

## Supporting Information

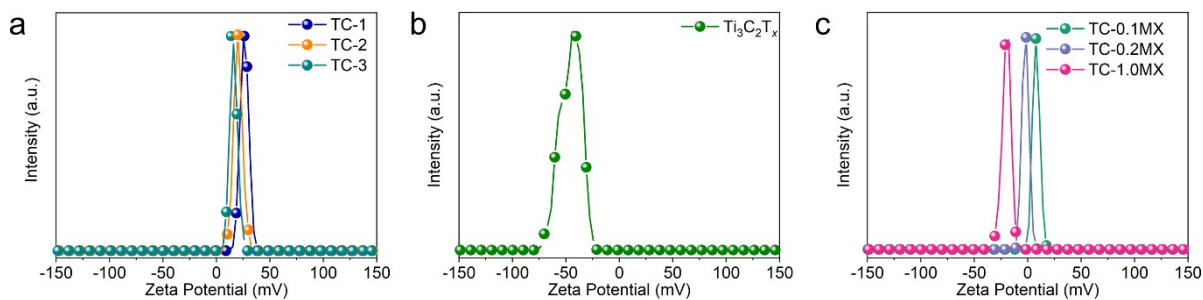
### On the Role of Plasmonic $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in Enhancing Photoredox Catalysis

Guanshun Xie<sup>a</sup>, Chuang Han<sup>b</sup>, Fei Song<sup>a</sup>, Yisong Zhu<sup>a</sup>, Xuanyu Wang<sup>a</sup>, Jialin Wang<sup>a</sup>, Zhenjun Wu<sup>c</sup>, Xiuqiang Xie<sup>a,\*</sup>, Nan Zhang<sup>a,\*</sup>

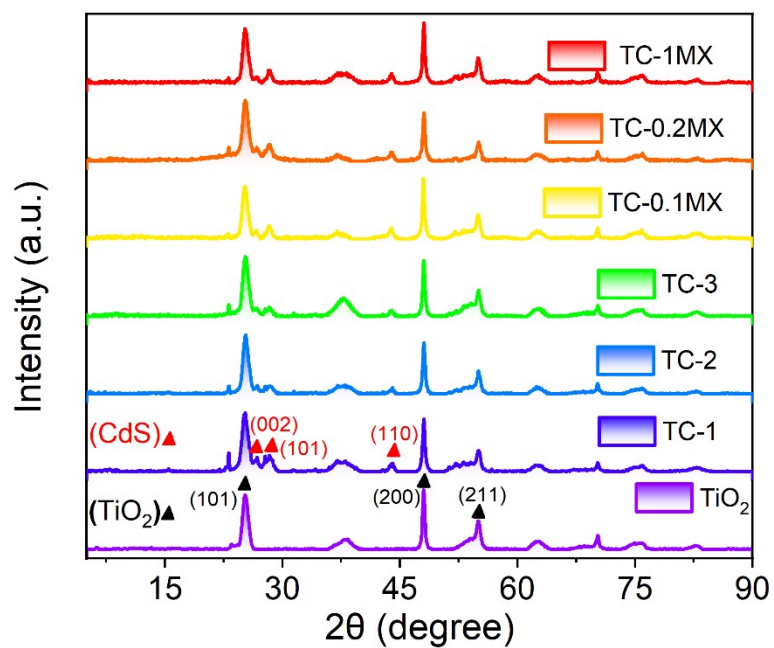
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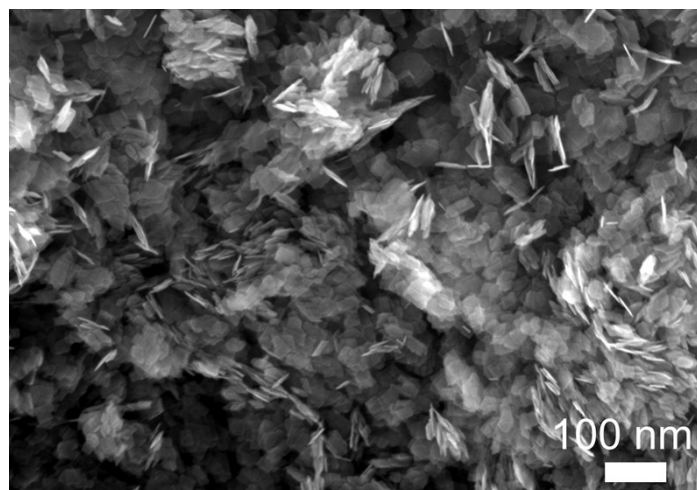
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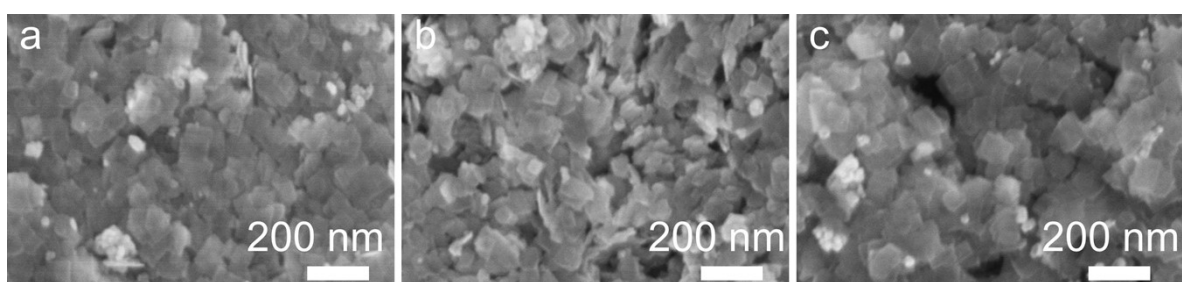
**Figure S1.** Zeta potentials of the as-prepared samples.



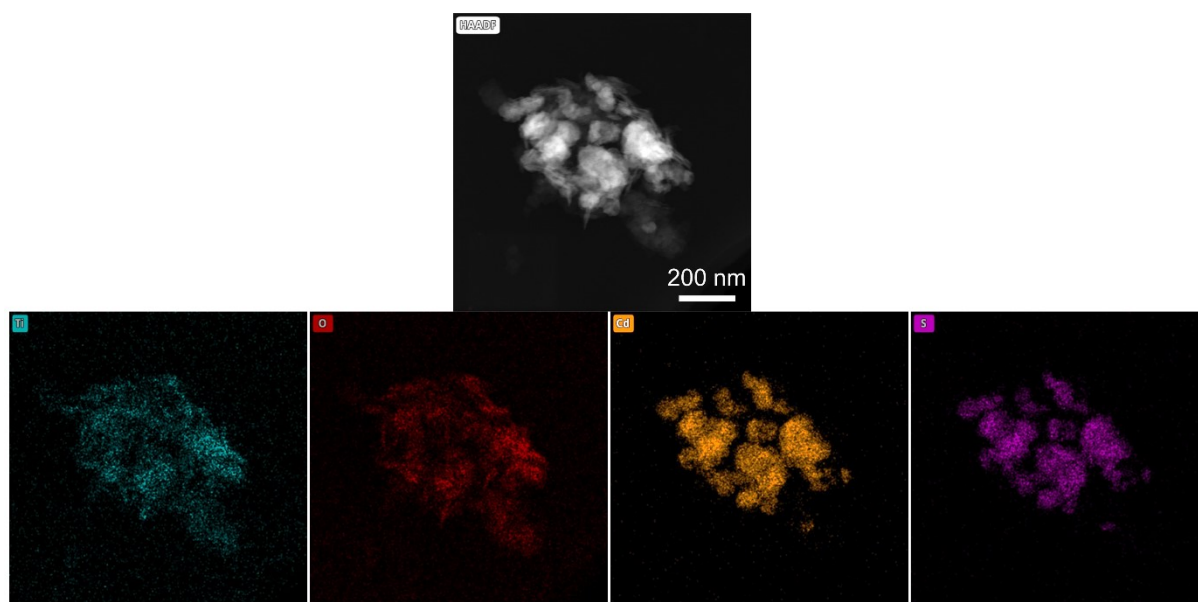
**Figure S2.** XRD patterns of  $\text{TiO}_2$ , TC, and TC-MX composites.



