Supplementary Information (SI) for Chemical Communications.

Supporting Information

Mesostructured TiO_2 with Abundant Oxygen Vacancies for Excellent Photocatalytic Hydrogen Production under Mild Conditions

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Author Contributions

C. Y. W., J. H. X. F. Z. and D. L. did the experiments of synthesis and photocatalytic performance. Z. L. did the TEM and photoelectrochemical characterizations. Y. L. conceived the project, provided the idea, and designed the experiments. L. Y. W. helped with the NMR measurements and corresponding analysis. G. T. helped with the TEM, STEM measurements and corresponding analysis. X. Y. Y. conceived the project, supported the scientific and technological platform. S. F. H. revised the paper. C. Y. W., J. H., and Y. L. wrote and revised the paper. All the authors discussed the results and analyzed the data.

Experimental section

Materials

Titanium butoxide (TBT) (≥98%, Shanghai Test), acetate (≥99.5%, Shanghai Test), 1-butyl-3-methylimidazolium tetrafluoroborate ([OMIm][BF_4]) (≥99%, Lanzhou Greenchem ILs) and commercial anatase TiO_2 nanoparticles (designed as Nano-TiO_2, Aldrich). All chemicals were used as obtained from commercial sources without further purification and distilled water was used in the whole experiment.

Synthesis and purification of OM-TiO_2-600

In a typical synthesis, 1 mL distilled water (DW) was mixed with 25 mL acetic acid in a 50 mL sealed Teflon-lined stainless steel autoclave. After stirring for five minutes, 1 mL [OMIm][BF_4] was added to the mixed solution. Next, 2 mL TBOT was added to the mixed solution and left to stir for 10 minutes. The autoclave was sealed and heated to 180 °C for 24 h. After cooling to room temperature, the sample was obtained through centrifugal separation, washed three times with water and ethanol, respectively, and then dried at 60 °C for 12 h to obtain the OM-TiO_2. The OM-TiO_2 sample was finally calcined at 600 °C in air for 4 h. The products were donated as mesoporous TiO_2 (TiO_2-OM-600). Commercial anatase TiO_2 was chosen for comparison.

Characterization

The sample's morphology was investigated by scanning electron microscopy (FE-SEM, S-4800, HITACHI) at 5 kV. To identify the TiO_2 phases, powder X-ray diffraction (XRD) patterns were obtained by a D8 Advance X-ray diffractometer (Bruker, Germany) with Cu-Kα radiation (λ = 0.15406 nm) operated at 40 kV, 40 mA. Transmission electron microscopy (TEM) experiments were conducted on a JEM-2100F STEM/EDS electron microscope operated at 200 kV. Thermogravimetric analysis (TGA) was performed using a STA449F3 thermal analysis instrument at a temperature ramping rate of 10 °C/min in air. The nitrogen adsorption and desorption isotherms of TiO_2 samples were measured using a Micromeritics ASAP 3020 system. The specific surface area was measured at -196 ^{o}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. Fourier-transform infrared (FT-IR) spectra were obtained with a Nicolet 6700 spectrometer. Electron paramagnetic resonance (EPR) measurements were performed at the X-band using a JEOL FA 2000 spectrometer. ^{1}H MAS and 2D 1H TQ-SQ and DQ-SQ 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 ^{1}H $\pi/2$ pulse length of 1.65 us and a recycle delay of 4 s. ^{19}F MAS NMR spectra was carried out in a 2.5 mm MAS probe on a Bruker AVANCE-III 500 spectrometer with a sample spinning rate of 30 kHz, a ^{19}F $\pi/2$ pulse length of 1.9 us and a recycle delay of 1 s. X-ray photoelectron spectroscopy (XPS) measurements of samples were performed on a PHI Quantera II, (ULVAC-PHI, Japan) for chemical composition analysis, all binding energies were calibrated to the C1s peak at 284.8 eV. UV-visible diffuse-reflectance spectrum (UV-Vis DRS) were measured on a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). The photoluminescence spectra (PL) were recorded on LS 55 (PERKINELMER) with an excitation wavelength of 320 nm. Electrochemical impedance spectroscopy (EIS) analysis was conducted by an Autolab PGSTAT302N working station (Metrohm, Switzerland) using a three-electrode configuration with the above photoanode as a working electrode, Ag/AgCl electrode as a reference electrode and platinum foil as the counter electrode. The transient photocurrent response vs time was measured under chopped UV-vis light irradiation.

