Supporting Information

TiO_2/Ti_3C_2 intercalated with g-C_3N_4 nanosheets as 3D/2D ternary heterojunctions photocatalyst for enhanced photocatalytic reduction of nitrate with high N_2 selectivity in aqueous solution

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S1. Experimental section

Materials

The Ti_3AlC_2 powder was produced by Beijing Forsman Technology Co., Ltd. 49 % HF aqueous solution was produced by Sinopharm Chemical Reagent Co., Ltd. Urea, KNO_3 and Rhodamine B (RhB) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Formic acid aqueous solution was obtained from Tianjin Fuchen Chemical Reagent Factory. Nitrogen (N_2, 99.99 %) was supplied by Qingdao Heli Gas Co., Ltd. All solvent used in this study was deionized (DI) water, which generated by the instrument of SW AC–520, Japan. All materials were used directly without further treatment.

Characterizations

The typical morphology and microstructure of the composites were observed by a scanning electron microscope (SEM, Hitachi S4800 and JSM-6510LV) and a transmission electronic microscopy (TEM, FET Tecnai G2 F20). X-ray diffraction (XRD) patterns were characterized by an X-ray diffractometer (D8 ADVANCE, Bruker). Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 670) were obtained to study the chemical structure of samples. X-ray photoelectron spectra (XPS, Escalab 250xi, Thermo Scientific) were obtained to reveal the situation of the surface chemical state and composition of photocatalysts. The information of Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) of the materials was obtained by nitrogen adsorption apparatus (ASAP2020, Micromeritics). The corresponding pore size distribution curves were characterized by the Barret-Joyner-Halender (BJH) method. The UV-vis diffused reflectance spectra (DRS) of the samples were described by UV-vis spectrophotometer (UV2550, Shimadzu).

Transient photocurrent responses (TPR), electrochemical impedance spectroscopy (EIS), and Mott-Schottky (M-S) plots were characterized by electrochemical workstation (CHI760e Instruments). The prepared samples, Ag/AgCl electrode and platinum-wire electrode were taken as the working electrodes, reference electrode and counter electrode, respectively. In the process of electrochemical measurements, the slurry of photocatalysts were coated onto the indium tin oxide (ITO) conductive glasses to effect as the working electrodes. During the experiments of TPR, the 300 W Xenon lamp was used as the light source. The M-S plots were tested at the frequency varying from 1000 to 2000 Hz.

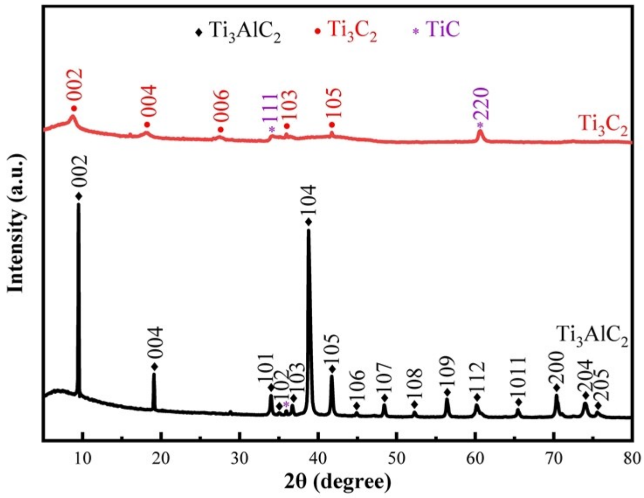

Fig. S1. XRD patterns of Ti_3AlC_2 and Ti_3C_2.