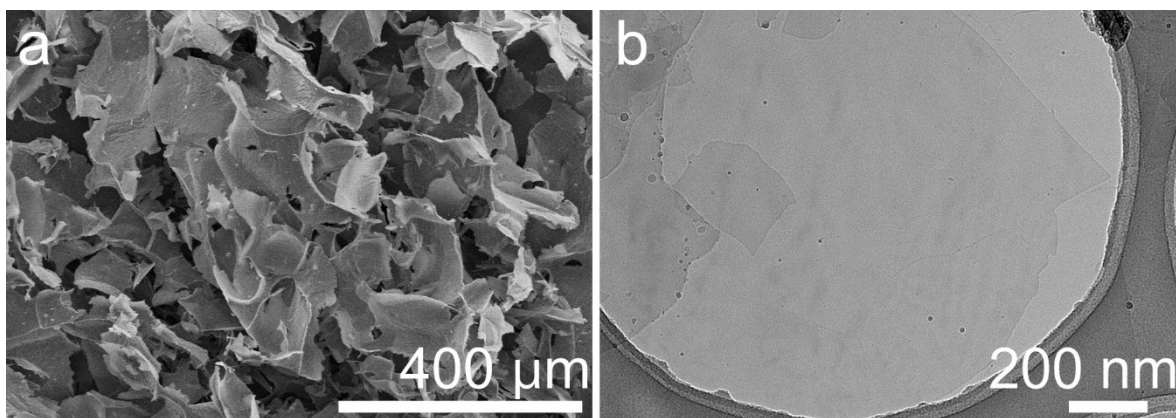
**Figure S3.** SEM image of  $\text{TiO}_2$  nanosheets.



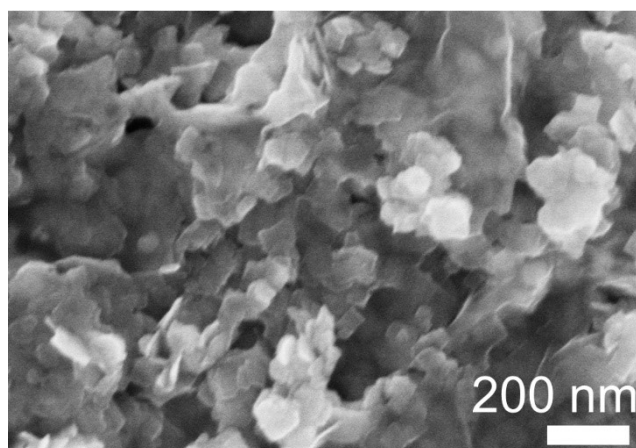
**Figure S4.** SEM images of (a) TC-1, (b) TC-2, and (c) TC-3.



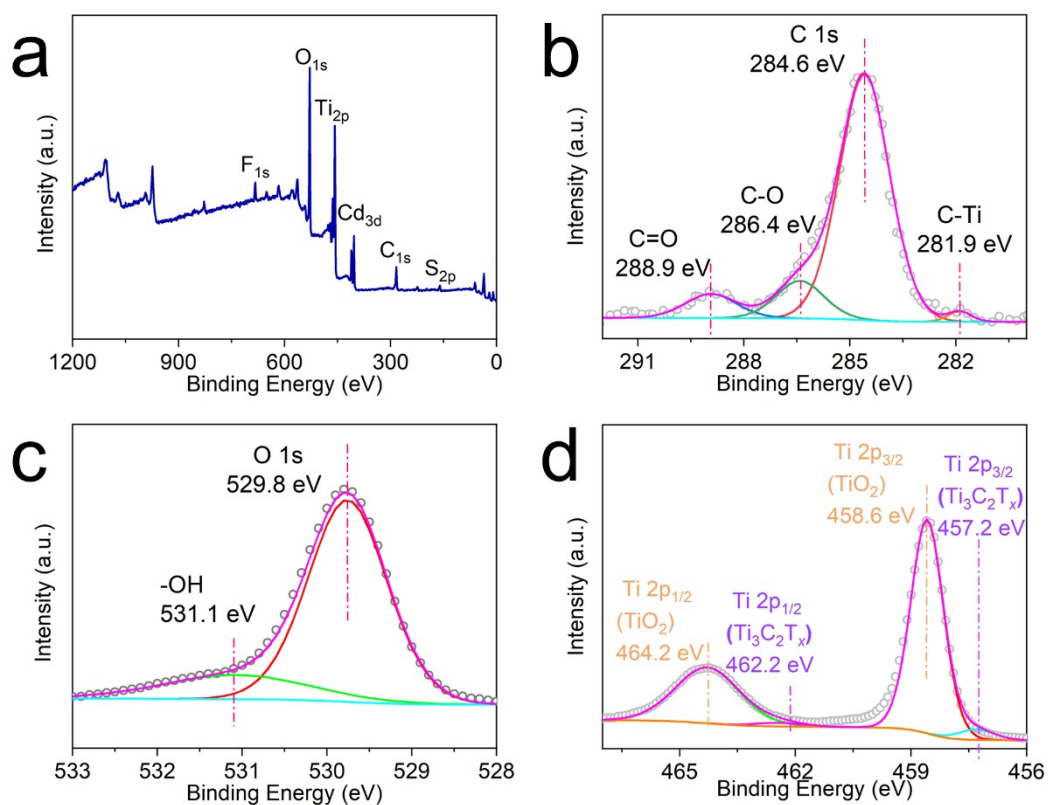
**Figure S5.** HAADF-STEM image of TC-2 with the corresponding Ti, O, Cd, and S EDX mapping results.



