

## Electronic Supplementary Information (ESI)

### New insights into interfacial photocharge transfer in $\text{TiO}_2/\text{C}_3\text{N}_4$ heterostructures: effects of facet and defect

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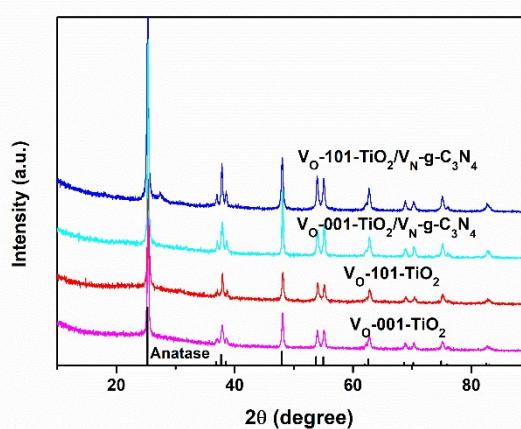
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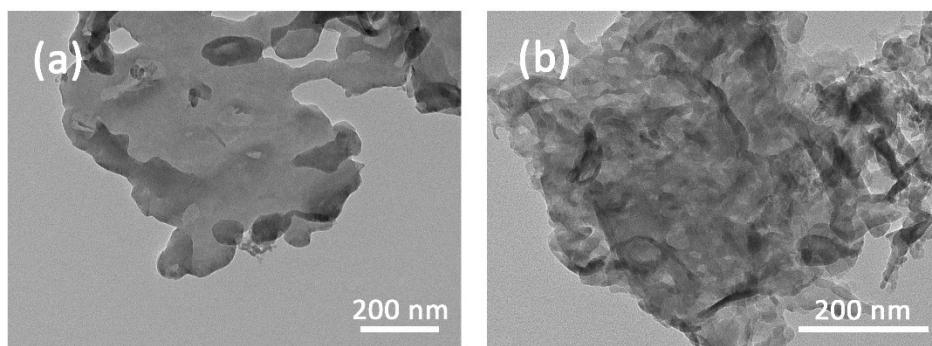
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**Fig. S1.** XRD patterns of different types of  $\text{V}_2\text{O}_5\text{-}\text{TiO}_2$  and  $\text{V}_2\text{O}_5\text{-}\text{TiO}_2/\text{V}_N\text{-g-C}_3\text{N}_4$  heterostructures.



**Fig. S2.** TEM images of  $\text{g-C}_3\text{N}_4$  (a) and  $\text{V}_N\text{-g-C}_3\text{N}_4$  (b).

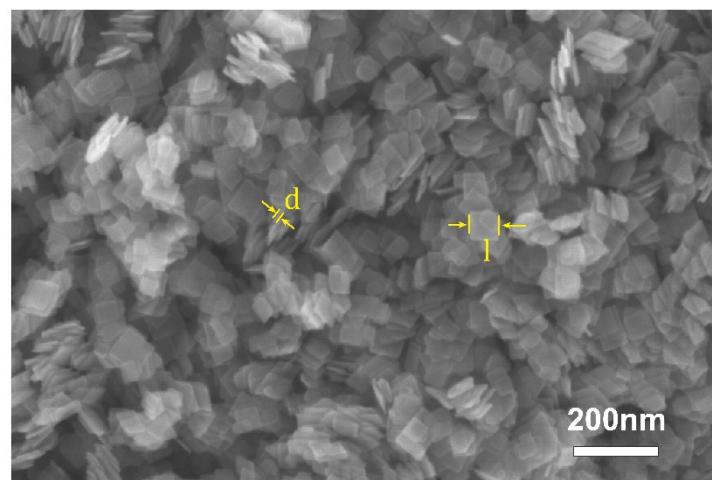
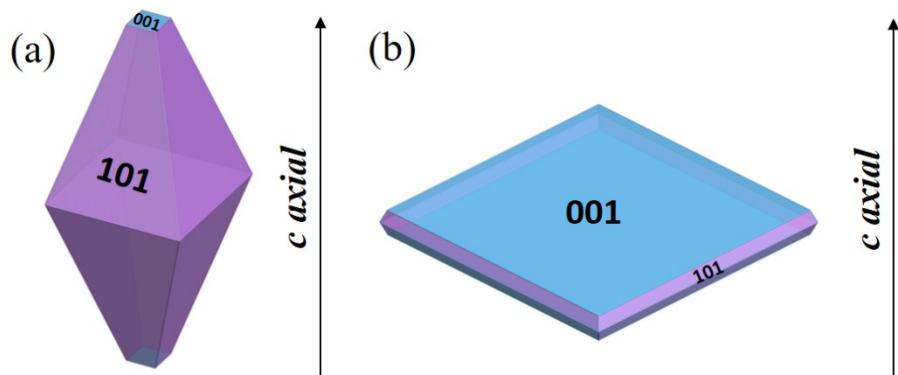
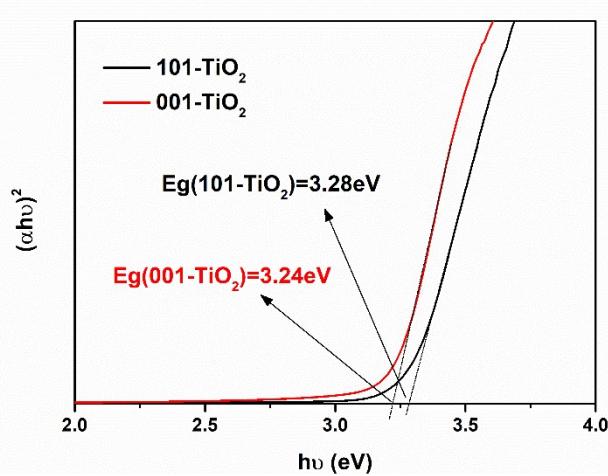