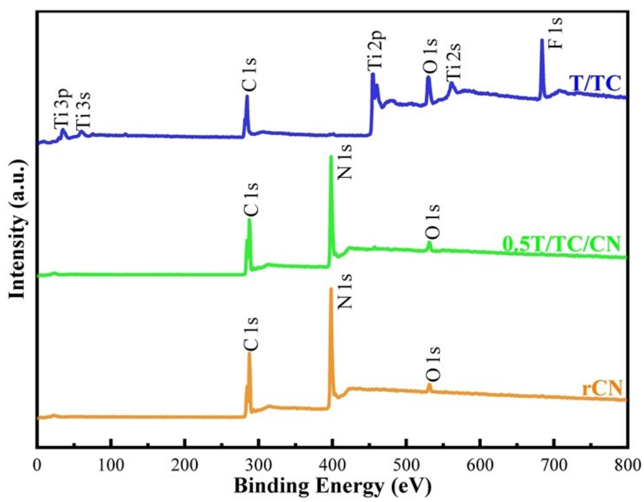

Fig. S2. XPS survye spectra of rCN, T/TC and 0.5T/TC/CN samples.

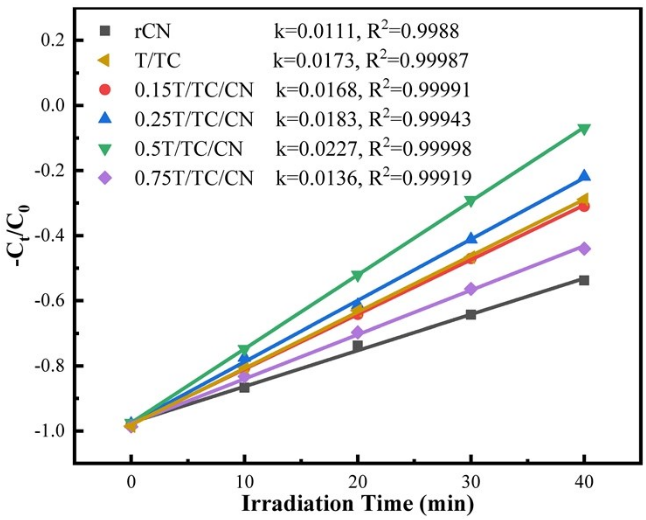

Fig. S3. Kinetic fit for the photocatalytic reduction of nitrate with different photocatalysts.

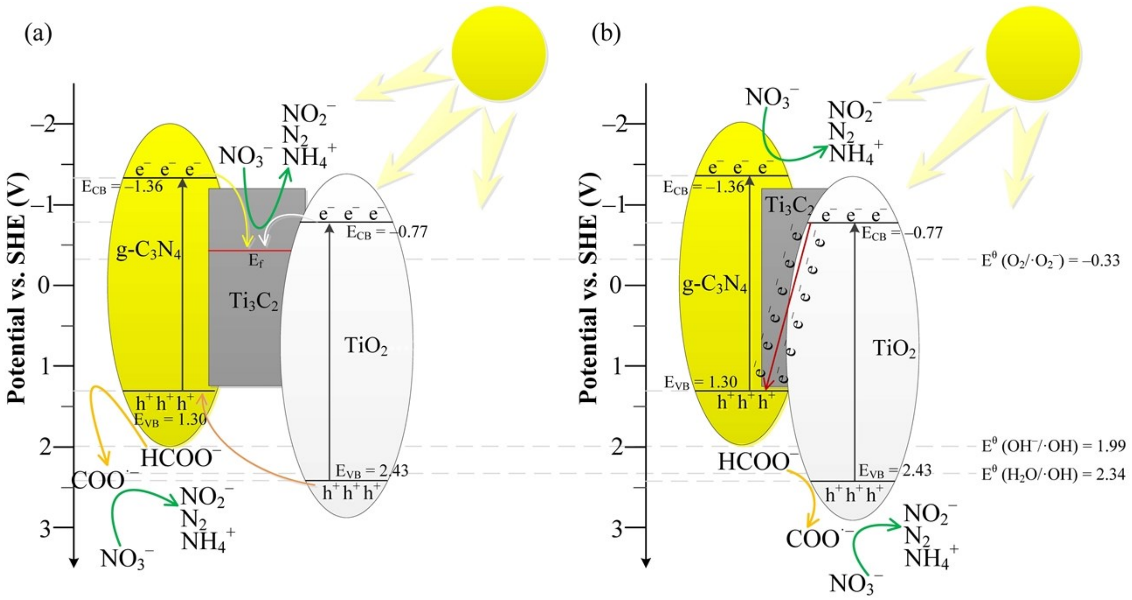

Fig. S4. The possible mechanisms for photocatalytic reduction of nitrate and charge transfer pathways over 0.5T/TC/CN: II-scheme heterojunction (a) and Z-scheme heterojunction (b).