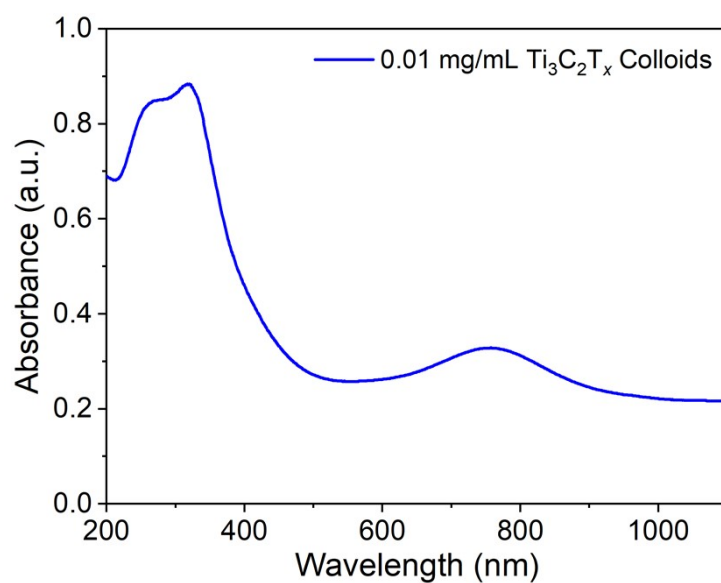
**Figure S6.** (a) SEM and (b) TEM images of  $\text{Ti}_3\text{C}_2\text{T}_x$ .



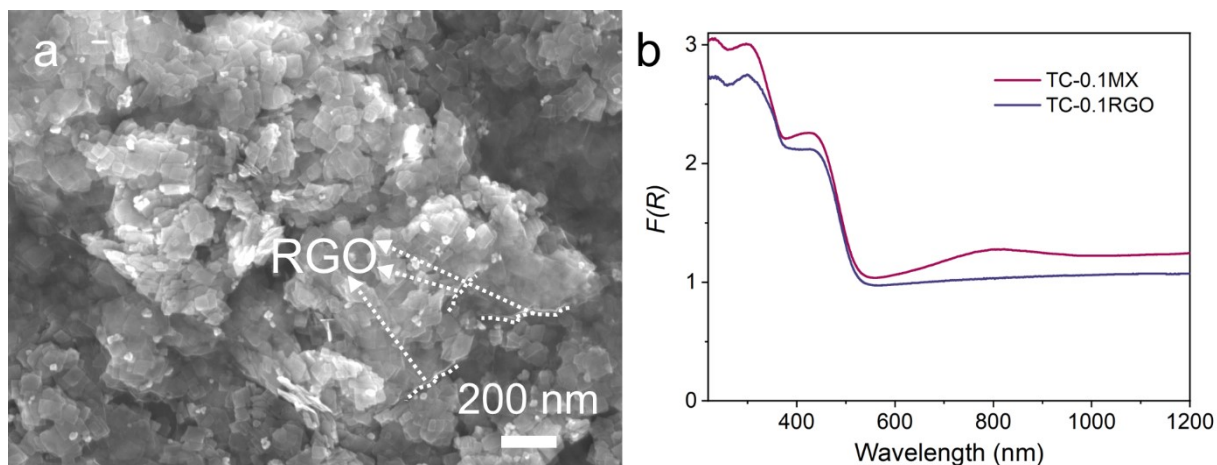
**Figure S7.** SEM image of TC-0.1MX.



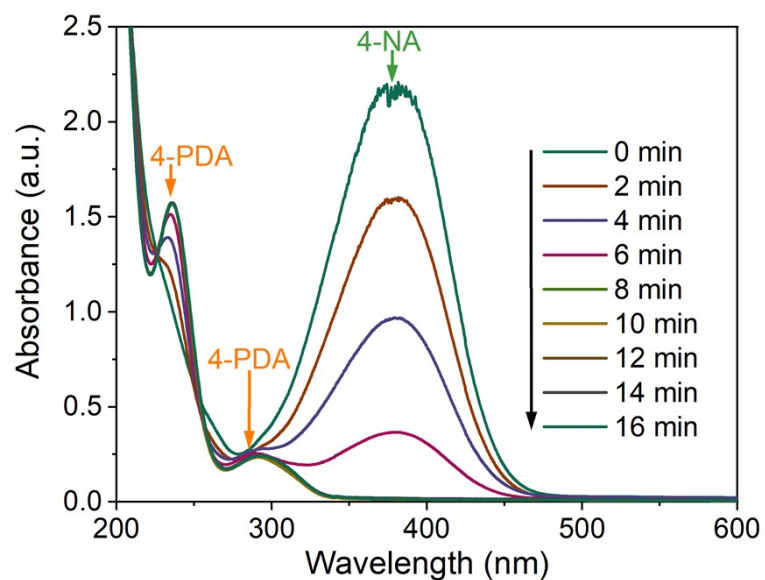
**Figure S8.** XPS spectrum of TC-0.1MX: (a) Survey, (b) C 1s, (c) O 1s and (d) Ti 2p.



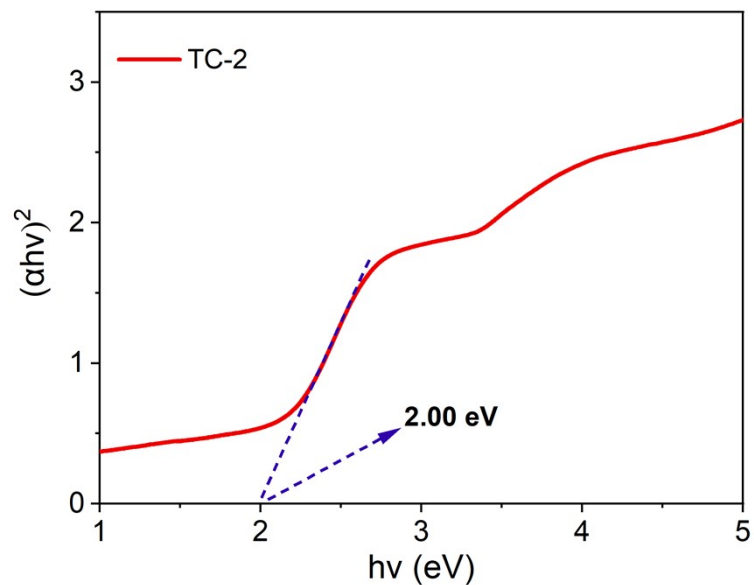
**Figure S9.** Ultraviolet-visible-NIR light absorption spectrum of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> colloid.



**Figure S10.** (a) SEM image of TC-0.1RGO. (b) UV-vis diffuse reflectance spectra (DRS) of TC-0.1MX and TC-0.1RGO composites.