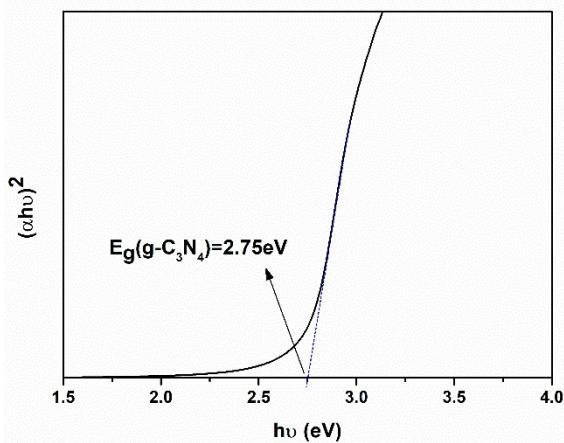
Fig. S3. SEM image of 001-TiO<sub>2</sub> nanosheets. The average length (l) and average thickness (d) of nanosheets are determined to be 55 and 5nm, separately.



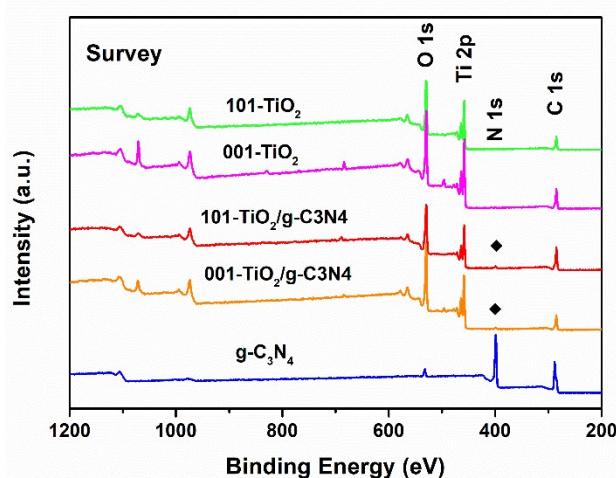
**Fig. S4.** Schematic illustration of 101-TiO<sub>2</sub> (a) and 001-TiO<sub>2</sub> (b).



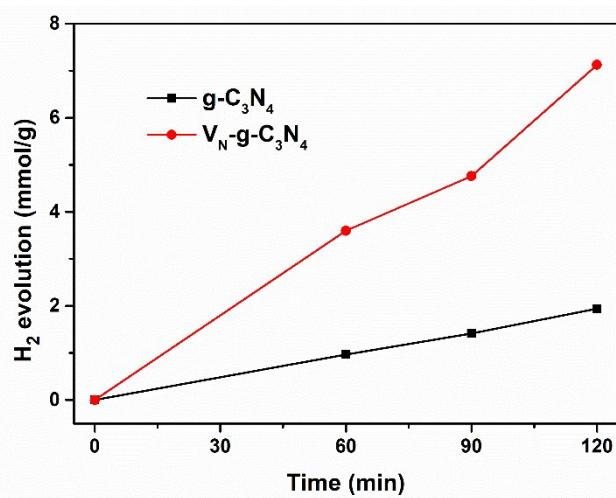
**Fig. S5.** Kubelka-Munk function curves plotted against photon energy for 101- and 001-faceted TiO<sub>2</sub>.



