Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

2D/2D Heterojunction of Ti_3C_2/g-C_3N_4 Nanosheets for Enhanced Photocatalytic Hydrogen Evolution

Tongming Su,*[a,b] Zachary D. Hood,[b,d] Michael Naguib,[c] Lei Bai,[b,f] Si Luo,[b] Christopher M. Rouleau,[b] Ilia N. Ivanov,[b] Hongbing Ji,[a,e] Zuzeng Qin,*[a] and Zili Wu*[b]

[a]School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

[b]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

[c]Department of Physics and Engineering Physics, Tulane University, New Orleans, Louisiana 70118, USA

[d]Electrochemical Materials Laboratory, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

[e]School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China

[f]West Virginia University, Department of Chemical and Biomedical Engineering, Morgantown, West Virginia 26506, USA

***Corresponding author:** Tel: +1(865)576-1080.

E-mail: sutm@gxu.edu.cn (T. Su); qinzuzeng@gxu.edu.cn (Z. Qin); wuz1@ornl.gov (Z. Wu).

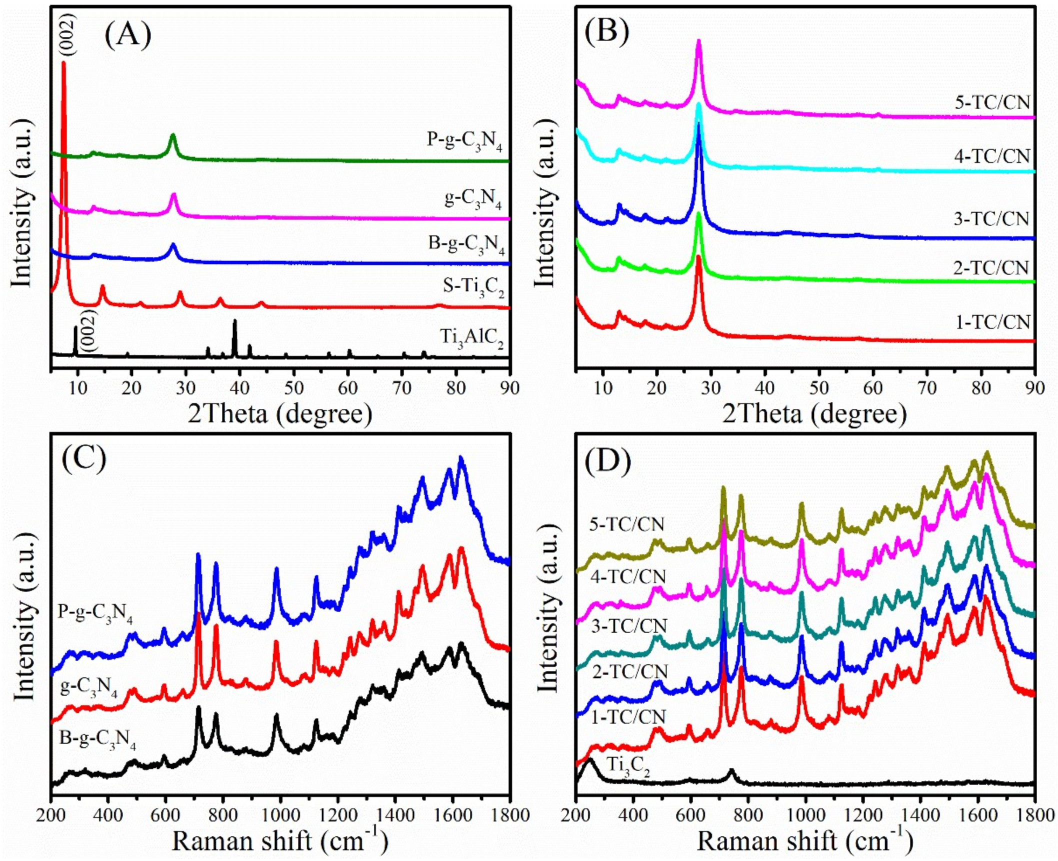

Figure S1. XRD patterns (A, B) and Raman spectra (C, D) of Ti_3AlC_2, S-Ti_3C_2, g-C_3N_4, B-g-C_3N_4, P-g-C_3N_4, and 2D/2D Ti_3C_2/g-C_3N_4 composites.

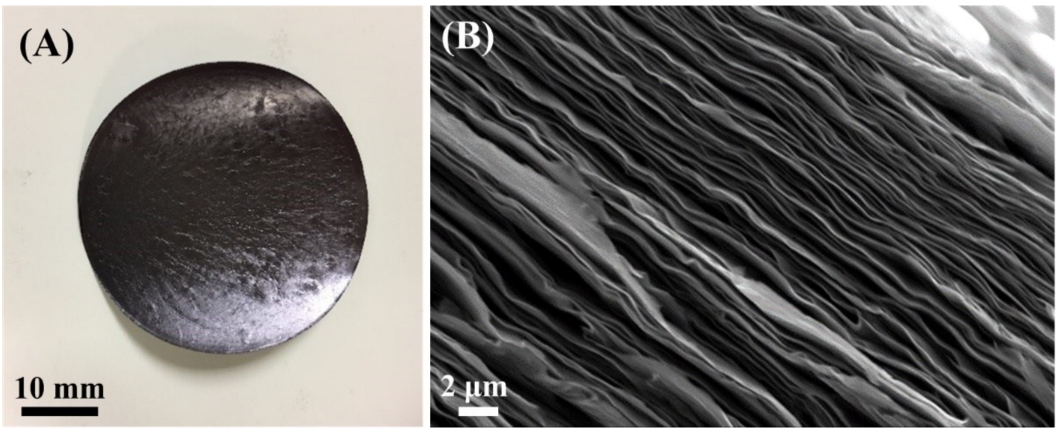

Figure S2. The photograph (A) and the cross-sectional SEM image (B) of the S-Ti_3C_2.