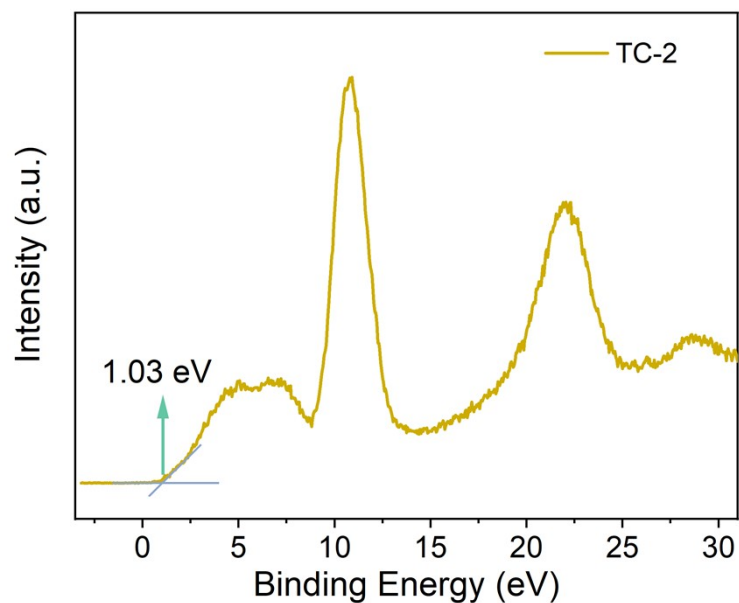


**Figure S11.** UV-vis absorption spectra of 4-NA aqueous solution over TC-0.1MX nanocomposite under visible light irradiation ( $\lambda > 420$  nm) with the addition of ammonium formate as quencher for photogenerated holes under  $N_2$  purge.



**Figure S12.** Transformed plots based on the Kubelka–Munk function versus photon energy for TC-2.

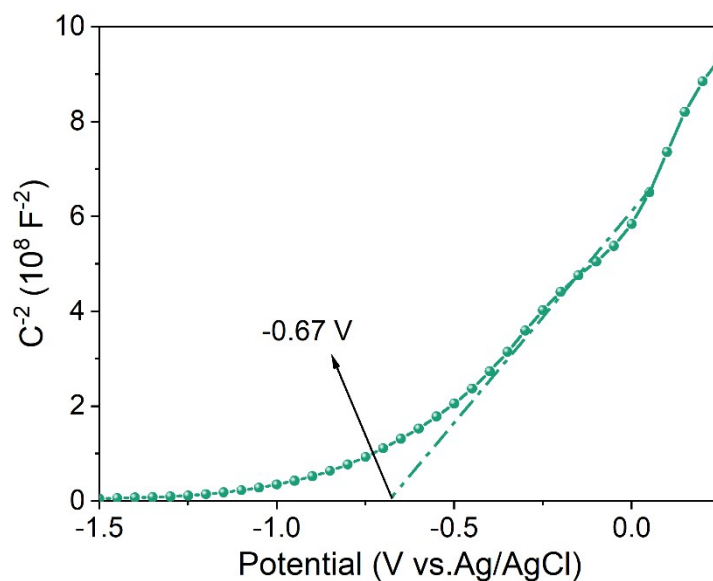
**Note:** As  $\text{TiO}_2$  has no light absorption in the visible region of  $\text{TiO}_2@\text{CdS}$  (**Figure 2c**), the  $E_g$  obtained corresponds to CdS.



**Figure S13.** XPS valence band spectrum of TC-2.

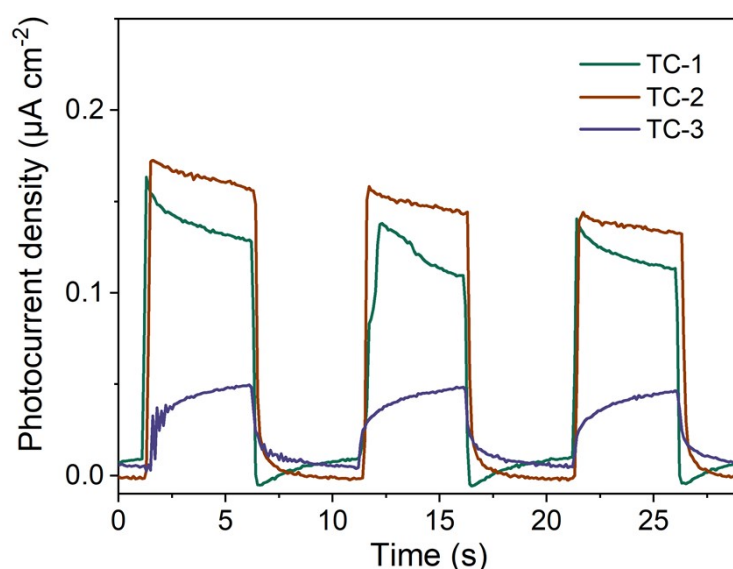
**Note:** The valence band energy ( $E_{\text{VB}}$ ) of  $\text{TiO}_2@\text{CdS}$  composite is attributed to CdS by XPS, because CdS is coated on the surface of CdS and the XPS detection depth is only  $\sim 5$  nm.