Photocatalytic measurements

The photocatalytic H_2 production was measured using a closed circulation system (Prefect light Labsolar 6A) with a 300 W Xe lamp (PLS-SXE-300C lamp) placed 10 cm away from the suspension. The amount of 20 mg of sample was dispersed in a water/methanol mixture (3:1, v/v, 80 mL) and 5.2 μL of H_2PtCl_6 (0.1 mmol/L) was added after transfer into a quartz container with an inner diameter of 7 cm. The produced H_2 was analyzed by an Agilent 7890 A gas chromatograph (GC) with a thermal conductivity detector (TCD). Photocatalytic reaction under the -10 °C was carried out in a closed container connected with a cooling liquid circulator pump and 20 wt.% of NaCl aqueous solution was used to prevent freezing. Water was used as a circulator liquid to maintain temperature at about 80 °C and 25°C, while ethanol was used as a cooling liquid to keep the temperatures at about -10 °C. The seawater was obtained from the South China Sea and filtered to remove the particles and algae before use.

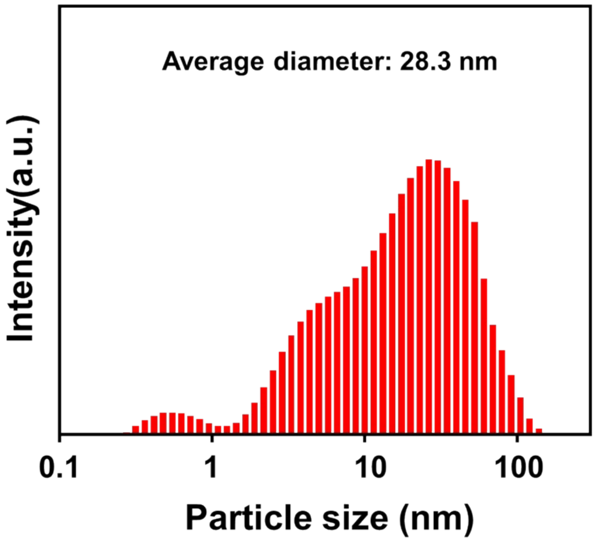

Fig. S1. Size distribution curves of TiO_2-IL oligomers in acetic acid solution.

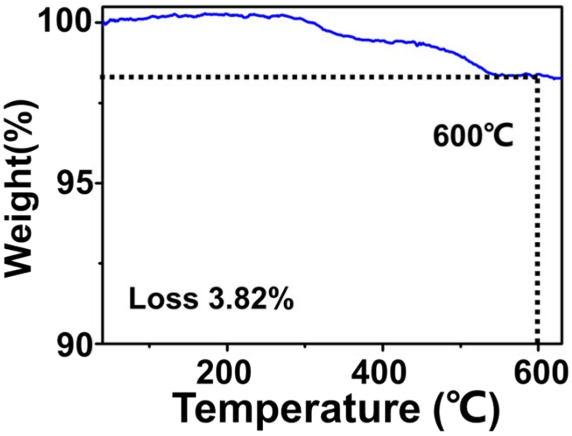

Fig. S2. TGA image of TiO_2-OM.