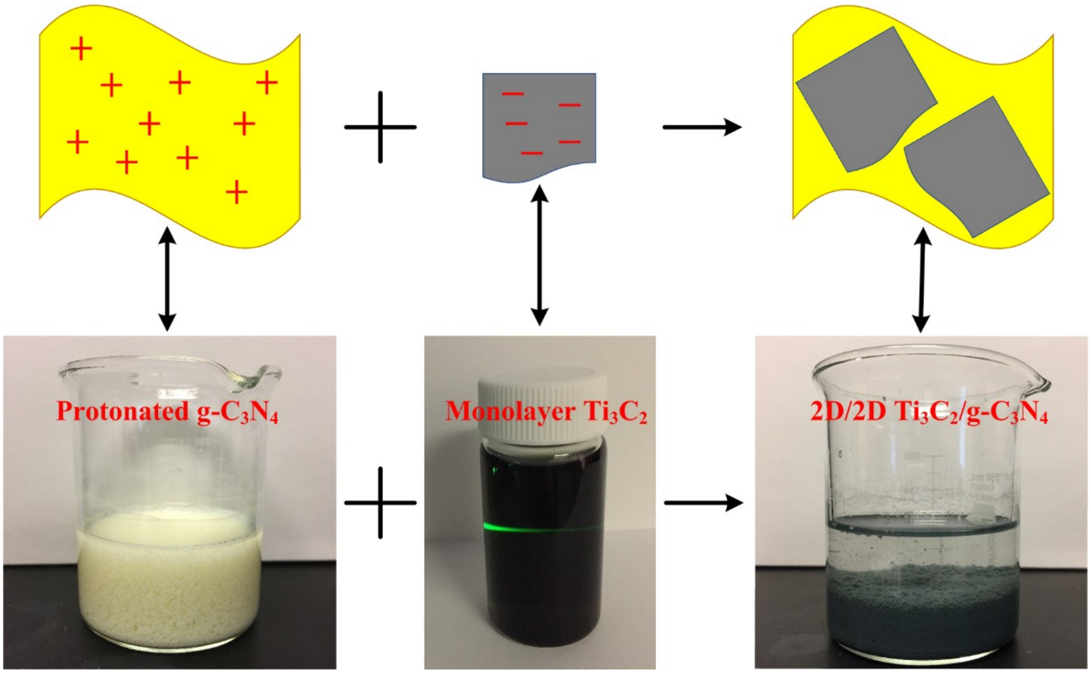

Figure S3. Synthesis of 2D/2D Ti_3C_2/g-C_3N_4 via electrostatic self-assembly approach.

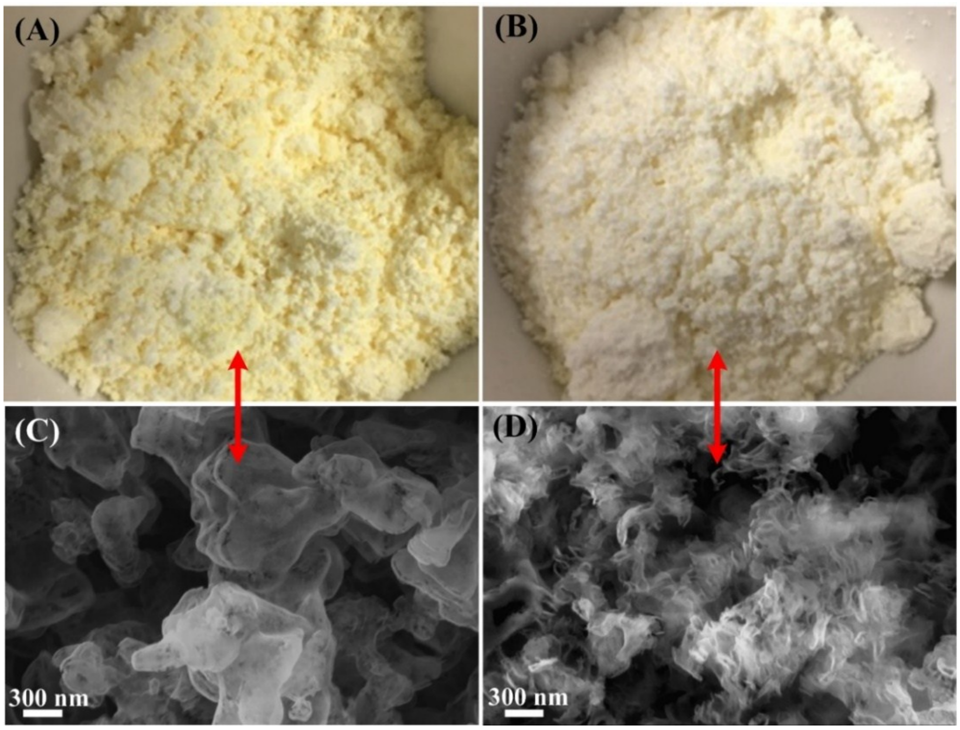

Figure S4. The photographs and SEM images of the B-g-C_3N_4 (A, C) and g-C_3N_4 (B, D).