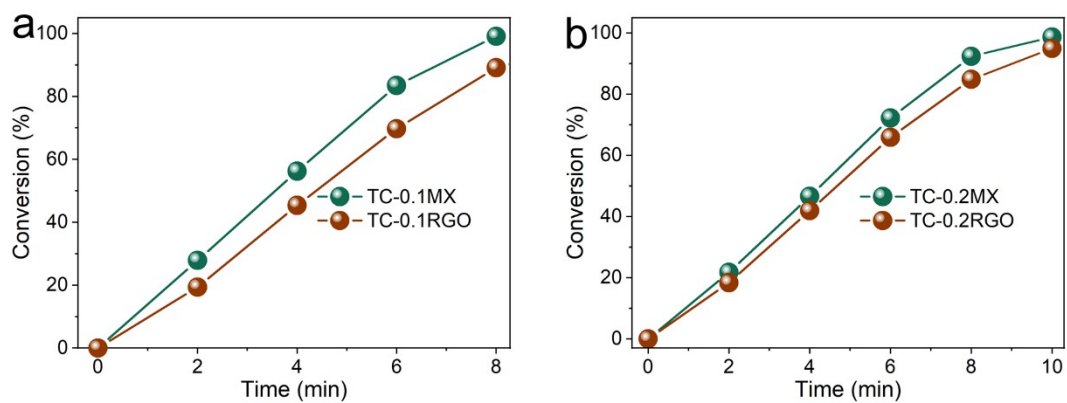


**Figure S14.** Mott-Schottky plots of TiO<sub>2</sub>.

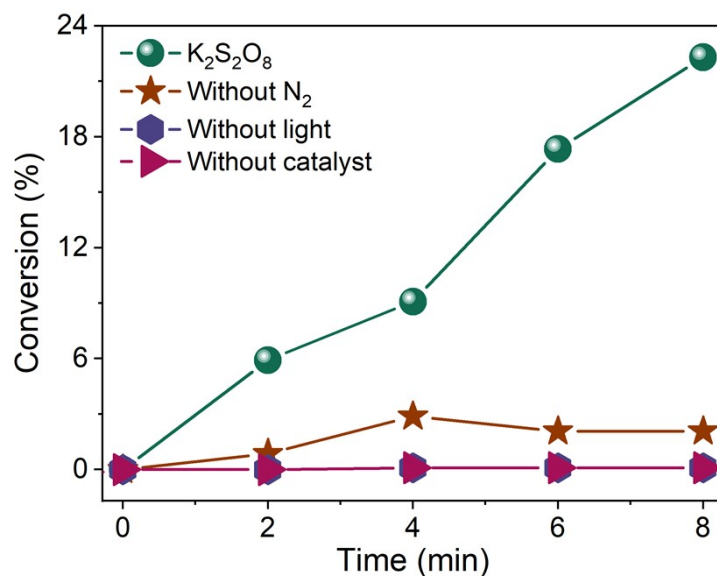
**Note:** It is seen from **Figure S14** that the flat-band potential of TiO<sub>2</sub> is estimated to be around  $-0.67 \text{ V}$  versus Ag/AgCl (pH = 6.8, for 0.2 M Na<sub>2</sub>SO<sub>4</sub> electrolyte). It is known that the bottom of conduction band in n-type semiconductors is more negative by about  $-0.2 \text{ V}$  than the flat band potential<sup>[1]</sup>. The conduction band of TiO<sub>2</sub> is calculated to be  $-0.27 \text{ V}$  versus normal hydrogen electrode (NHE, pH = 0)<sup>[2]</sup>.



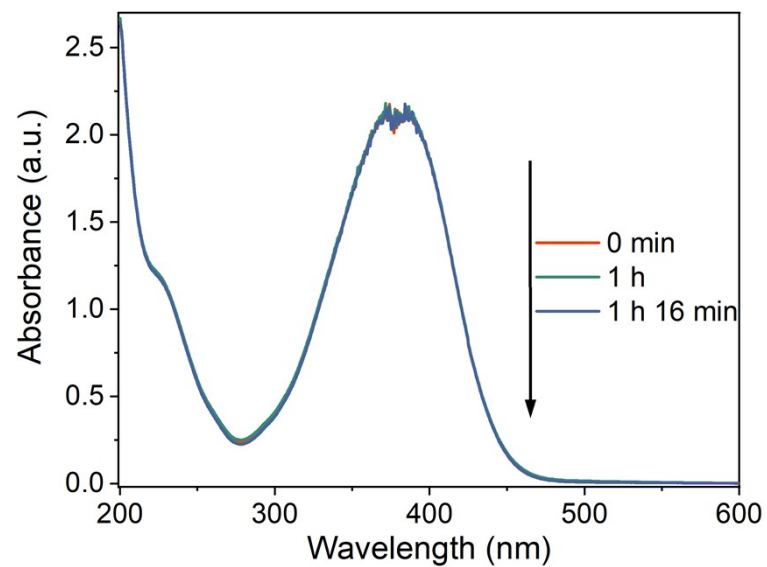
**Figure S15.** Photocurrent densities of TC-1, TC-2, and TC-3 under visible-NIR light irradiation ( $\lambda > 420 \text{ nm}$ ).



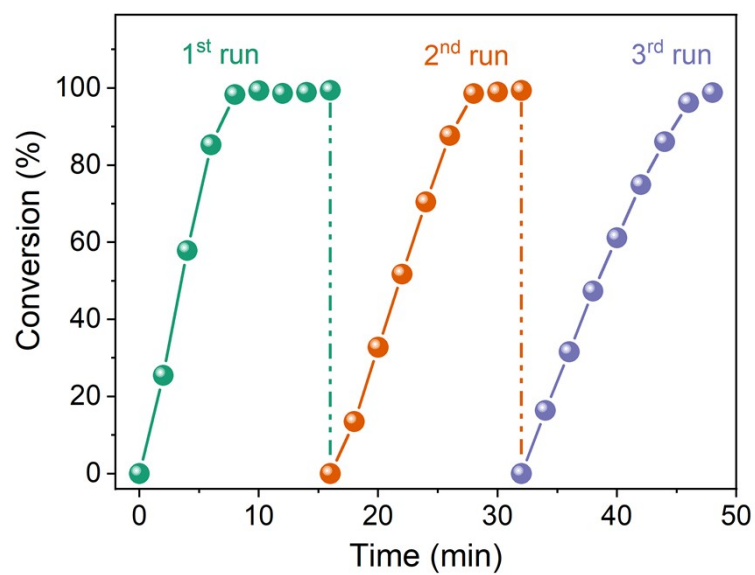
**Figure S16.** Photoactivities of TC-0.1RGO a) and TC-0.2RGO b) composites for the selective reduction of 4-nitroaniline (4-NA) to 4-phenylenediamine (4-PDA) in water with the addition of ammonium formate as a hole scavenger and  $N_2$  purging in water under visible-NIR light irradiation ( $\lambda > 420$  nm).



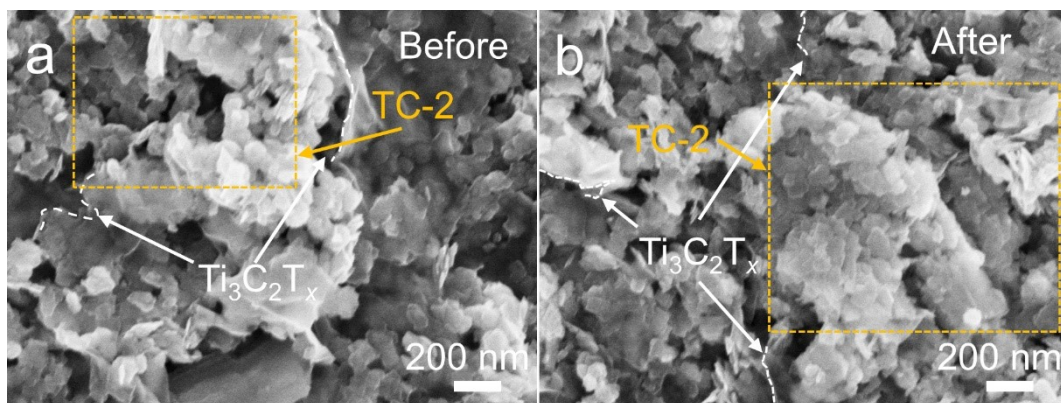
**Figure S17.** Control experiments for photocatalytic reduction of 4-NA over TC-0.1MX: reaction with  $K_2S_2O_8$  as a scavenger for electrons, and reaction without the purge of  $N_2$ , without light, without catalyst.



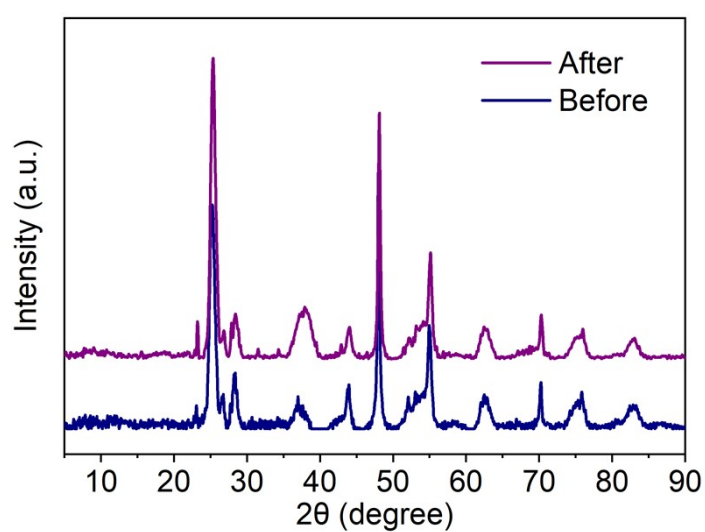
**Figure S18.** UV-vis absorption spectra of 4-NA over TC-0.1MX under adsorption equilibrium.