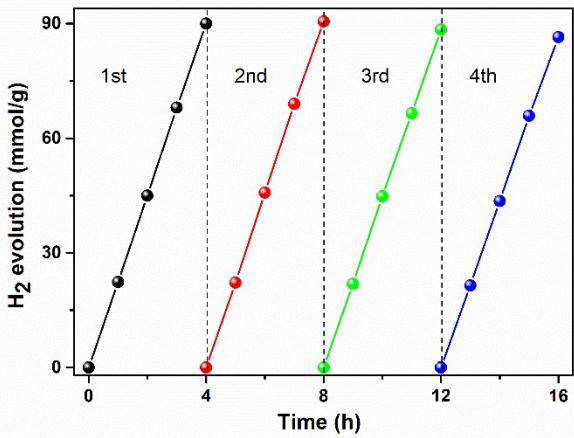
**Fig. S6.** Kubelka-Munk function curve plotted against photon energy for  $g\text{-C}_3\text{N}_4$ .



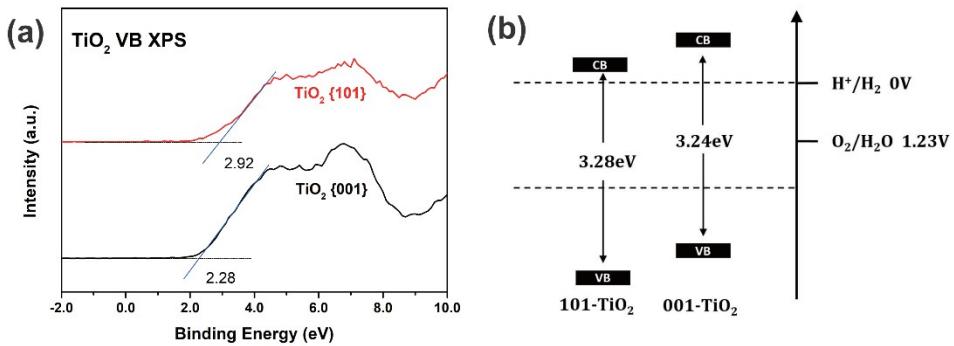
**Fig S7.** XPS survey spectra of  $g\text{-C}_3\text{N}_4$ , 101-TiO<sub>2</sub>, 001-TiO<sub>2</sub>, 101-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> and 001-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>.



**Fig. S8.** Time course of photocatalytic H<sub>2</sub> evolution over  $g\text{-C}_3\text{N}_4$  and  $V_N\text{-}g\text{-C}_3\text{N}_4$ .



**Fig. S9.** The recyclability tests of the  $\text{V}_\text{O}$ -101- $\text{TiO}_2$ / $\text{V}_\text{N}$ -g- $\text{C}_3\text{N}_4$  for hydrogen evolution.



**Fig. S10.** (a) Valence-band (VB) XPS spectra of 101- and 001-faceted  $\text{TiO}_2$ . (b) Band positions of 101- $\text{TiO}_2$  and 001- $\text{TiO}_2$ .

**Table S1.** Calculated facet percentage of 101- $\text{TiO}_2$  and 001- $\text{TiO}_2$

Sample	$\text{l}/\text{nm}$	$\text{d}/\text{nm}$	{001} facets %	{101} facets %
101- $\text{TiO}_2$	13	24	2.7	97.3
001- $\text{TiO}_2$	55	5	82.8	17.2

**Table S2.** Elemental analysis of g- $\text{C}_3\text{N}_4$  and  $\text{V}_\text{N}$ -g- $\text{C}_3\text{N}_4$

Samples	N (wt%)			C (wt%)	C/N mole ratio
	C-N-C	N-(C) <sub>3</sub>	C-N-H <sub>x</sub>		
g- $\text{C}_3\text{N}_4$	21.03	25.09	12.36	41.52	0.710
$\text{V}_\text{N}$ -g- $\text{C}_3\text{N}_4$	33.00	15.53	8.19	43.18	0.761