Supporting Information

Spatially Distributed Carbon Quantum Dots in TiO_2 for Photothermal-Assisted Hydrogen Production from Seawater

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EXPERIMENTAL SECTION

Chemicals

Commercial 40 nm anatase TiO_2 nanoparticles (designated as Comm-TiO_2, AR), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, AR, Pt ≥37.5%), glycerol (AR), citric acid ($C_6H_8O_7$, AR), urea (CH_4N_2O, AR), Nafion perfluorinated resin solution (Polymer Content: 5.0-5.4%, Water Content: 42-48%, VOC Content:47-53%, Total Acid Capacity:1.03-1.12 meq/g) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.. Sodium hydroxide (NaOH, AR, ≥96.0%), hydrochloric acid (HCl, 36 wt%, AR) and ethanol (C_2H_5OH, AR, 95%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Distilled water was used in the whole experiments.

Synthesis

Preparation of CQDs (Carbon Quantum Dots): In a typical synthesis, 0.21 g citric acid and 0.18 g urea were stirred in 5 ml of deionized water to achieve uniformly dispersed solution. Then, the mixture was transferred to a Teflon-lined autoclave, and heated to 160 °C for a duration of 4 h. After the autoclave was cooled to room temperature naturally, the mixed solution was dried at 100 °C. The obtained product via centrifugation, subjected to three cycles of washing with water and ethanol, and finally dried at 60 °C. The obtained black solid named as CQDs.

Preparation of CQDs@TNF (CQDs loaded mesoporous titanium dioxide nanofibers): 10.5 g NaOH and 0.5 g commercial 40 nm anatase TiO_2 nanoparticles were added into a Teflon-lined autoclave. Then, the CQDs were added to the mixture at mass fractions of 1%, 2%, 3% and 4%, respectively. 30 mL of deionized water was

added into the Teflon-lined autoclave while stirring to achieve uniform dispersions. The mixture was heated at 120 °C for 24 h. After the autoclave was cooled to room temperature naturally, the obtained product was filtered and stirred overnight in 0.1 M HCl solution. The product was washed with deionized water several times, filtered, and dried at 80 °C. Then the resulting solid were calcined at 500 °C for 1 h in an argon atmosphere (named as TNF, 1%C@TNF, 2%C@TNF, 3%C@TNF, and 4%C@TNF, respectively), and the heating rate to the target temperature is 1 °C min^{-1}.

Preparation of TNF: Titanium dioxide nanofibers (TNF) were synthesized using the above method except without the addition of CQDs.

Preparation of CQDs/TNF: For comparison, TNF and CQDs were added to pure water at a fixed mass ratio, stirred for 1 h, centrifuged at high speed (1000 r/min) for 10 min, and then dried to obtain CQDs/TNF.

Characterization

The sample morphology was characterized by field emission scanning electron microscope (FE-SEM, Hitachi S-4800) and transmission electron microscope (TEM, Talos F200S). X-ray diffraction patterns (XRD) were obtained using a D8 ADVANCE X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm), a tube current of 40 mA and a voltage of 40 kV at a scan rate of 0.1 °/s^{-1}. The porous structure was investigated by N_2 adsorption/desorption at liquid nitrogen temperature (TriStar TM II 3020, Micromeritics) and the samples were degassed at 120 °C for 12 h before the measurements. Fourier-transform infrared (FT-IR) spectra were obtained with a Nicolet Avatar 360 spectrometer. Ultraviolet-visible spectroscopy diffuse reflectance spectra

(UV-vis DRS) were obtained by a UV-vis spectrophotometer (Lambda 750 S). X-ray photoelectron spectra (XPS) of the samples were recorded on a PHI Quantera II (Thermo Fisher-K-Alpha, America) using a monochromated Al-Kα X-ray source, all binding energies were calibrated to the C1s peak at 284.8eV. Electron paramagnetic resonance (EPR) measurements were performed at the X-band using a JEOL FA 2000 spectrometer. The modulation amplitude was 0.1 mT, the microwave power was 1 mW, and the experimental temperature was 295 K. ^{1}H MAS, 2D ^{1}H DQ-SQ and 3D ^{1}H DQ-SQ spectra were recorded in a 1.9 mm MAS probe on a Bruker AVANCE-III 500 spectrometer with a sample spinning rate of 35 kHz, a ^{1}H π/2 pulse length of 1.65 us and a recycle delay of 5 s. All the samples were measured with the same parameters and same amount.

Photocatalytic activity evaluation

Photocatalytic H_2 production was performed in a closed circulation system using a PLS-SXE-300D lamp (300W Xe lamp with the full spectrum, 100 mW cm^{-2}, Beijing Perfectlight Technology Co., Ltd.). The lamp was 10 cm away from the reaction solution. Typically, 20 mg of sample was suspended in 80 mL of an aqueous solution containing 75 mL seawater (or water, 3.5 wt.% NaCl solution), 5 mL glycerol and 5.2 μL H_2PtCl_6 (100 mmol/L). Glycerol is used as a sacrificial agent in the hydrogen production tests. The mixture was sealed in a quartz vessel and vacuumed for 30 min to remove the dissolved oxygen, a continuous magnetic stirrer and circulating cooling water was applied during the experiment. The produced H_2 was analyzed by an Agilent 7890 A gas chromatograph (GC) with a thermal conductivity detector (TCD). The H_2

production rate was calculated by normalizing the total amount of H_2 evolved by the total catalyst mass (20 mg CQDs@TNF) and the irradiation time. Each experiment was repeated at least three times, and the reported values represent the mean ± standard deviation.