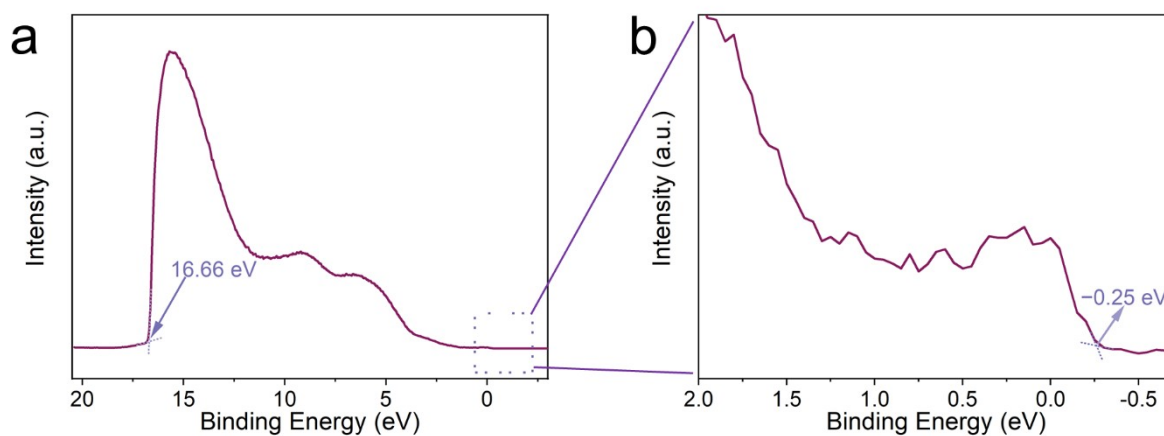
**Figure S19.** Stability test of TC-0.1MX.



**Figure S20.** SEM images of (a) the original TC-0.1MX sample, and the TC-0.1MX sample after (b) three-cycle photocatalysis reactions.



**Figure S21.** XRD patterns of the TC-0.1MX sample before and after three-cycle photocatalysis reactions.



**Figure S22.** Ultraviolet photoelectron spectra (UPS) of the synthesized  $Ti_3C_2T_x$  MXene.

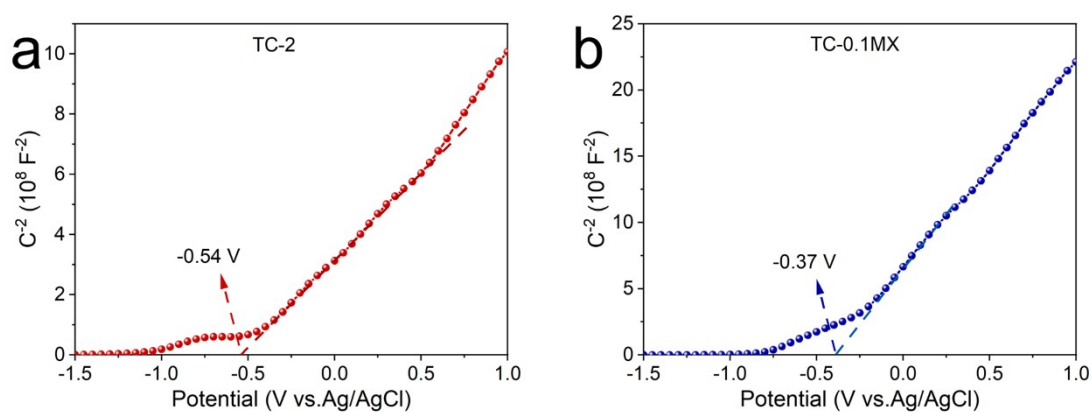
**Note:** The excitation source was He I ( $h\nu = 21.22$  eV) and a negative bias of  $-9.8$  eV was applied during the UPS measurement. The following formula is used to calculate the work function ( $\Phi$ ) of  $\text{Ti}_3\text{C}_2\text{T}_x$ :

$$\Phi = h\nu - W = 21.22 - 16.91 = 4.31 \text{ eV}$$

where  $W$  is the width of the UPS spectrum. Then, the Fermi level ( $E_F$ ) of  $\text{Ti}_3\text{C}_2\text{T}_x$  is calculated as follows<sup>[3]</sup>:

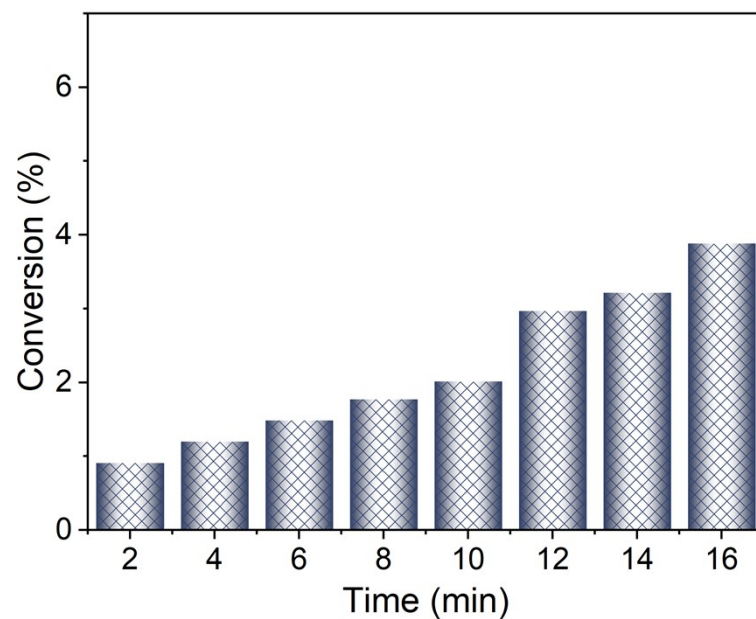
$$E_F = E_{\text{vac}} - \Phi$$

where  $E_{\text{vac}}$  is the energy of a stationary electron at vacuum level (assumed as 0 eV). Therefore, it can be estimated that the  $E_F$  of the  $\text{Ti}_3\text{C}_2\text{T}_x$  is located at  $-4.31$  eV vs. vacuum level. According to the relationship between the  $E_{\text{vac}}$  and the normal electrode potential ( $E_{\text{NHE}}$ ),  $E_{\text{vac}} = -E_{\text{NHE}} - 4.44$ <sup>[3]</sup>, the  $E_F$  of  $\text{Ti}_3\text{C}_2\text{T}_x$  is thus determined to be  $-0.13$  V vs. normal hydrogen electrode.

