sun light (SSL)” in this article). And the degradation process was monitored using UV-Vis spectroscopy method by measuring the absorption of the by-product solution sampled from the system every 10 min. The degradation experiments of Methyl Orange (MO) and Methylene Blue (MB) were conducted the same as that of RhB except that the pH was adjusted to 10.0 in MO solution and 3.33 in MB solution.

On the other hand, the dark Fenton reactions were carried out in totally darkness from the beginning of mixing the catalysts with the dye solution. And only the lowest catalyst concentration ([Ti] = 10ppm) was adopted to ensure the degradation process slow enough. To be specific, take RhB as the example, 5 ml of the as-prepared mp-MXene/TiO_{2-x} NDs solution was dropped into a quartz tube containing 15 ml RhB to make [Ti] and [RhB] equal to 10 ppm and 30 mg/L, respectively. Correspondingly, P25 of 16.7 mg/L suspended in 30 mg/L RhB was prepared for comparison. The Fenton reaction started by adding H_2O_2 after an adsorption-desorption equilibrium process of 2h. 200 μl solution was sampled every 10 min to measure the UV-Vis absorption after removing the catalyst via centrifugation. The degradation process lasted two hours. The “dark-light converting-condition-reactions” were performed similar as that in the dark condition except that the first hour was kept in totally dark while the second hour was exposed to 500W Xe lamp with a cooling system.

5 Figures and captions

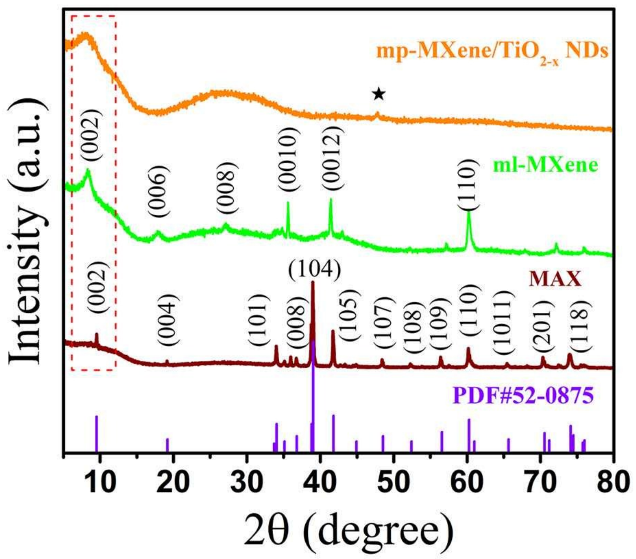

Fig. S1 XRD patterns of the pristine MAX, multi-layer MXene and the prepared mp-MXene/TiO$_{2-x}$ NDs.

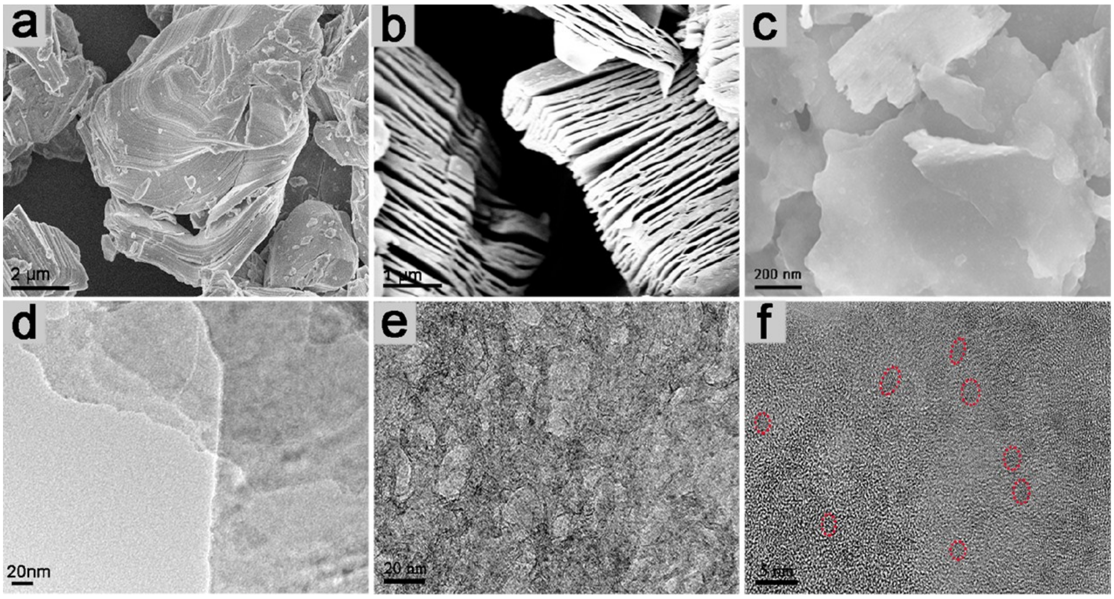

Fig. S2 SEM images of the pristine MAX (a), multi-layer MXene (b) and delaminated mono-layer MXene (c); TEM images of delaminated mono-layer MXene (d) and the prepared mp-MXene/TiO$_{2-x}$ NDs (e), high-resolution TEM image of the prepared mp-MXene/TiO$_{2-x}$ NDs (f).