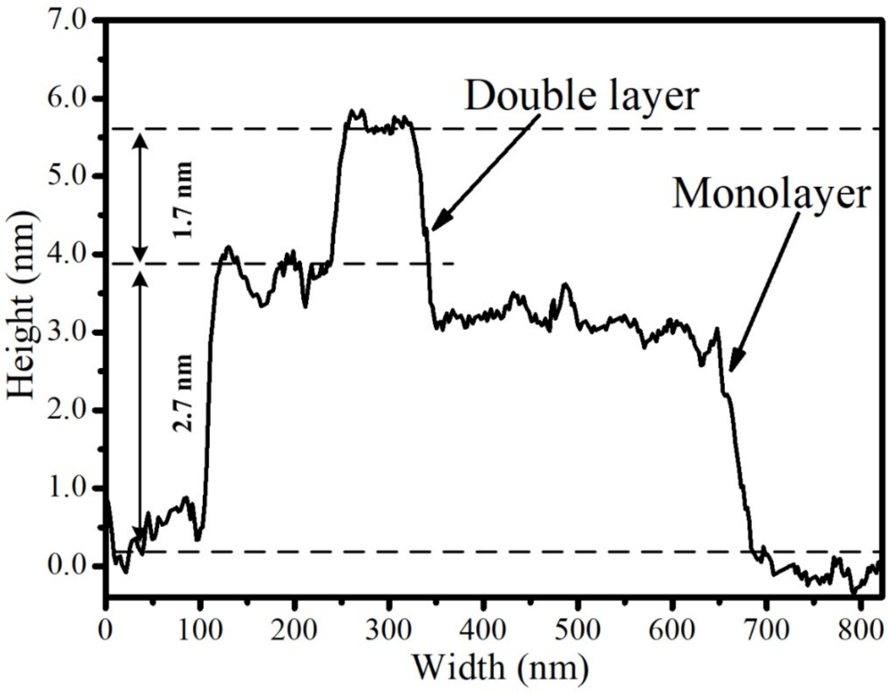

Figure S5. AFM height profile of a representative monolayer Ti_3C_2 deposited on Si wafer.

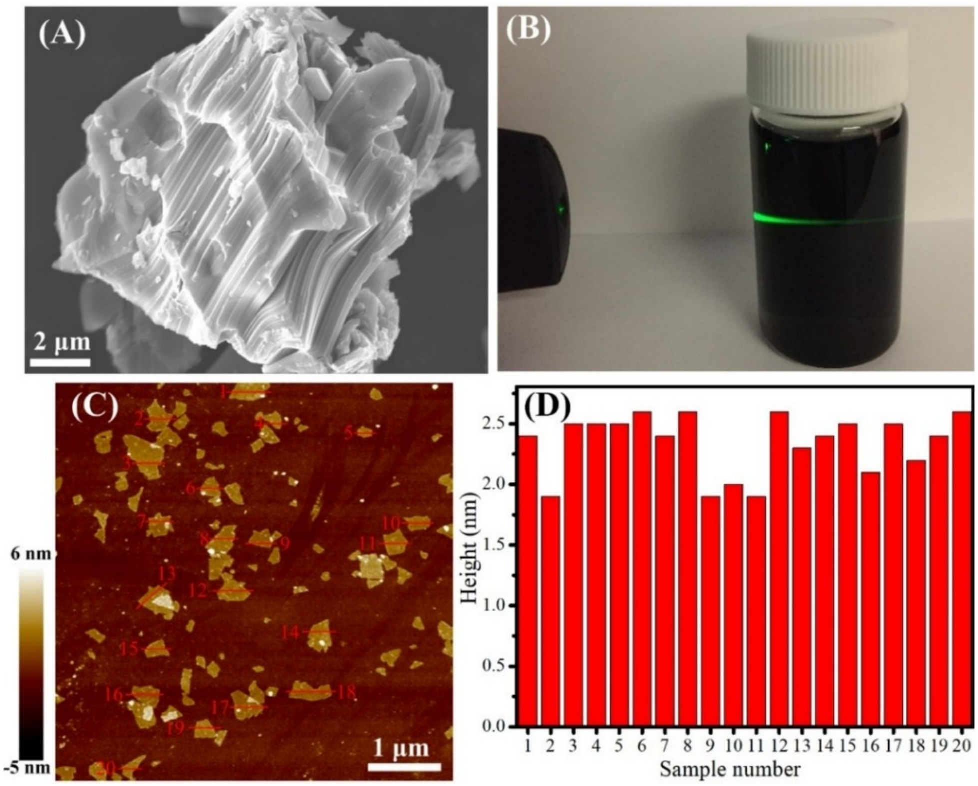

Figure S6. SEM image of Ti_3AlC_2 (A), photograph of the Ti_3C_2 flakes dispersion in water showing an apparent Tyndall effect (B), AFM images (C) and thickness (D) of different Ti_3C_2 flakes.

