Electronic Supplementary Information

Heterojunctions in g-C_3N_4 and TiO_2(B) Nanofibres with Exposed (001) Plane and Enhanced Visible-Light Photoactivity

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NCLS calculation and rational selection between g-C_3N_4 and TiO_2 nanofibres

In view of crystallography, planar matching between the two involved phases must obey a basic rule that there are some planes roughly parallel to each other and sharing similar planar spacing. It is known that g-C_3N_4 is a graphite-type 2-dimensional six-fold symmetric layered material with lattice parameter of a = 1.42 nm. Near coincidence site lattice (NCSL) is a traditional and powerful crystallographic conception for phase transformations. NCSL is a super lattice at the interface between two adjacent phases and is the structure of the interface. The NCSL is two-dimensional periodic lattice wish a certain symmetry and a certain coincidence site mutliplicity (Σ) which is inversely to interfacial energy.

Here, TiO_2(B) and anatase are used for comparison. The crystal structures of TiO_2(B), anatase and g-C_3N_4 are shown in Table S1. Based on our previous study [1,2], as shown in Figure S1, the exposal plane of TiO_2(B) nanofibre is (001) and that of anatase is (100).

Table S1 Crystal structures of TiO_2(B), anatase and g-C_3N_4

Phase	Bravias lattice	Lattice parameters			
		a (nm)	b (nm)	c (nm)	Beta (°)
TiO_2(B)	Monoclinic	1.192	0.374	0.651	107.29
anatase	Tetragonal	0.374	0.374	0.953	
g-C_3N_4	Hexagonal	1.420			

The NCSL lattice of two phases can be generated as follows. As shown in Scheme S1A, the unit cell of phase 1 (2) in orthogonal coordinates has the two basic vectors, where phase 1 is TiO2(B) or Anatase, and phase 2 is g-C3N4.

Phase 1: $R_1 = [a,0]$, $R_2 = [0,b]$

Phase 2: $R_1' = [c,0]$, $R_2' = [0,d]$

The schematic illustration of an arbitrary superlattice of phase 1 (2) is displayed in Scheme S1B.

Phase 1: $V_1 = mR_1 + nR_2 = [ma, nb]$, $V_2 = [nb, -ma]$, and $V_2 \perp V_1$

Phase 2: $V_1' = pV_1' + qV_2' = [pc, qd]$, $V_2' = [qd, -pc]$, and $V_2' \perp V_1'$

If phase 2 is able to superimpose over the super lattice of phase 1, the superlattice of phase 2 has to rotate a special angle θ and the rotated phase 2 has two basic vectors:

Phase 2: $V_1'' = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos \end{pmatrix} V_1' = \begin{bmatrix} pc\cos\theta - qd\sin\theta \\ pc\sin\theta + qd\cos\theta \end{bmatrix}$,

$$V_2'' = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} V_2' = \begin{bmatrix} pc\sin\theta + qd\cos\theta \\ qd\sin\theta - pc\cos\theta \end{bmatrix}, \text{ and } V_2'' \perp V_1''$$

It could be deduced that since both superlattices are overlapped,

$$V_1 // V_1'' ; V_2 // V_2''$$
$$|V_1| = |V_1''| ; |V_2| = |V_2''|$$

From $V_1 // V_1''$, we can get equation (1)

$$\begin{cases} pc\cos\theta - qd\sin\theta = ma \\ pc\sin\theta + qd\cos\theta = nb \end{cases} \text{ and } \ tg\theta = \frac{npbc - mqad}{mpac + nqbd} \qquad (1)$$

From $V_1 \perp V_1''$, we can get equation (2)

$$(ma)^2 + (nb)^2 = (pc\cos\theta - qd\sin\theta)^2 + (pc\sin\theta + qd\cos\theta)^2 \ \text{ and}$$

$$m^2a^2 + n^2b^2 = p^2c^2 + q^2d^2 \qquad (2)$$

The inverse of coincidence site mutliplicity (Σ) is the ratio of volume between unit cell and superlattice

$$\Sigma = \frac{V_{super-cell}}{V_{unit-cell}} = \frac{\sqrt{(ma)^2 + (nb)^2}\sqrt{(nb)^2 + (-ma)^2}}{ab} = \frac{(ma)^2 + (nb)^2}{ab} \qquad (3)$$