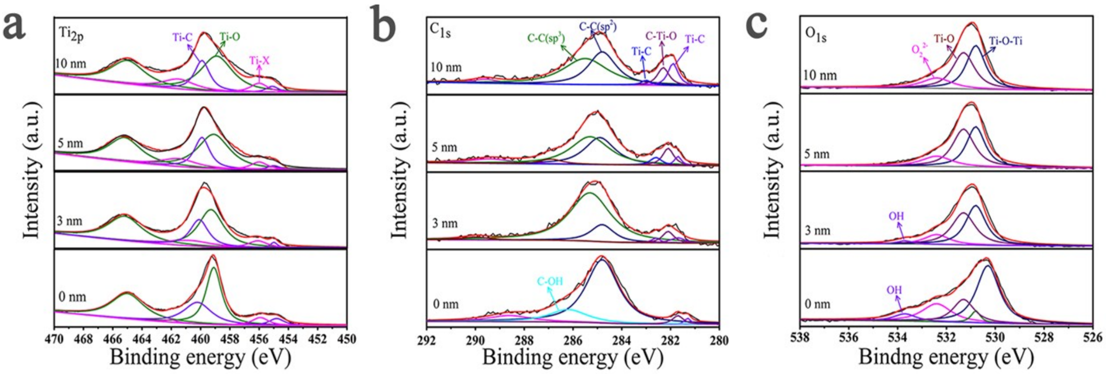

Fig. S3 Depth profiling XPS spectra of the intermediate product during the process of synthesizing mp-MXene/TiO_{2-x} NDs in (a) Ti 2p region, (b) C 1s region and (c) O 1s region.

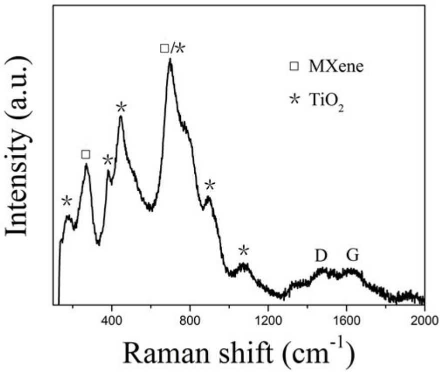

Fig. S4 Raman spectrum of mp-MXene/TiO_{2-x} NDs.

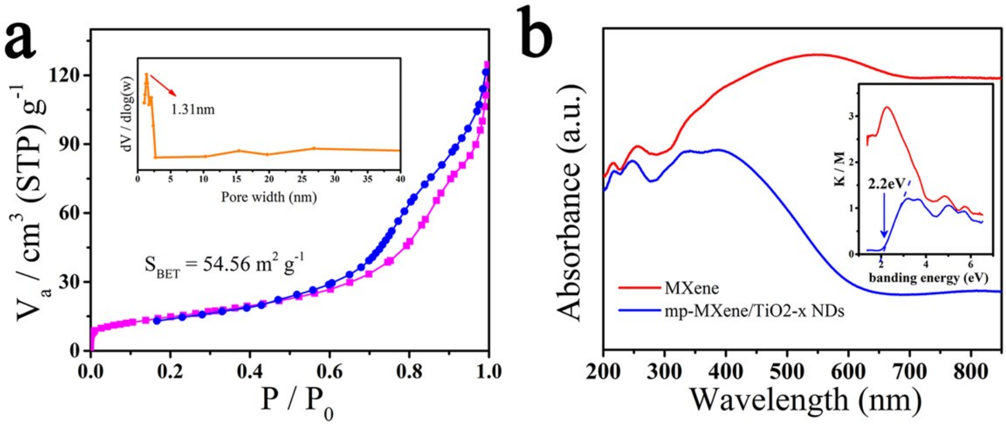

Fig. S5(a) N_2 adsorption-desorption isotherms of mp-MXene/TiO_{2-x} NDs. Inset is the pore width distribution analysis; (b) UV-Vis diffuse reflection spectrum of ml-MXene and mp-MXene/TiO_{2-x} NDs and the band gap analysis (the inset).

