Supporting Information

Interfacial co-existence of oxygen and titanium vacancies in nanostructured TiO2 for enhancement of the carrier transport

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Author Contributions

Y.L. and Y.X.L carried out the experiments. X.Y.Y. conceived the project, provided the idea, and designed and guided the experiments. B.L.S. conceived the project, supported scientific and technological platform. Y.X.L., L.H., and Y.Z.L helped with the measurements. X.L.L., L.Y.W. and J.W.L. helped with the NMR measurements and corresponding analysis. X.H.Y helped with the CO₂ reduction measurement. H.Z. and G.T. performed the TEM characterizations. Y.L and X.Y.Y. wrote and revised the paper. C.J. and S.L. revised the paper. All the authors discussed results and analyzed the data, and have given approval to the final version of the manuscript.

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Section 1. Experimental

1.1 Materials

Hexadecylamine (90%, Sigma-Aldrich) and titanium (IV) isopropoxide (TIP, 95%) were purchased from Aladdin Industrial Co., China. Other chemical reagents were of analytical grade and supplied from Sinopharm Chemical Reagent Co., Ltd., China. Graphene oxide (GO) was synthesized from graphite powder by the modified Hummers method.

1.2 Preparation of TiO₂ (first), TiO₂@rGO (first), TiO₂ and TiO₂@rGO

TiO₂ precursor was synthesized by the sol-gel method using hexadecylamine as a surfactant according to a previous report.¹⁶ In a typical procedure, 400 mg TiO₂ precursor was dispersed in a mixture of 20 mL ethanol and 20 mL H₂O. With stirring, a varying amount of the prepared GO dispersion was added into the above dispersion and autoclaved in a Teflon-lined stainless steel vessel at 180 °C for 12 h. The weight ratios of GO to TiO₂ precursor were 0.25 *wt*.%, 0.5 *wt*.%, 1.0 *wt*.%, 1.5 *wt*.%, 2.0 *wt*.%, and 5.0 *wt*.%. After cooling to room temperature, the obtained precipitates were collected and washed with ethanol and deionized water. The as-prepared samples were calcinated at 500 °C for 2 h in an Ar atmosphere (denoted as TiO₂@rGO (first)) and then at 350 °C for 1 h in an air atmosphere (denoted as TiO₂@rGO). For comparison, the TiO₂ (first) and TiO₂ were synthesized by the same procedure in the absence of GO.

*1.3 Preparation of TiO*₂*-rGO (core-shell structure without any vacancy)*

Thin layer reduced graphene oxide (rGO) ethanol solution was purchased from Nanjing XFNANO Materials Tech Co.,Ltd., China and used in this procedure only. To fabricate the coreshell structure of TiO₂-rGO without interfacial vacancy, different amount of TiO₂ were dispersed in diluted rGO ethanol solution with stirring for 30 min, filtered and collection. The weight ratios of rGO to TiO₂ were 0.25 *wt.*%, 0.5 *wt.*%, 1.0 *wt.*%, 1.5 *wt.*%, 2.0 *wt.*%, and 5 *wt.*%.

1.4 Preparation of rGO and $TiO_2+rGO(mix)$

The GO dispersion was hydrothermally treated at 180 °C for 12 h. After cooling to room temperature, the obtained precipitate was collected and calcinated at 500 °C for 2 h in an Ar atmosphere and then at 350 °C for 1 h in an air atmosphere (denoted as rGO). The $TiO_2+rGO(mix)$ composite was synthesized by mixing of TiO_2 and rGO through grinding.

Section 2. Characterization

The samples morphology observation was performed on a scanning electron microscope (SEM, S-4800, HITACHI), a transmission electron microscopy (TEM, JEOL-2100F) with a field emission gun operated at 200 kV. The powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 1.54182$ Å). The specific surface area was derived from N₂ sorptions measurements at -196 °C on a Micromeritics ASAP 3020 system according to the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated from the adsorption isotherm branch using the Barrett-Joyner-Halenda (BJH) method. Electron paramagnetic resonance (EPR) measurements were performed at the X-band using a JEOL FA 2000 spectrometer. The microwave frequency was 9.163 GHz, the modulation amplitude was 0.1 mT, the microwave power was 1 mW, and the experimental temperature was 295 K. 2D ¹H DQ MAS NMR spectra were carried out in a 1.9 mm MAS probe on a Bruker AVANCE-III 500 spectrometer with a sample spinning rate of 40 kHz, a ¹H $\pi/2$ pulse length of 1.75 us and a recycle delay of 5 s. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantera II, (ULVAC-PHI, Japan). For chemical composition analysis, all binding energies were calibrated to the C 1s peak at 284.8 eV. The photoluminescence spectra (PL) were recorded on an LS55 (PERKIN-ELMER) with an excitation wavelength of 230 nm. UV-vis di □use reflection spectrum(UV-vis DRS) was measured on a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). Time-resolved photoluminescence emission spectra (TRPL) were recorded at 410 nm with a 286 nm excitation on a fluoromax-4 spectrofluorometer (HORIBA Scientific). Thermogravimetric analyses (TGA, NETZSCH STA 449F3) were performed in the range of 30-1000 °C at a heating rate of 5 °C min⁻¹.