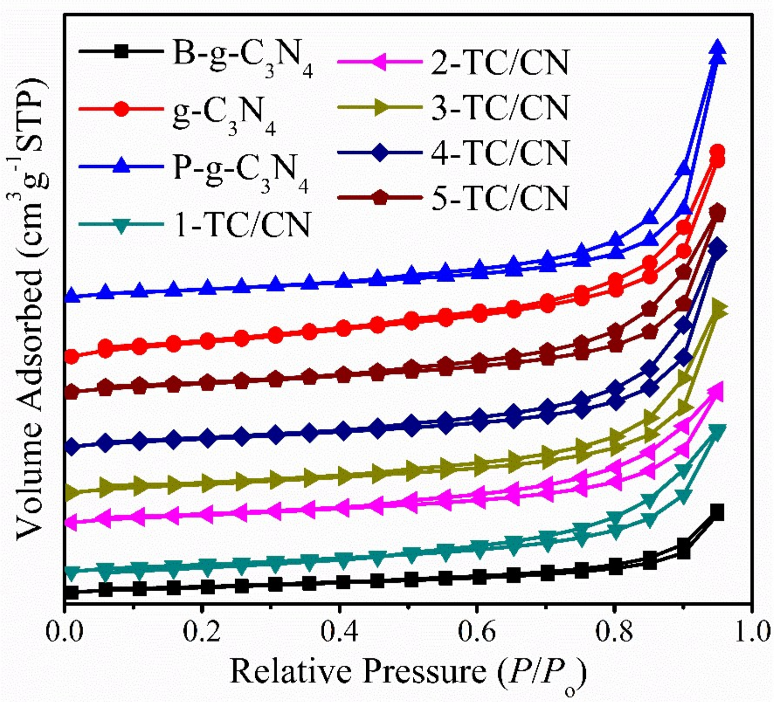

Figure S7. N_2 adsorption-desorption isotherms of B-g-C_3N_4, g-C_3N_4, P-g-C_3N_4, and 2D/2D Ti_3C_2/g-C_3N_4 composites.

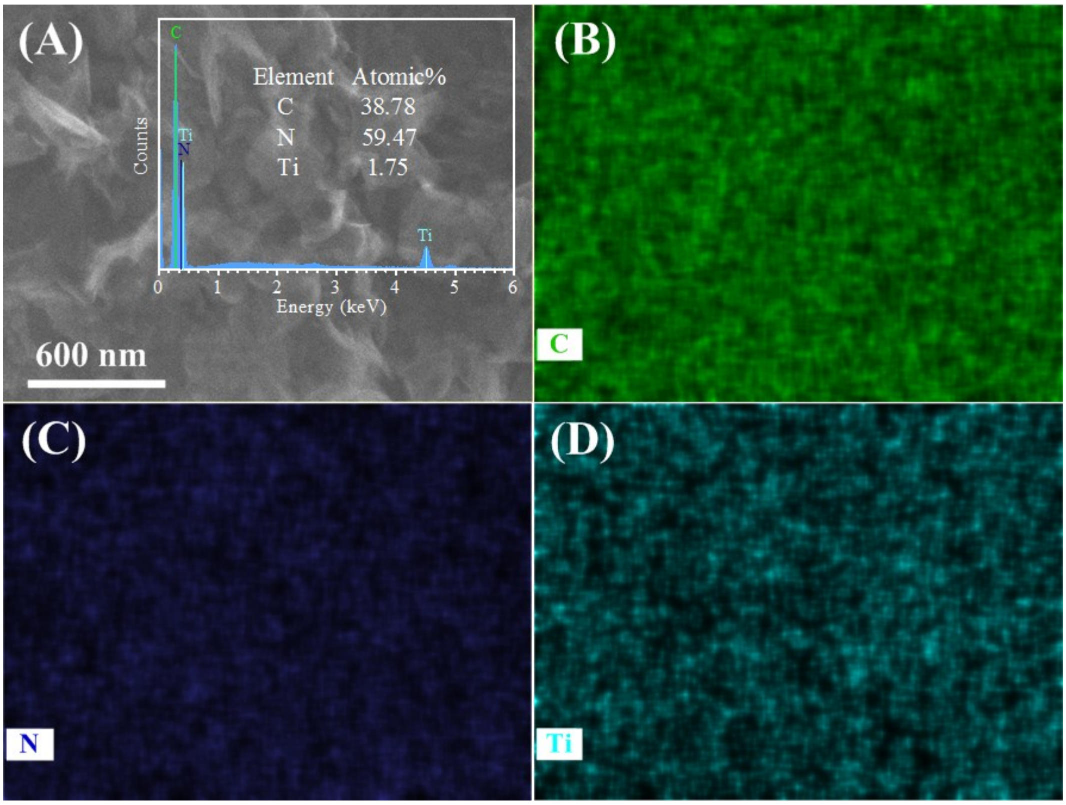

Figure S8. EDS spectrum and corresponding elemental mappings for 3-TC/CN.

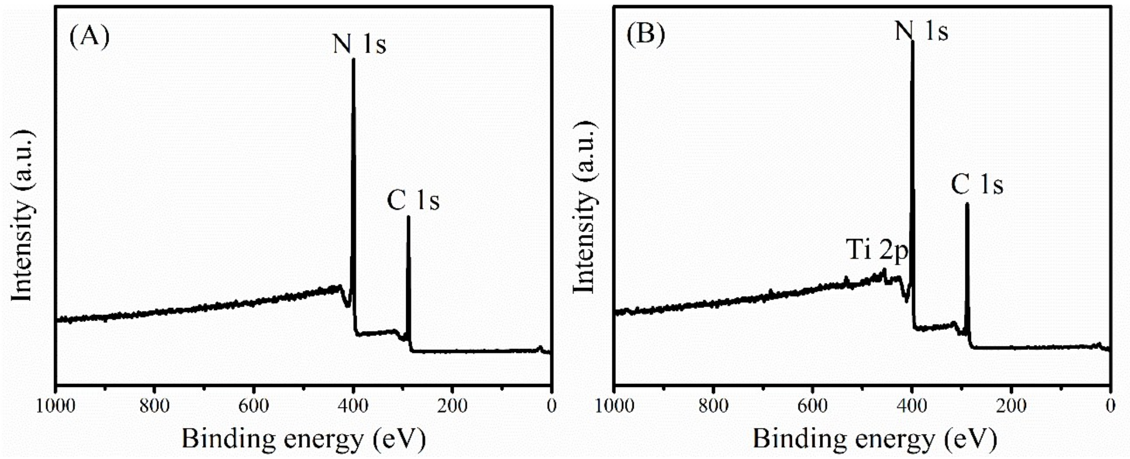

Figure S9. XPS survey spectra of g-C_3N_4 (A) and 3-TC/CN (B).