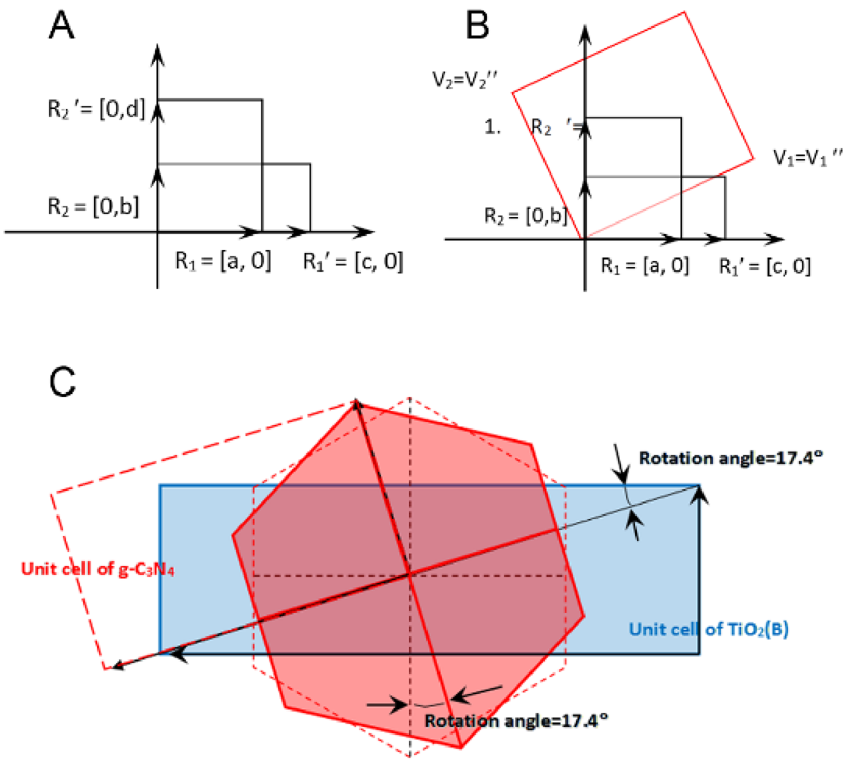
The equations (1)-(3) are the basic equations for NCSL lattice. It can be used for g-C_3N_4/TiO_2(B) and anatase/g-C_3N_4 systems. It is noticed that (001) plane of TiO_2(B) and (100) plane of anatase are both 2-fold symmetry while (001) plane of g-C_3N_4 is 6-fold symmetry. So the unit cell for g-C_3N_4 needs careful choosing so that the cell shows 2-fold symmetry. Thus, it can be chosen $R_1' = [2\bar{1}\bar{1}0] = [c, 0]$, $R_2' = [01\bar{1}0] = [0, \sqrt{3}c]$. The detailed parameters for calculation NCSL are shown in Table S2.

Table S2 NCSL calculation for systems TiO_2(B)/g-C_3N_4 and Anatase/g-C_3N_4

System	Unit cell		Unit cell		NCSL							
	Cell 1	Cell 2	Cell 1	Cell 2	Cell 1		Cell 2		Σ	Rotation Angle	TEM result	Diffe.
	R_1	R_2	R_1'	R_2'	m	n	p	q				
TiO_2(B)/g-C_3N_4	$(a,0)$	$(0,b)$	$(c,0)$	$(0,d)$	2	2	0	1	7	$tg\theta = a/$ θ=17.4°	17.4°	0.0°
Anatase/g-C_3N_4	$(a,0)$	$(0,b)$	$(c,0)$	$(0,d)$	0	3	1	1	23	$tg\theta = c/$ θ=30°	N/A	N/A

Remarks: a=0.374 nm, b=1.192 nm, c=1.42 nm, d=c$\sqrt{3}$=2.46nm.