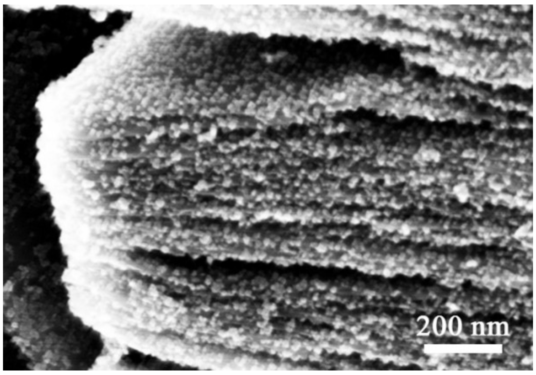

Fig.S6 SEM image of the TiO_2-Ti_3C_2.

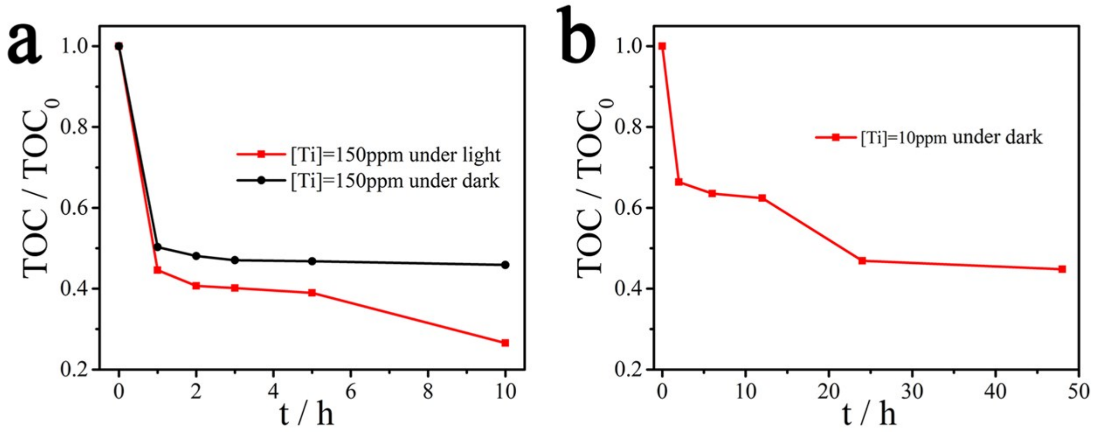

Fig. s7 TOC removal analysis during RhB degradation process using mp-MXene/TiO_{2-x} NDs at a concentration of (a) [Ti] = 150 ppm, [H_2O_2] = 0.7mM under dark and light, respectively; and (b) [Ti] = 10 ppm, [H_2O_2] = 0.047mM under dark.

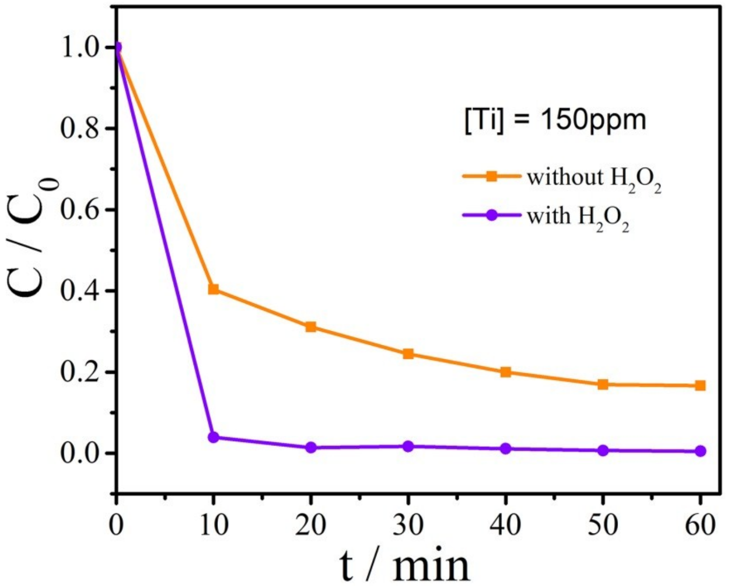

Fig. S8 Degradation of RhB (30 mg/L) on mp-MXene/TiO_{2-x} NDs ([Ti] = 150 ppm) with and without the attendance of H_2O_2.