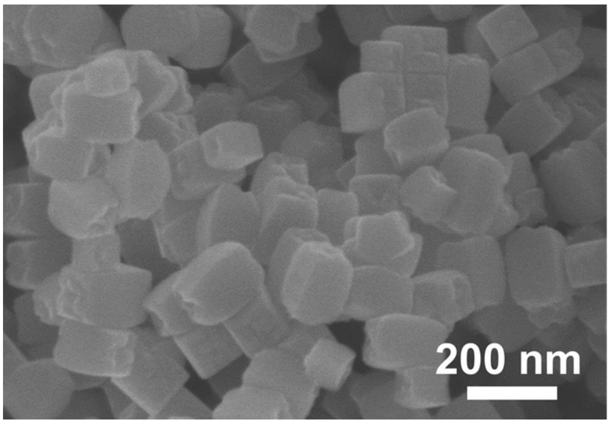

Fig. S3. SEM image of OM-TiO_2

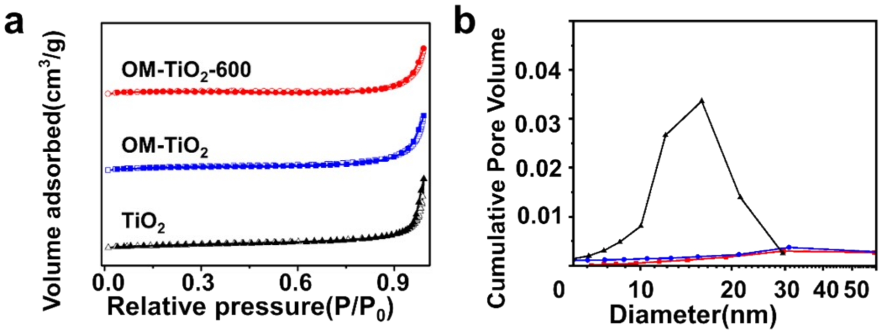

Fig. S4 N_2 adsorption-desorption isotherm (a) and pore size distribution (b) of the TiO_2、OM-TiO_2 and OM-TiO_2-600.

Table S1 The BET specific surface area of different TiO_2 photocatalysts

Samples	BET surface area, m^2/g	Pore volume, cm^3/g	Pore size, nm
TiO_2	24.5	0.054	14.8
OM-TiO_2	13.2	0.044	/
OM-TiO_2-600	9.3	0.029	/

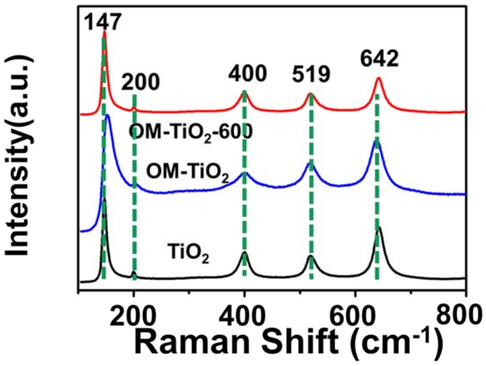

Fig. S5. Raman spectra of OM-TiO_2-600、OM-TiO_2 and commercial TiO_2

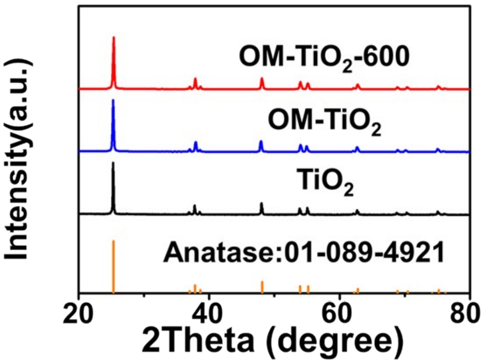

Fig. S6. XRD patterns of commercial TiO_2、OM-TiO_2 and OM-TiO_2-600.