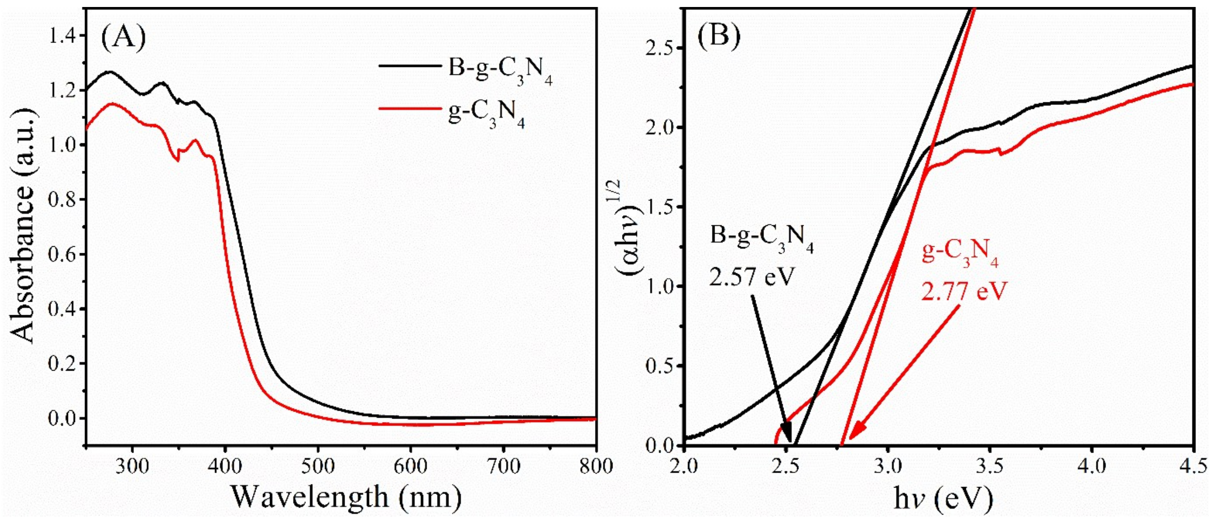

Figure S10. UV-vis absorption spectra and the corresponding Tauc plot of B-g-C_3N_4 and g-C_3N_4.

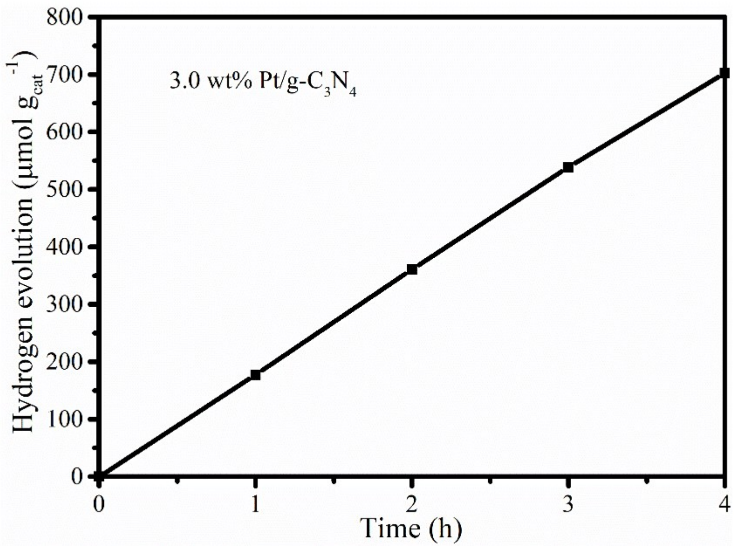

Figure S11. Photocatalytic hydrogen evolution over 3.0% Pt/g-C_3N_4.

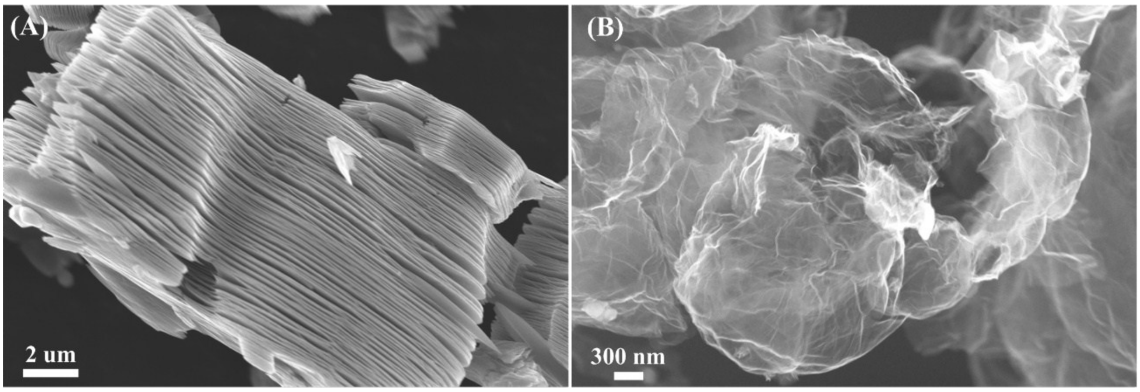

Figure S12. SEM images of multilayer Ti_3C_2 (A) and monolayer graphene (B).