Table S1. Photocatalytic reduction of nitrate in previous literatures.

Photocatalysts	$[NO_3^{-}\text{-}N]_0$ /($mg_N \cdot L^{-1}$)	Hole scavenger	Conversion (%)	Irradiation time/(min)	Selectivity (%)			Ref.
					NO_2^{-}-N	NH_4^{+}-N	N_2	
Mn_2O_3/g-C_3N_4	20	Magnetic field	94.5	120	-	-	93.2	1
Pd/$GdCrO_3$	8.4	Formic acid	98.7	100	0	0	100	2
AgCl/TNT	8.4	Formic acid	94.5	30	0.2	7.1	92.9	3
TiO_2(P90)	100	Formic acid	＞88	-	-	-	＞94	4
Ag/TiO_2(25)	100	Formic acid	71.7	30	11.5	0.167	83.7	5
TiO_2(P25)	11.2	Formic acid	52.5	120	23	6	38.1	6
Pt-Cu/TiO_2	14	Benzene	63.3	240	1	1	90	7

Photocatalysts	**$[NO_3^--N]_0$ /($mg_N \cdot L^{-1}$)**	**Hole scavenger**	**Conversion (%)**	**Irradiation time/(min)**	**Selectivity (%)**			**Ref.**
					NO_2^--N	**NH_4^+-N**	**N_2**	
TiO_2(P25)	3.5	Bio-electrons	60	1440	0	4	96	8
Cu/TiO_2(P25)	10	Glycerol	98	120	0	2	98	9
Cu/TiO_2	8.4	Formic acid	93.73	120	-	-	0	10
Cu_2O/TiO_2(P25)	22.4	Oxalic acid	57.6	180	12.4	45.7	41.9	11
Pt/TiO_2+SnPd/Al_2O_3	14	Glucose	23	720	3	22	75	12
Ag/TiO_2(P25)	100	Formic acid	100	180	0	4	96	13
Ag/TiO_2(P25)	100	Formic acid	99.6	240	2.3	9.3	88.4	14
Pd-Cu/TiO_2(P25)	22.4	CO_2+H_2+Humic acid	100	240	0	<2	> 98	15
Pd-Cu/TiO_2(P25)	11.2	H_2+Formic acid	39-100	60	0	0-13.7	86.3-	16

Photocatalysts	**$[NO_3^{-}\text{-}N]_0$ /$(mg_N \cdot L^{-1})$**	**Hole scavenger**	**Conversion (%)**	**Irradiation time/(min)**	**Selectivity (%)**			**Ref.**
					NO_2^{-}-N	**NH_4^{+}-N**	**N_2**	
							100	
Sn-Pd/Pt/TiO_2(P25)	140	Ethanol	23	240	0	24	76	17

Table S2. Texture properties of the prepared photocatalysts.

Photocatalysts	S_{BET} ($m^2 \cdot g^{-1}$)	V_{pore} ($cm^3 \cdot g^{-1}$)	D_{pore} (nm)
rCN	90.4175	0.486570	21.52549
T/TC	7.6879	0.034164	17.77535
0.5T/TC/CN	30.1255	0.166963	22.16890

Table S3. Performance of photocatalytic nitrate reduction over different photocatalysts..

Photocatalysts	Conversion of NO_3^{-}-N (%)	Yield of NO_2^{-}-N ($mg_N \cdot L^{-1}$)	Yield of NH_4^{+}-N ($mg_N \cdot L^{-1}$)	Selectivity of N_2 (%)
rCN	46.23	4.04	2.91	84.99
T/TC	71.13	1.08	2.70	94.67
0.15T/TC/CN	69.00	2.46	2.70	92.30
0.25T/TC/CN	78.13	1.11	6.04	90.51
0.5T/TC/CN	93.03	0.56	3.21	96.62
0.75T/TC/CN	55.99	3.6	2.32	88.77

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