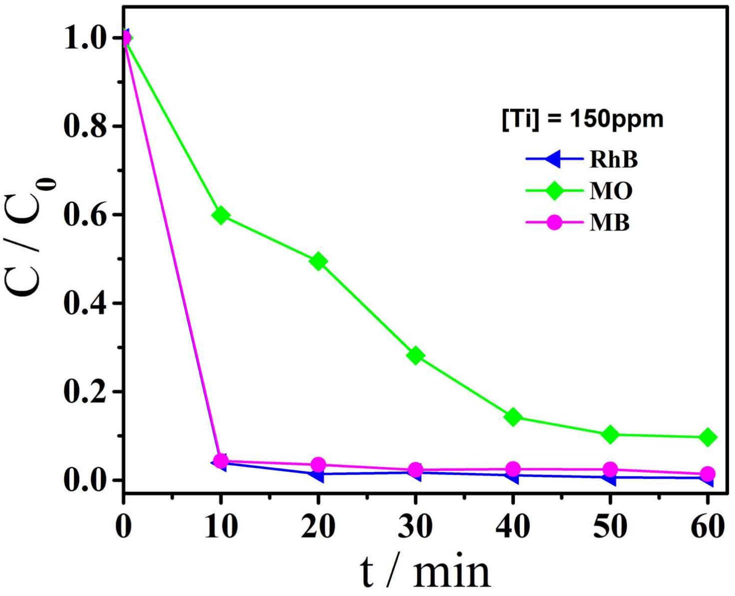

Fig. S9 Degradation of RhB (30 mg/L), MO(30 mg/L) and MB(30 mg/L) upon mp-MXene/TiO_{2-x} NDs ([Ti] = 150 ppm, [H_2O_2] = 0.7 mM) at a pH of 5.78 , 10 and 3.33 respectively with simulated sunlight irradiation.

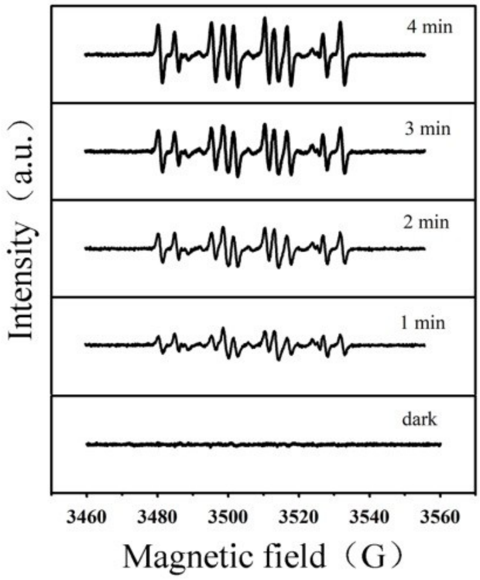

Fig. S10 EPR signal of superoxide radicals (• O^{2-}) generated in mp-MXene/TiO_{2-x} NDs & H_2O_2 system measured at different time before and after exposed to light.

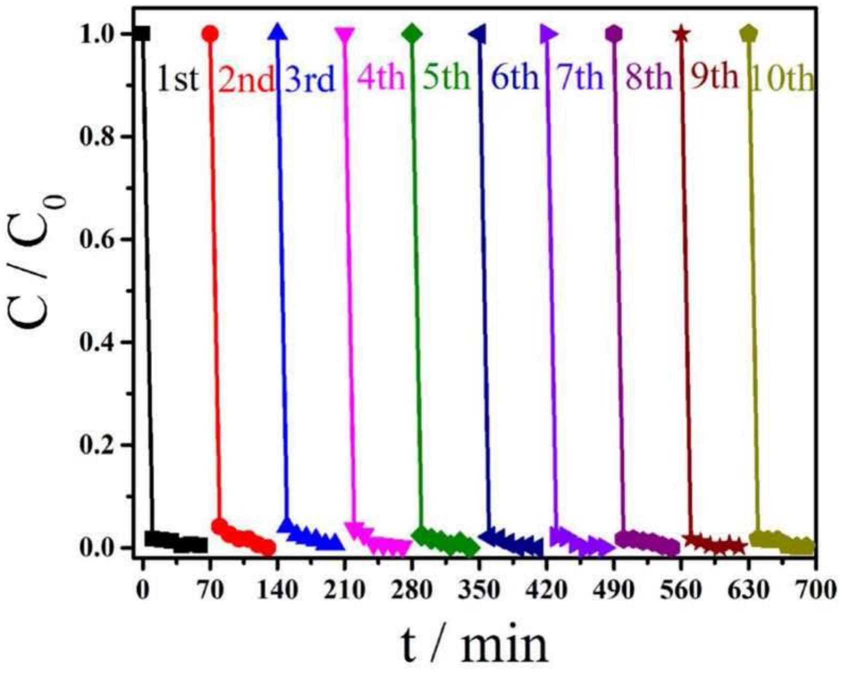

Fig. S11 Degradation of RhB (30 mg/L) on mp-MXene/TiO_{2-x} NDs ([Ti] = 150 ppm, $[H_2O_2]$ = 0.7 mM) in different cyclic runs.