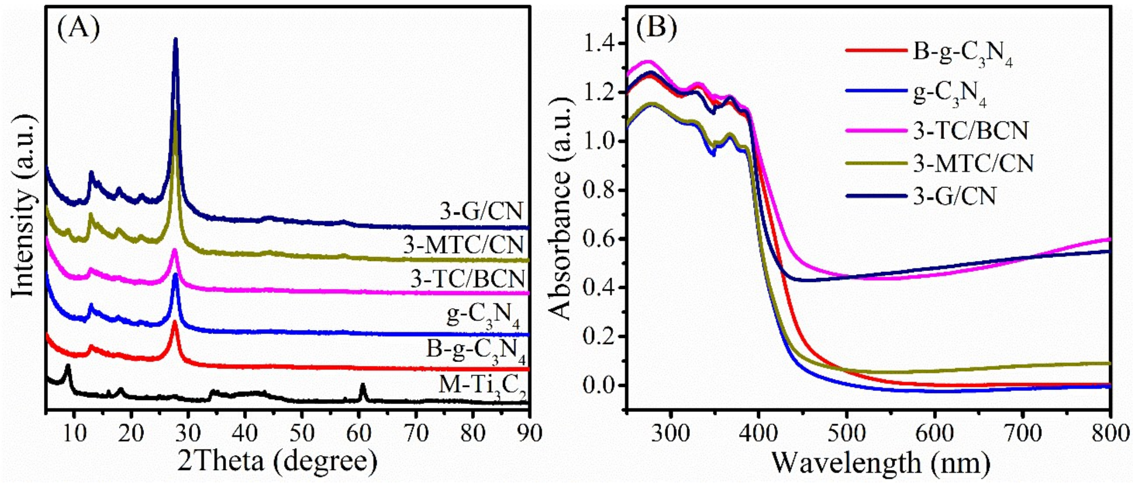

Figure S13. XRD patterns (A) and UV-vis absorption spectra (B) of B-g-C_3N_4, g-C_3N_4, 3-TC/BCN, 3-MTC/CN, and 3-G/CN.

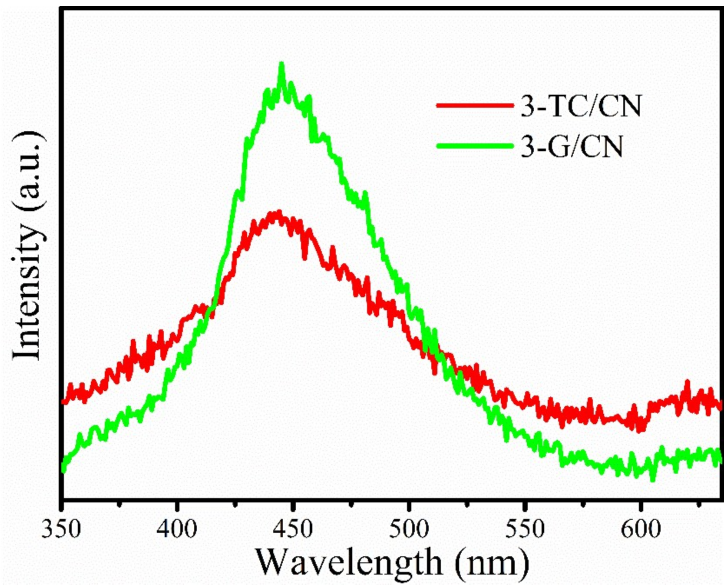

Figure S14. PL spectra of 3-TC/CN and 3-G/CN.