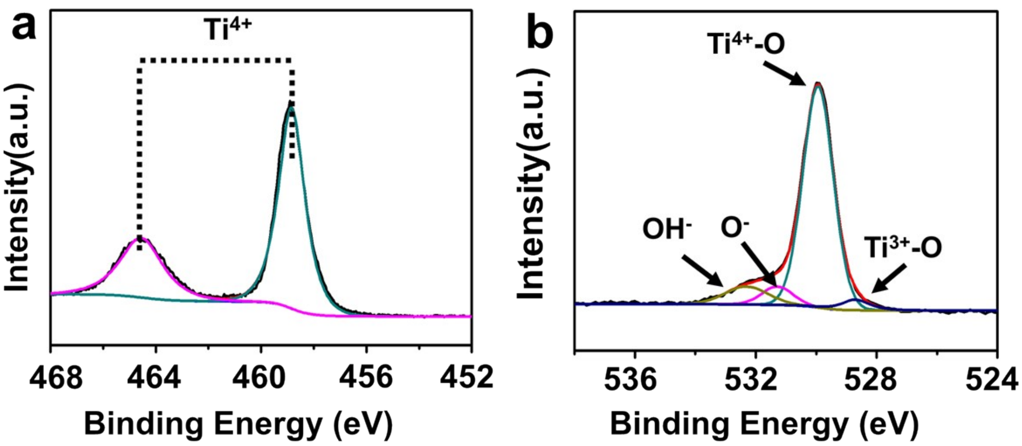

Fig. S7. (a) Ti 2p XPS of OM-TiO_2, (b) O 1s XPS spectrum of OM-TiO_2-600

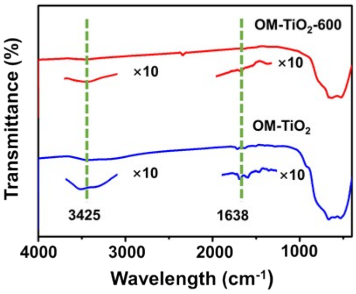

Fig. S8. FT-IR spectra of OM-TiO$_2$-600、OM-TiO$_2$.

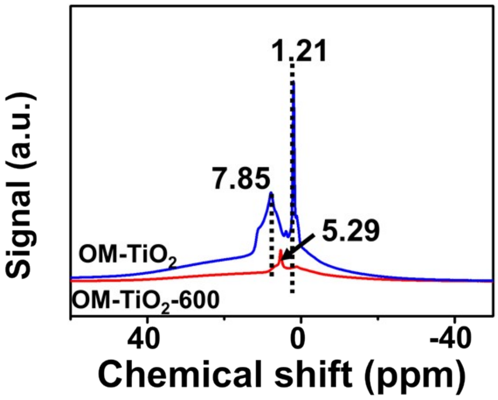

Fig. S9. ^{1}H NMR spectra of OM-TiO_2 and OM-TiO_2-600.

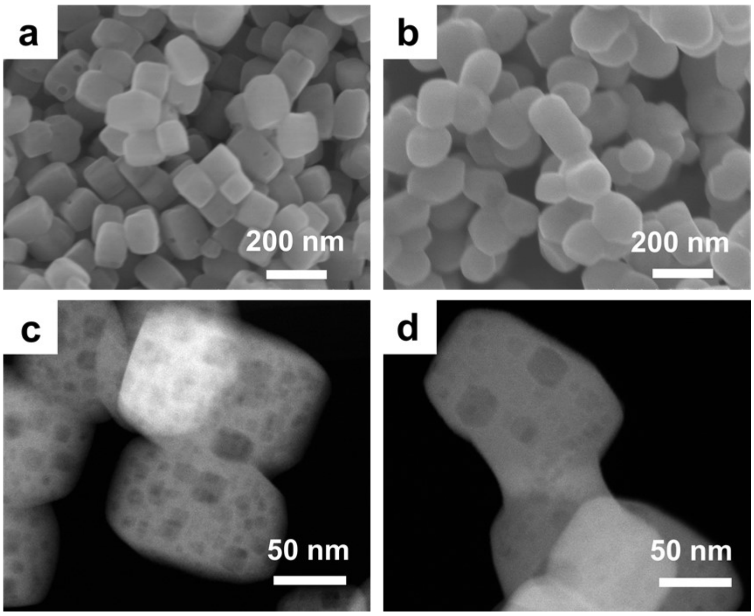

Fig. S10. SEM images of (a) OM-TiO_2-600-700, (b) OM-TiO_2-600-800, HAADF-STEM images of (c) OM-TiO_2-600-H and (d) OM-TiO_2-600-S.