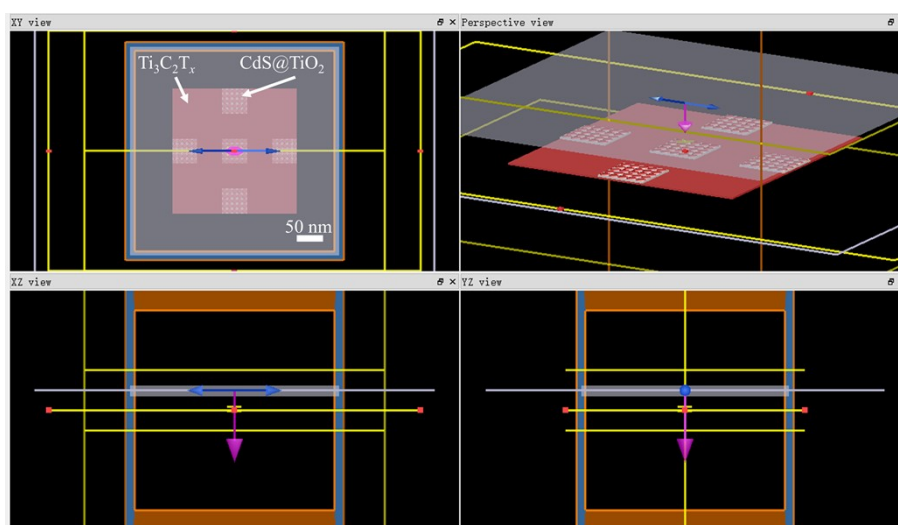


**Figure S23.** Mott-Schottky plots of TC-2 and TC-0.1MX.

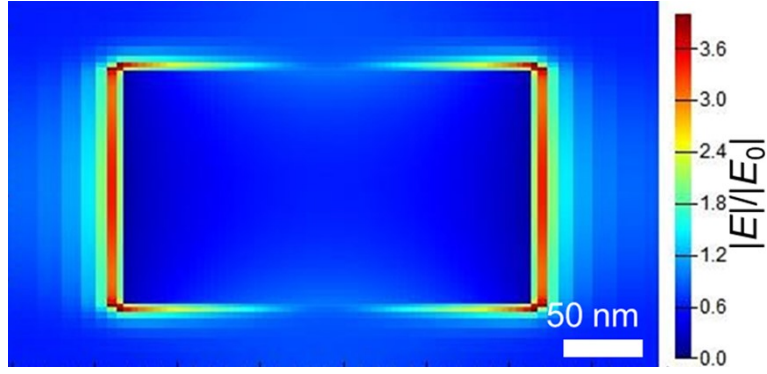
**Note:** The flat band potential is obtained from the Mott-Schottky curve corresponding to the apparent Fermi level after the Fermi-level equilibration of the different components.



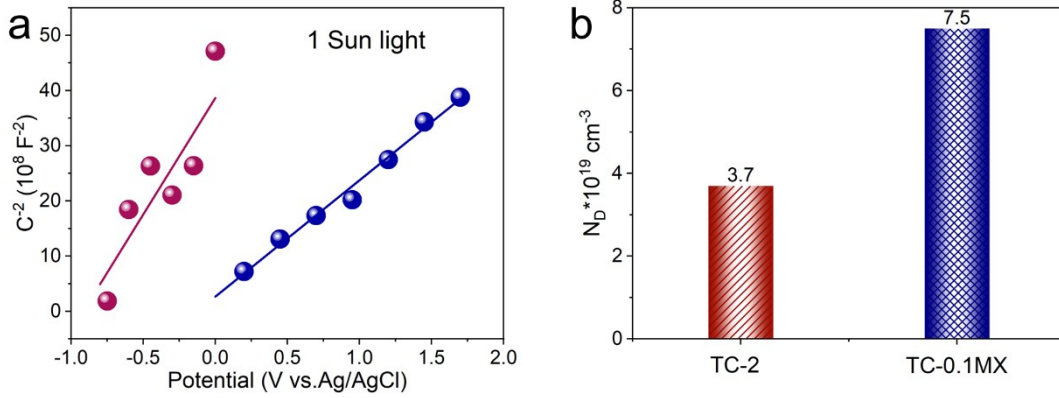
**Figure S24.** Photoactivities of TC-0.1MX for selective reduction of 4-NA under light irradiation ( $\lambda > 780$  nm) at room temperature.



**Figure S25.** The finite-difference time-domain (FDTD) model consisting of CdS deposited to  $\text{TiO}_2$  and then loaded to  $\text{Ti}_3\text{C}_2\text{T}_x$ .



**Figure S26.** FDTD simulation of the near-field distributions of  $\text{Ti}_3\text{C}_2\text{T}_x$ .

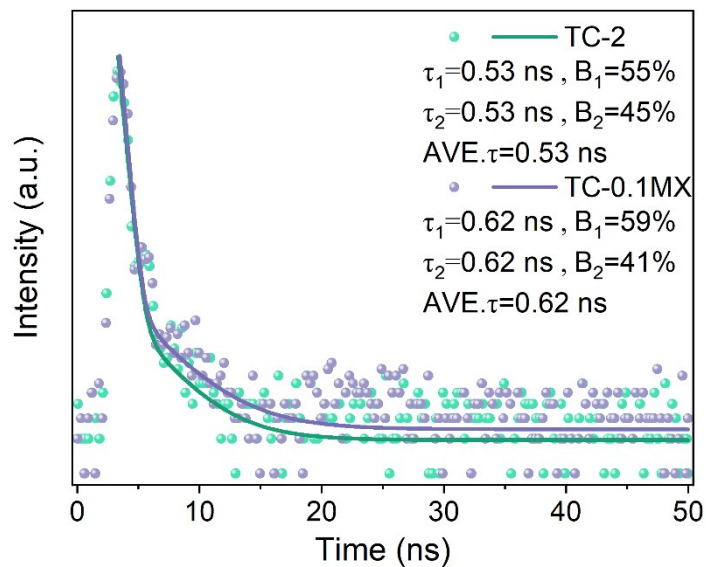


**Figure S27.** (a) Mott-Schottky plots for TC-2 and TC-0.1MX composites under 1 sun irradiation and (b) corresponding calculated results of the photo-induced carrier concentration.