Obviously, the coincidence site density 1/Σ of TiO_2(B)/g-C_3N_4 system is much lower than that of anatase/g-C_3N_4 system. It is expected that the TiO_2(B)/g-C_3N_4 system is more favorite and stable than the anatase/g-C_3N_4 system. It is also predicted a rotation angle θ=17.4° between TiO_2(B) and g-C_3N_4. This is the induced angle between [010]TiO_2(B) and [2-1-10] g-C_3N_4. That means there must be a pair of planes parallel and sharing same planar spacing. The departure angle of plane (110) and (020) is exactly 17.4°. The planar spacing of plane (110) is 0.355nm, the same as (22-40) plane. Scheme S1C shows such prediction of orientation relationship between TiO_2(B) and g-C_3N_4. This is well coincident with TEM experimental observation.



Scheme S1. (A) the unit cell of phase 1 (2) in orthogonal coordinates. (B) an arbitrary superlattice of phase 1 (2). (C) prediction of orientation relationship between TiO_2(B) and $g-C_3N_4$.

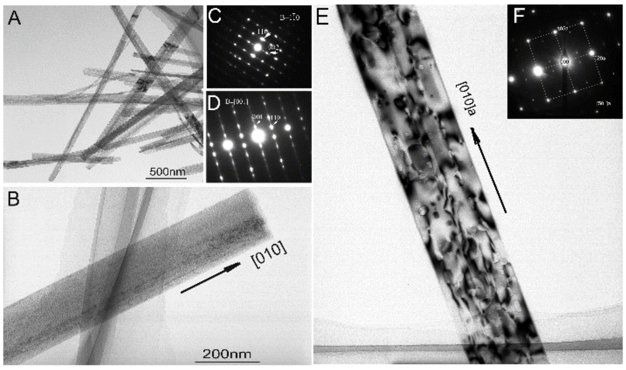


Fig. S1 TEM image of TiO_2(B) with exposed (001) plane (A,B,C,D) and anatase fibers with exposed (100) plane (E,F).

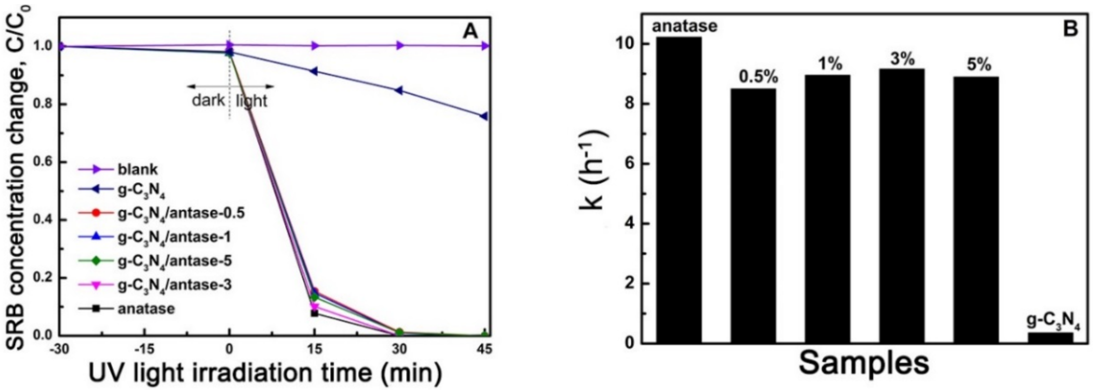


Fig. S2 (A) Photocatalytic degradation of SRB (C_0 = 25μmol L^{-1}) under UV light irradiation. (B) Average reaction rate constants *k* for photodegradation on SRB over g-C_3N_4/TiO_2(anatase) samples with different mass rations.