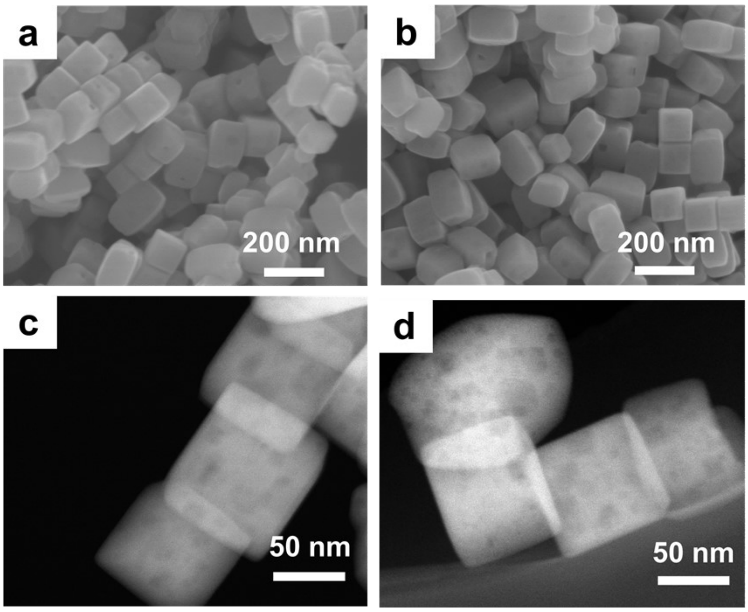

Fig. S11. SEM images of (a) OM-TiO_2-600-H and (b) OM-TiO_2-600-S, HAADF-STEM images of (c) OM-TiO_2-600-700, (d) OM-TiO_2-600-800,

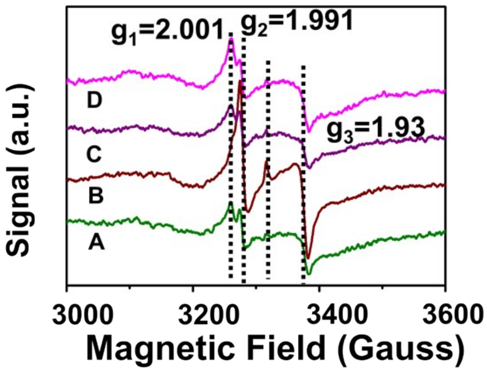

Fig. S12. EPR spectra of (A) OM-TiO_2-600-700, (B) OM-TiO_2-600-800, (C) OM-TiO_2-600-H and (D) OM-TiO_2-600-S.

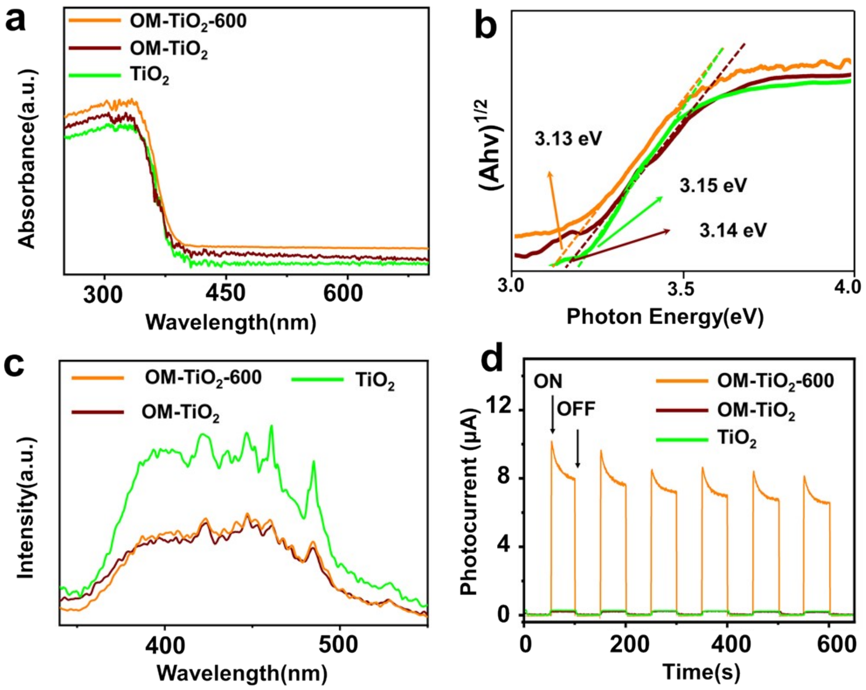

Fig. S13. (a) UV-vis diffuse reflection spectra, (b) the corresponding Tauc plot *vs hv* curve; (c) photoluminescence (PL) spectra and (d) Transient photocurrent responses of commercial TiO_2, OM-TiO_2 and OM-TiO_2-600.