Section 3. Photocatalytic H₂ production experiment

Photocatalytic H₂ production was performed in a closed circulation system using a PLS-SXE-300C lamp (Beijing perfectlight Technology Co., Ltd.) with a UV-vis light (λ =320-780nm) intensity of *ca*. 158 mW cm⁻². The lamp was 10 cm away from the reaction solution. All the samples were loaded with 0.5 *wt*.% Pt by an *in situ* photo-deposition method. A portion of 20 mg of the sample was suspended in a reaction vessel containing 40 mL of H₂O and 40 mL of methanol, to which the chloroplatinic acid (H₂PtCl₆) solution (51.6 µL, 5 mM) was added. Continuous magnetic stirring and water cooling were applied during the experiment. The produced H₂ was analyzed by an Agilent 7890A gas chromatograph (GC) with a thermal conductivity detector. Photocatalytic H₂ production from artificial seawater was carried out by using simulated seawater instead of H₂O and methanol mixture. The artificial seawater was prepared by dissolving 27.21 g of NaCl, 3.81 g of MgCl₂, 1.66 g of MgSO₄, 1.404 g of CaSO₄, 0.577 g of K₂SO₄, 0.2124 g of K₂CO₃, and 0.08 g of MgBr₂ in 1 L of distilled water, which was reported elsewhere.^{1, 2}

The apparent quantum yield (AQY) was measured and calculated by the following equation using a PLS-SXE-300C Xe lamp with 365 nm band-pass filter (20 mW cm⁻²):

$$AQY = \frac{Number of \ evolved \ H \ molecules \times 2}{Number \ of \ incident \ photos} \times 100\%$$
(1)

Section 4. Photocatalytic CO₂ reduction experiment

The photoreduction of CO_2 was carried out in a 225 mL cylindrical glass reactor with 100 mg catalysts tiled on a glass sheet (1.5 cm × 5.5 cm) under ultraviolet-visible light irradiation. A PLS-SXE-300C lamp was used as the light source. The glass reactor was located 15 cm away from the light source and remained vertical to the light beam. The glass sheet with the catalysts was placed into the reactor, fixing it on the underface of the light source. The reactor was continuously inflated

with CO₂ gas (99.999 %) at a flux of 0.3 L min⁻¹ for at least 45 min, which was enough to ensure that the reactor was injected into the reactor was utterly full of CO₂ gas. Then 1.5 ml deionized water was injected into the reactor and the light source was turned on. Every 2 h, 0.4 mL gas of the reactor was extracted to measure the produced amount of CH_4 and CO by a gas chromatograph.

Section 5. Photo-electrochemical measurement

All photo-electrochemical measurements were carried out on an Autolab PGSTAT302N working station (Metrohm, Switzerland) using a three-electrode configuration with sample photocatalyst as a working electrode, saturated calomel electrode (SCE) as a reference electrode and Pt foil as the counter electrode. The supporting electrolyte used was 0.5 M Na₂SO₄ solution (pH=6.5). A PLS-SXE-300C lamp was placed 10 cm away from the working electrode that operated as a light source and the light intensity was calibrated to 158 mW cm⁻². The working electrodes were prepared by dispersing catalyst (5 mg) and Nafion solution (30 μ L, 5 *wt*.%) in H₂O/ethanol mixed solvent (1 mL, 1:1 v/v) with at least 10 min of sonication to form a homogeneous ink. The working electrode was prepared by drop-casting the above ink (50 μ L) onto FTO glass with an area of 1 cm². Electrochemical impedance spectroscopy (EIS) analysis was evaluated at open circuit potentials over a frequency range of 100 kHz to 0.1 Hz with an amplitude of 10 mV. The transient photocurrent response vs time was measured under chopped UV-vis light irradiation.

The photocathodic protection performance for 304 stainless steel (304 SS) was carried out with two couple cells connected by a Nafion membrane. The corrosion cell containing a NaCl (3.5 wt.%) electrolyte and the photolysis cell filled with a mixed electrolyte of Na₂S (0.1 M) and NaOH (0.2 M). The 304 SS (working electrode), SCE (reference electrode) and Pt (electrode) were placed

in corrosion cell while our samples in the photolysis cell and connected to the working electrode by a conducting wire. A PLS-SXE-300C lamp was placed 10 cm away from the sample electrode. Section 6. SEM and TEM images, N₂ adsorption, XPS, PL emission, comparison of photocatalytic H₂ activity, TRPL, OCP and TG measurements.



Fig. S1. (a) The original HRTEM image of Fig. 1e, with no added colors. (b) The original inverse FFT image of Fig. 1f.