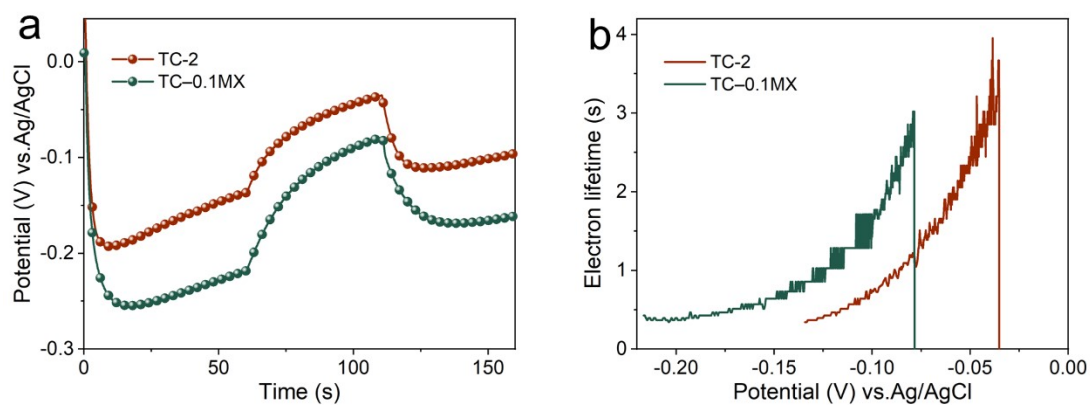
**Note:** As shown in **Figure S27**, the slope of  $C^{-2}$  vs.  $V$  in the Mott-Schottky plot of TC-0.1MX decreases as compared to that of TC-2, indicating the increase of charge carriers density. The charge carriers density ( $N_D$ ) is calculated to be  $3.7 \times 10^{19}$  and  $7.5 \times 10^{19} \text{ cm}^{-3}$  for TC-2 and TC-0.1MX, respectively, according to the following equation<sup>[4]</sup>.

$$N_D = \frac{2}{e\epsilon\epsilon_0} \left( \frac{d(1/C^2)}{dV} \right)^{-1}$$

where  $e$  is the elementary electronic charge,  $\epsilon$  is the dielectric constant (8.99 for  $\text{CdS}$ <sup>[5]</sup>),  $\epsilon_0$  is the permittivity in vacuum,  $C$  is the capacitance, and  $V$  is the applied potential.

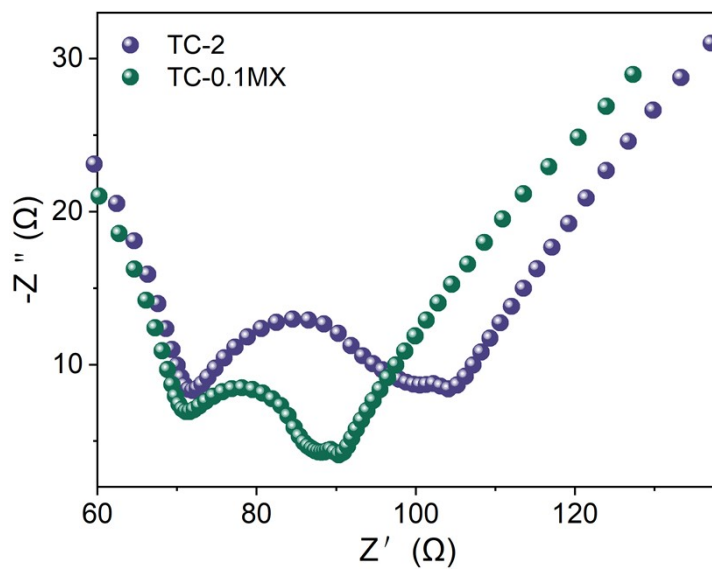


**Figure S28.** Time-resolved PL decay of TC-2 and TC-0.1MX.

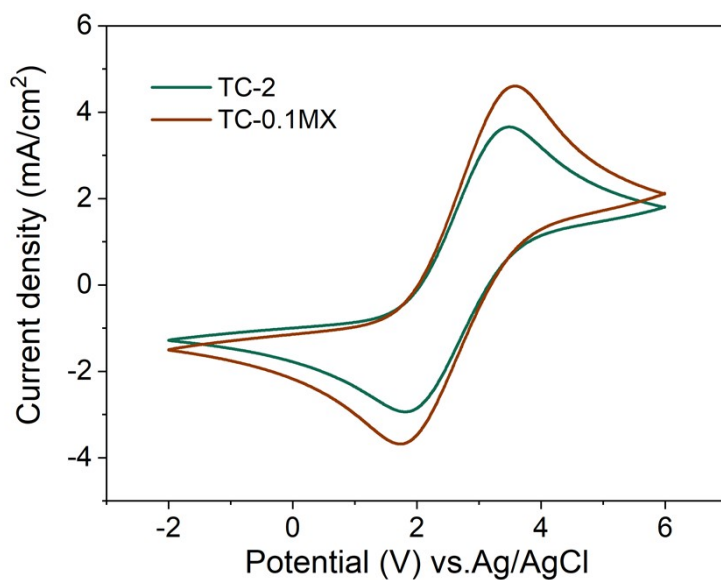


**Figure S29.** (a) Decay curves of photovoltage, and (b) electron lifetime of TC-2 and TC-MX composites.

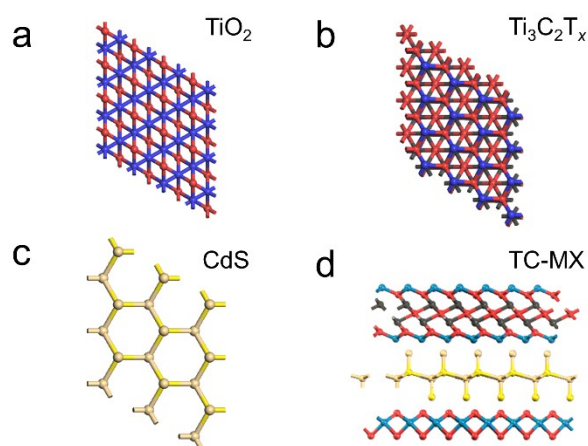




**Figure S30.** EIS Nyquist plots of the samples.



**Figure S31.** Cyclic voltammetry curves of TC-2 and TC-0.1MX composites at different scan rates.



**Figure S32.** The top view of optimized calculation models of (a)  $\text{TiO}_2$ , (b)  $\text{Ti}_3\text{C}_2\text{T}_x$  and (d) TC-MX.

**Table S1.** XRD intensities of  $\text{TiO}_2$  (224) and CdS (110) for different TC composites

| Entry                                      | TC-1 | TC-2 | TC-3 |
|--|------|------|------|
| $\text{TiO}_2$ (224)                       | 266  | 260  | 235  |
| CdS (110)                                  | 545  | 460  | 344  |
| Ratio of $\text{TiO}_2$ (224) to CdS (110) | 0.49 | 0.57 | 0.68 |

## References

- [1] Y. Matsumoto, *J. Solid State Chem.* **1996**, *126*, 227.
- [2] Y. Xu, M. A. A. Schoonen, *Am. Mineral.* **2000**, *85*, 543.
- [3] J. Y. Li, Y. H. Li, F. Zhang, Z. R. Tang, Y. J. Xu, *Appl. Catal. B: Environ.* **2020**, *269*, 118783.
- [4] Z. Xu, Y. Lin, M. Yin, H. Zhang, C. Cheng, L. Lu, X. Xue, H. J. Fan, X. Chen, D. Li, *Adv. Mater. Interfaces* **2015**, *2*, 1500169.
- [5] C. Han, Z. R. Tang, J. Liu, S. Jin, Y. J. Xu, *Chem. Sci.* **2019**, *10*, 3514.