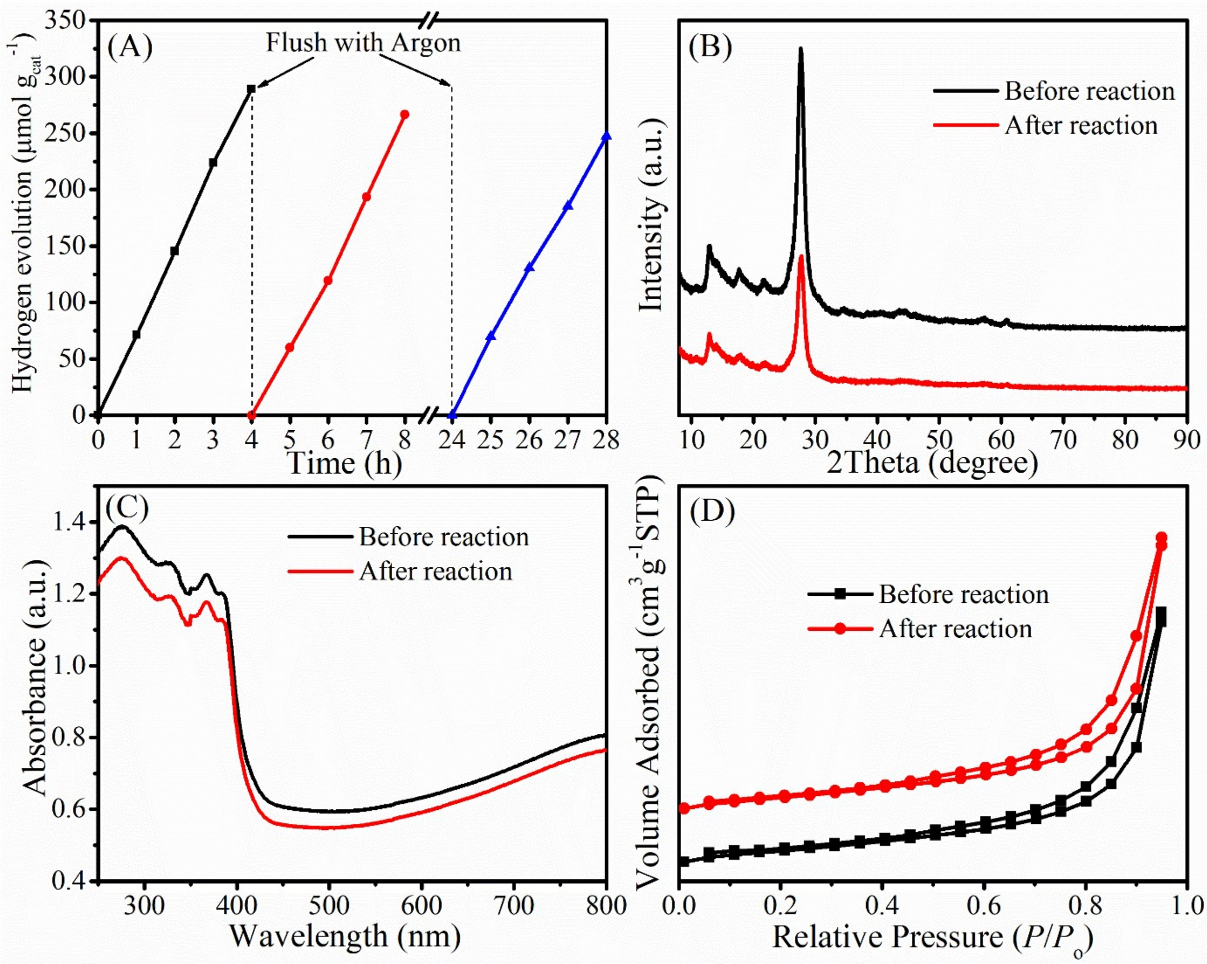

Figure S15. Stability of photocatalytic hydrogen production over 3-TC/CN (A); XRD patterns (B), UV-vis absorption spectra (C), and N_2 adsorption-desorption isotherms (D) of 3-TC/CN before and after reaction.

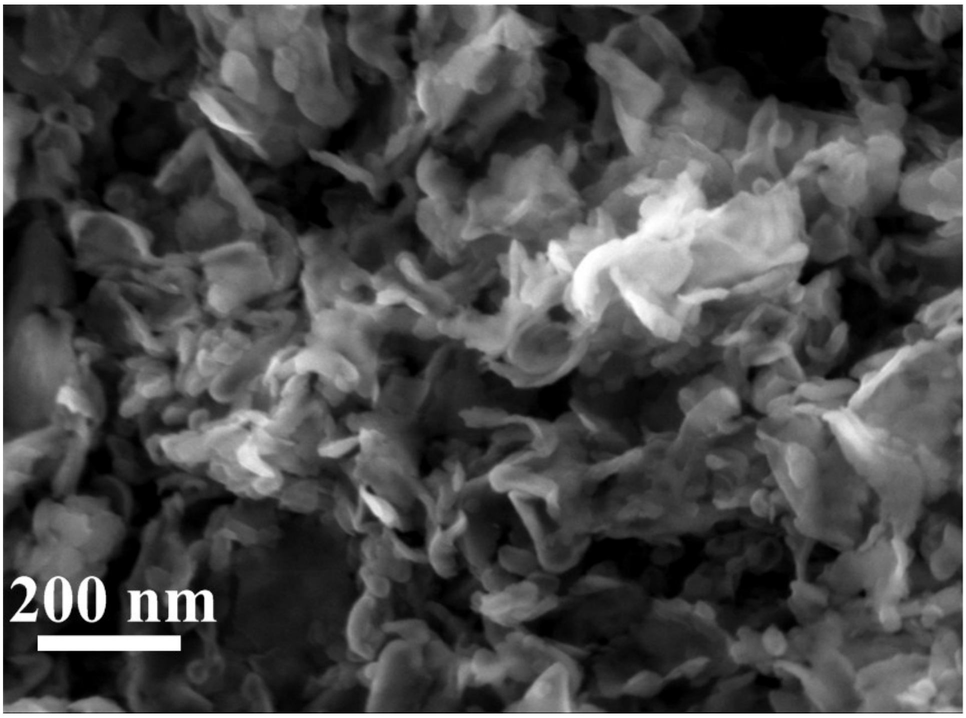

Figure S16. SEM image of 3-TC/CN after reaction.

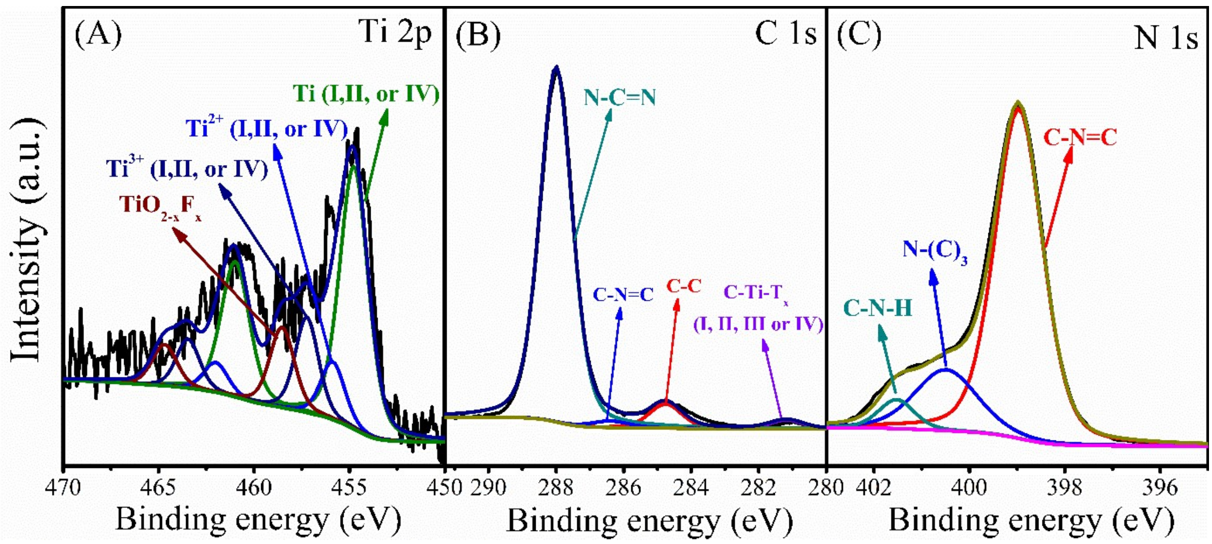

Figure S17. XPS spectra of Ti 2p (A), C 1s (B) and N 1s (C) peaks in 3-TC/CN after reaction.