Fig. S2. Nitrogen adsorption-desorption isotherm curves and diameter distribution curve (inset) of TiO_2 and $TiO_2@rGO$.

Sample	specific surface area	Average	pore	Pore volume
	$(m^2g^{-1})^{a}$	diameter		(cm ³ g ⁻¹) ^c
		(nm) ^b		
TiO ₂ @rGO	119	13		0.29
TiO ₂	92	13		0.25

Table S1. Nitrogen adsorption-desorption measurements analysis data

^a Specific surface areas (BET) were calculated from five adsorption points in the pressure range $P/P_0 = 0.05-0.3$.

^b Calculations for pore size distributions were done with the ASAP 3020 using the BJH model.

^c Total pore volumes were calculated from the N₂ adsorption isotherm at $P/P_0 = 0.99$.



Fig. S3. Raman spectra of TiO_2 and $TiO_2@rGO$, the inset shows the D and G bands of GO and $TiO_2@rGO$.



Fig. S4. the surface molar ratio of Ti:O from XPS of TiO₂ (first), TiO₂, TiO₂@rGO (first) and TiO₂@rGO from XPS.

Table S2. The peak area and molar ratio on the surface of TiO_2 (first), TiO_2 , TiO_2 @rGO (first) and TiO_2 @rGO from Fig. S4.

Sample	Lattice titanium area	Lattice oxygen area	O/Ti ratio
TiO ₂ (first)	205247 a	150717 ^b	1.88±0.02 °
TiO ₂	205857 ^a	152773 ^b	1.90±0.02 °
TiO ₂ @rGO (first)	140913 ^a	101729 ^b	1.85±0.02 °
TiO ₂ @rGO	202469 ^a	154430 ^d	1.95±0.02 °

 $^{\rm a}$ Combined Ti $2p_{3/2}$ and Ti $2p_{1/2}$ XPS peak areas.

^b Ti-O peak area.

^c The relative sensitivity factors for Ti and O element are 2.001 and 0.78.

^d Combined Ti-O and O^{-} peak areas.



Fig. S5. PL spectra of different samples.



Fig. S6. TGA curve of TiO₂@rGO (first) and TiO₂@rGO measured in air atmosphere. The TiO₂@rGO (first) shows 2.8 % of weight loss at the range of 300-450 °C mainly due to the combustion of unstable carbon and the TiO₂@rGO has no weight loss at these temperatures, ³ indicating the unstable carbon species in TiO₂@rGO might be efficiently removed during the calcination at 350 °C in air flow. Besides, the slight weight loss observed at 500-650 °C in both samples is attributed to the combustion of rGO, the weight percentage of rGO is determined to be 0.5 % in these samples.

Table S3. Photocatalytic H₂ production rates of $TiO_2@rGO-1.5\%$, $TiO_2-rGO-0.5\%$, $TiO_2+rGO(mix)$ and TiO_2 under visible light irradiation (400 nm cutoff filter), indicating that all the TiO_2 and the composites of TiO_2 and rGO show photocatalytic activity only at ultraviolet region.

Example	TiO ₂ @rGO- 1.5%	TiO ₂ -rGO-0.5%	TiO ₂ +rGO (mix)	TiO ₂
H ₂ production rate (mmol g ⁻¹ h ⁻¹)	<0.05	<0.05	<0.05	< 0.05



Fig. S7. UV-vis di \Box use reflection spectra of a) TiO₂ (first), TiO₂, TiO₂@rGO (first) and TiO₂@rGO, b) p25 and TiO₂-rGO with different amount of rGO coating.



Fig. S8. Photostability of H₂ production of TiO₂-CQDs-rGO and V_{Ti} @CQDs@rGO, each cycle run 5 h.



Fig. S9. 2D ¹H DQ MAS NMR spectrum of $TiO_2@rGO$ after 5 cycles (25h) photocatalytic reaction.



Fig. S10. TRPL spectra of TiO₂ (first), TiO₂, TiO₂@rGO (first) and TiO₂@rGO, p25 and TiO₂-rGO-0.5%.



Fig. S11. OCP variations of 304 SS coupled with i) $TiO_2@rGO$, ii) $TiO_2@rGO$ (first), iii) TiO_2 and iv) TiO_2 (first) photoelectrodes.

Table S4. Photo-electrochemical parameters from the polarization curves of the bare 304 SS and 304 SS coupled with TiO_2 (first), TiO_2 , TiO_2 @rGO (first), TiO_2 @rGO electrodes under UV-vis light irradiation.

Sample	E _{corr} (mV vs. SCE)	j _{corr} (µA cm ⁻²)
304 SS	-76	0.40
TiO ₂ (first)	-276	2.19
TiO ₂	-327	5.27
TiO ₂ @rGO (first)	-366	3.85
TiO ₂ @rGO	-501	6.00

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