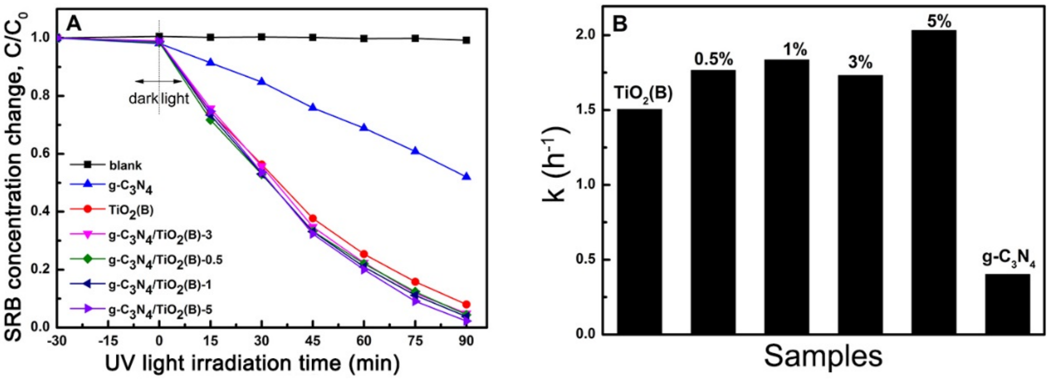


Fig. S3 (A) Photocatalytic degradation of SRB (C_0 = 25 μmol L^{-1}) under UV light irradiation. (B) Average reaction rate constants *k* for photodegradation on SRB over g-C_3N_4/TiO_2(B) samples with different mass ratios.

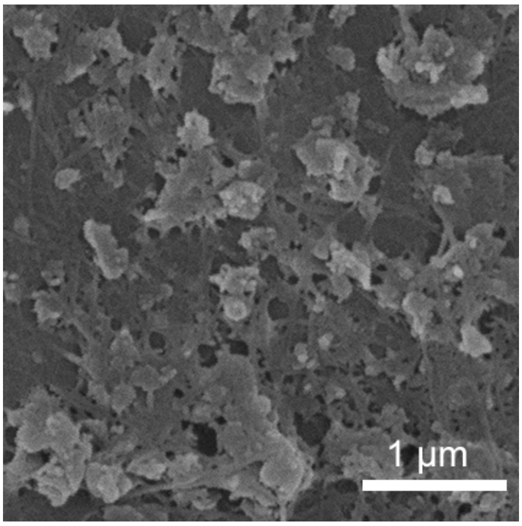


Fig. S4 SEM of the g-C_3N_4 after sonication

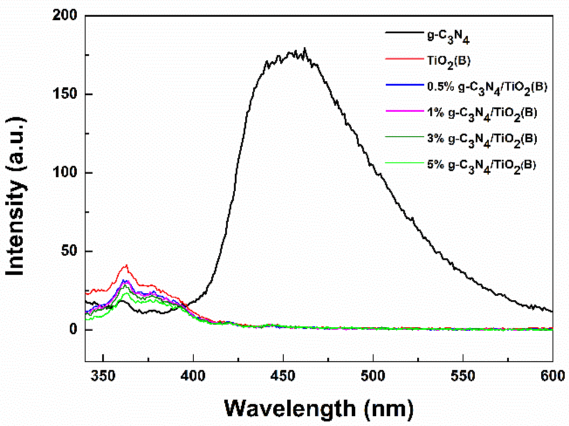


Fig. S5 Room -temperature photoluminescence spectra of the g-C_3N_4, TiO_2(B) and g-C_3N_4/TiO_2(B) samples under 324 nm excitation.

References

1. D. J. Yang, J. Zhao, H. W. Liu, Z. F. Zheng, M. O. Adebajo, H. X. Wang, X. T. Liu, H. J. Zhang, J. C. Zhao, J. Bell and H. Y. Zhu, *Chem. Eur. J.*, 2013.
2. D. J. Yang, H. W. Liu, Z. F. Zheng, Y. Yuan, J. C. Zhao, E. R. Waclawik, X. B. Ke and H. Y. Zhu, *J. Am. Chem. Soc.*, 2009, **131**, 17885.