Supporting information for

**Photocatalytic Properties of Graphdiyne and Graphene Modified TiO₂: From
Theory to Experiment**

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Table S1 Super cell parameters and mismatches of the composites

	a (Å)	b (Å)	c (Å)	Mismatch (%)
TiO ₂ (101)-GD	9.85	16.71	25	3.82
TiO ₂ (110)-GD	9.49	16.22	25	0
TiO ₂ (001)-GD	18.93	15.77	25	4.02
TiO ₂ (101)-GR	10.02	21.98	25	3.17
TiO ₂ (110)-GR	10.36	10.36	25	5.31
TiO ₂ (001)-GR	21.98	11.80	25	4.04

Figure S1 Structure of TiO₂-GD and TiO₂-GR composites

Table S2 Bond length of C-O and Ti-C, band gap and Fermi energy of the composites

	C-O bond length range(Å)	Ti-C bond length range(Å)	Band gap (eV)	Fermi energy (eV)
(001)-GD	1.354~1.433	2.223~2.235	1.77	-5.19
(110)-GD	1.379~1.441	No bond	1.61	-4.99
(101)-GD	1.399~1.511	No bond	2.33	-5.41
(001)-GR	1.466~1.486	No bond	1.60	-4.82
(110)-GR	No bond	No bond	1.54	-5.62
(101)-GR	No bond	No bond	1.32	-5.51

Figure S2 The band structure and partial density of states for the composites, the Fermi energy is set as zero, (a) $\text{TiO}_2(101)\text{-GD}$, (b) $\text{TiO}_2(110)\text{-GD}$, (c) $\text{TiO}_2(101)\text{-GR}$, (d) $\text{TiO}_2(110)\text{-GR}$, The red lines represent CBM and VBM position of the composites.

Figure S3 characterization of the anatase TiO₂ nanosheets with exposed (001) facets.

SEM (a), TEM (b), and HR-TEM (c) images of the nanosheets, and (d) is the SAED pattern of (001) TiO₂.

Figure S4 Raman spectra of (a) $\text{TiO}_2(001)$, (b) $\text{TiO}_2(001)\text{-GR}$ and (c) $\text{TiO}_2(001)\text{-GD}$.

Figure S4 presents the Raman spectra of $\text{TiO}_2(001)$, $\text{TiO}_2(001)\text{-GR}$ and $\text{TiO}_2(001)\text{-GD}$. The $\text{TiO}_2(001)$ shows the distinct Raman bands at 143, 196, 395, 516 and 637 cm^{-1} . These bands can be attributed to the Raman-active modes of the anatase phase TiO_2 with the symmetries of E_g , E_g , B_{1g} , A_{1g} and E_g , respectively. It is obvious that there is no Raman bands of rutile phase TiO_2 (Figure S4a). The Raman peaks of $\text{TiO}_2(001)\text{-GD}$ at 1356 and 1593 cm^{-1} can be assigned to the vibration of aromatic rings of the GD substrates. The Raman spectrum of $\text{TiO}_2(001)\text{-GR}$ shows the presence of D, G and 2D bands at 1350 , 1604 and 2700 cm^{-1} , respectively. G band is common to all the sp^2 carbon forms and provides information on the in-plane vibration of sp^2 bonded carbon atoms. The D band suggests the presence of sp^3 defects, which indicates the successful chemical modification of the graphite sheets.

Moreover, the weak and broad 2D band also suggests the existence of disorder. The above results reveal the successfully combination of the carbon substrates with TiO₂(001) catalysts.

Figure S5 FTIR spectroscopy of TiO₂(001), TiO₂(001)-GD and TiO₂(001)-GR. The shifts toward the long wavenumber below 1000 cm⁻¹ in the composite materials indicate the formation of C-O-Ti bond.

Figure S6 Plot of the remaining methylene blue (MB) in solution treated with different samples: Initial and equilibrated with $\text{TiO}_2(001)$, $\text{TiO}_2(001)$ -GD, $\text{TiO}_2(001)$ -GR composites in the dark after 30 min stirring. These composites have similar BET surface areas, which are 13.18, 13.49 and 14.21 respectively. The increase absorption of MB is mainly due to the π - π stacking between 2D carbon sheets and MB molecules.

Figure S7 The high-resolution XPS C1s spectra of graphene oxide