Table S2. Overview of the TiO_2-based photocatalysts in different solutions

Photocatalyst	Water Source	Activity (mmol h^{-1} g^{-1})	Light source	Reference
TiO_2	water	69.0	300 W xenon lamp	This work
	Artificial seawater	81.0		
	Seawater	72.0		
TiO_2	Artificial seawater	18.1	300 W Xenon lamp	ACS Nano 2023, 17, 18217
TiO_2/Cu_2O	Seawater	17.9		
TiO_2	water	57.9	300 W Xenon lamp	Chem. Eng. J. 2020, 400, 125909.
	Artificial seawater	46.6		
Pt/TiO_2 (P25)	water	58.0	LED UV light	Fuel, 2023, 354, 129248
SnO_2/TiO_2	water	16.7	300 W Xenon lamp	Chin. Chem. Lett. 2023, 34,107125
TiO_2	water	12.5	300 W xenon lamp	J. Am. Chem. Soc., 2024, 146, 1701
NiS_2/TiO_2	water	10.4	300 W Xenon lamp	Int. J. Hydrog. Energy, 2024, 91, 673
	Artificial seawater	12.5		
	seawater	12.0		
CoS_2/TiO_2	water	2.2		
	Artificial seawater	9.9		
	seawater	6.2		
SnS_2/TiO_2	water	1.6		
	Artificial seawater	2.5		
	Seawater	3.8		
Cu_2O/TiO_2	Water	11.0	300 W Xenon lamp	J. Alloy. Compd., 2021, 868, 159144
	Seawater	5.1		
TiO_2-rGO-Cu	Artificial seawater	16.1	300 W Xenon lamp	Chem. Phys. Lett, 2023, 822, 140498

Table S3 Overview of the TiO_2 and other photocatalysts under extreme temperature

Photocatalyst	Water Source	Activity (mmol h^{-1} g^{-1})	Temperature (°C)	Reference
TiO_2	NaCl/methanol solution	63.0	-10	This work
	NaCl/methanol solution	85.0	80	
TiO_2	NaCl/methanol solution	20	-20	ACS Appl. Mater. Inter. 2024, 16, 47695
		32	-10	
		39	80	
CNT/CdS	Water/triethanolamine	0.45	80 °C	Adv. Mater. 2020, 32, 1906361
Ti/TiO_2	Water/methanol	0.5	60	ACS Catal. 2015, 5, 4790
CoO	water	5.8	73	Nat. Commun. 2021, 12, 1343
$SnSe/ZnIn_2S_4$	Water/triethanolamine	5.7	73	Chem. Eng. J. 2021, 404, 126477
$Rh/SrTiO_3$:Ir	Water	5.0	67	J. Phys. Chem. C 2025, 129, 2381

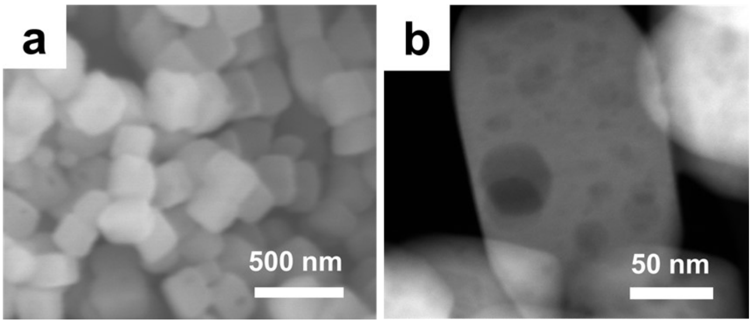

Fig. S14 (a) SEM image and (b) HAADF-STEM image of OM-TiO_2-600 after 100 h reaction