Table S1. BET specific surface areas of the different photocatalysts in this study.

Sample	BET specific surface area [$m^2\ g^{-1}$]
B-g-C_3N_4	58.0
g-C_3N_4	153.6
P-g-C_3N_4	79.0
1-TC/CN	73.8
2-TC/CN	76.6
3-TC/CN	82.0
4-TC/CN	83.1
5-TC/CN	84.3

Table S2. Results from XPS peak fitting for 3-TC/CN.

Region	BE [eV][a)]	Assigned to	Reference
Ti $2p_{3/2}$($2p_{1/2}$)	454.9 (461.2)	Ti (I,II, or IV)	1
	455.9 (462.0)	Ti^{2+}(I,II, or IV)	1
	457.2 (463.4)	Ti^{3+}(I,II, or IV)	1
	459.4 (465.6)	$TiO_{2-x}F_x$	1
C 1s	281.4	C-Ti-T_x(I, II, III or IV)	1
	284.8	C-C	2
	286.8	C-N=C	2
	288.0	N-C=N	3, 4
N 1s	399.0	C-N=C	2, 4
	400.5	N-$(C)_3$	2
	401.5	C-N-H	2, 4

a) (Values in parentheses correspond to the $2p_{1/2}$ component)

Table S3. Results from XPS peak fitting for 3-TC/CN after reaction.

Region	BE [eV][a)]	Assigned to	Reference
Ti $2p_{3/2}$($2p_{1/2}$)	454.8 (460.9)	Ti (I,II, or IV)	1
	455.9 (462.0)	Ti^{2+}(I,II, or IV)	1
	457.3 (463.5)	Ti^{3+}(I,II, or IV)	1
	458.6 (464.7)	$TiO_{2-x}F_x$	1
C 1s	281.2	C-Ti-T_x(I, II, III or IV)	1
	284.8	C-C	2
	286.4	C-N=C	2
	288.0	N-C=N	3
N 1s	399.0	C-N=C	2
	400.5	N-$(C)_3$	2
	401.5	C-N-H	2

[a)] (Values in parentheses correspond to the $2p_{1/2}$ component)

Table S4. Hydrogen evolution rates of Ti_3C_2/g-C_3N_4 composites and their corresponding AQY.

Sample	Hydrogen production rate (μmol h^{-1} g_{cat}^{-1})	AQY(%)
g-C_3N_4	7.1	0.08
1-TC/CN	25.8	0.29
2-TC/CN	56.6	0.63
3-TC/CN	72.3	0.81
4-TC/CN	42.5	0.47
5-TC/CN	12.6	0.14
3-TC/BCN	19.5	0.22
3-MTC/CN	33.9	0.38
3-G/CN	20.7	0.23

In this work, the cut-off of the visible light filter is greater than 400 nm. Hence, we use 400 nm as the wavelength as the solar simulated light source.

The energy of photon (E_{ph}) can be calculated by Equation (1).

$$E_{ph} = hv = \frac{hc}{\lambda} \quad (1)$$

where h is the Planck's constant (6.63×10^{-34} m^2kg/s), v is frequency, c is the speed of light (3×10^8 m/s), and λ is the wavelength of the light source (400 nm). The energy of photon for light source is determined to be 4.97×10^{-19} J.

The number of the photons (N_{ph}) irradiating per second on the reactor can be calculated by Equation (2).

$$N_{ph} = \frac{\Phi}{Eph} \quad (2)$$

where Φ is the light intensity (1.51 W, measured by a Newport 843-R power meter) hitting on the quartz reactor, E_{ph} is the energy of photon.

The number of electrons (N_e) that are effectively participated in the photocatalytic reaction can be determined from the hydrogen yield and are shown in Equation (3).

$$N_e = \text{hydrogen yield per hour} \times 2 \times \text{Avogadro's number} \qquad (3)$$

where hydrogen yield per hour is calculated by using the hydrogen yield to divide the corresponding number of hours.

The apparent quantum yield (AQY) can be calculated according to Equation (4).

$$\text{AQY [\%]} = \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \times 100\% = \frac{Ne}{Nph \times 3600} \times 100\% \qquad (4)$$

References:

1. J. Halim, K. M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen and M. W. Barsoum, Appl. Surf. Sci., 2016, **362**, 406-417.
2. X. Yue, S. Yi, R. Wang, Z. Zhang and S. Qiu, Sci. Rep., 2016, **6**, 22268.
3. Q. Y. Lin, L. Li, S. J. Liang, M. H. Liu, J. H. Bi and L. Wu, Appl. Catal. B: Environ., 2015, **163**, 135-142.
4. L. Shen, Z. Xing, J. Zou, Z. Li, X. Wu, Y. Zhang, Q. Zhu, S. Yang and W. Zhou, Sci. Rep., 2017, **7**, 41978.