Photoelectrochemical Measurements.

An electrochemical workstation (Autolab PGSTAT302N) was used to carry out the photoelectrochemical measurements, including the photocurrent tests and electrochemical impedance spectra (EIS), Photocurrent tests were carried out in a conventional three-electrode setup with a Pt foil as the counter electrode and a saturated silver-silver chloride (Ag/AgCl) reference electrode under a PLS-SXE-300D lamp. The working electrodes were prepared by dispersing catalysts (5 mg) and Nafion solution (5 μL, 5 wt%) in water/ethanol mixed solvent (500 μL, 1:1 v/v) followed by at least 10 min of sonication to form a homogeneous ink. The working electrode was prepared by drop-casting the above ink (50 μL) onto FTO glass with an area of 1 cm^2. EIS were obtained with a frequency range of 100 kHz to 0.01 Hz. The electrolyte in the corrosion cell was 3.5 wt% NaCl. The photoelectrochemical cell is a conventional three-electrode system.

Supplementary tables

Table S1. The BET surface area and pore distribution of TNF and CQDs@TNF.

Samples	S_{BET} (m^2/g)	Pore diameter (nm)
TNF	62	15
CQDs@TNF	158	15

Table S2. The concentrations of various ions in seawater and simulated seawater determined by ICP-MS and IC.

Samples	Na^+ (mg/L)	Cl^- (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
seawater	4921.1	10176.94	192.0	586.1
simulated seawater (3.5 wt.% NaCl solution)	10846.4	20502.82	/	/

Table S3. Summary of photothermal hydrogen production rate of TiO_2-based materials.

Photocatalyst	Light source	Sacrificial agent	System	Low temperature (°C)/H_2 production rate (mmol h^{-1} g^{-1})	High temperature (°C)/H_2 production rate (mmol h^{-1} g^{-1})	Ref.
CQDs@TNF	300 W Xe lamp	glycerol	seawater	25/28.2	80/100.8	Our work
Ti@TiO_2	100 W halogen lamp	methanol	water	35/5.8±1.2	60/10.4±1.8	(ACS Catal. 2015)[1]
Cu-TiO_2	300 W Xe lamp	/	water	25/trace amount	300/18.1*10^{-3}	(ACS Appl. Energy Mater. 2022)[2]
CDs/TCN	300 W Xe lamp	TEOA	seawater	7/7.97	26/11.92	(Chem. Eng. J. 2023)[3]
1% Cu_2O-rGO/TiO_2	300 W Xe lamp	methanol	water	25/3.8	90/17.8	(J. Colloid Interface Sci. 2022)[4]
Cu/TiO_2	300 W Xe lamp	methanol	water	30/2.86	100/24.16	(Int. J. Hydrogen Energy 2023)[5]
Ni_2P/TiO_2(B)	300 W Xe lamp	methanol	water	50/6.752	90/20.129	(Appl. Surf. Sci. 2020)[6]
TiO_2@CS	300 W Xe lamp	methanol	water	25/3.7	120/22.77	(Ind. Eng. Chem. Res. 2022)[7]

Note that the reported systems differ in light source, sacrificial agent, reaction temperature, water matrix, and reactor configuration. The comparison herein aims to demonstrate the performance of CQDs@TNF within the TiO2-based photothermal catalytic systems.

Table S4. The atomic concentrations of Ca and Mg in CQDs@TNF and commercial TiO_2 (Com-TiO_2) after the catalytic hydrogen production reaction, as determined by XPS.

Samples	Ca (Atomic %)	Mg (Atomic %)
CQDs@TNF	trace	trace
commercial TiO_2 (Com-TiO_2)	1.23	1.69

Supplementary figures

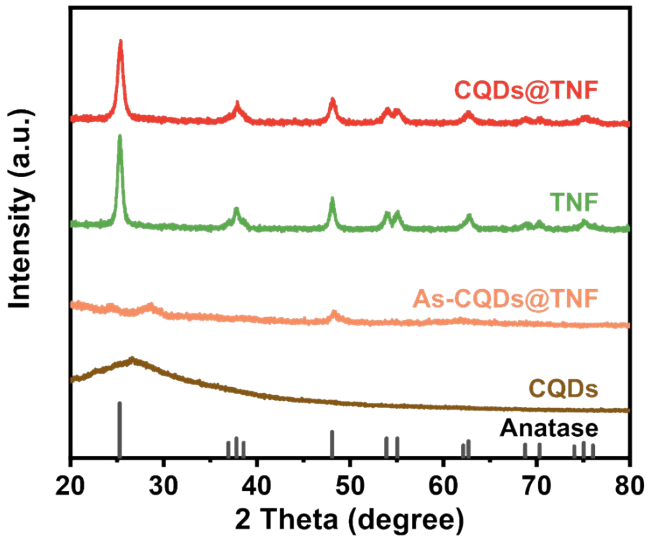

Fig. S1. XRD patterns of CQDs, As-CQDs@TNF, TNF and CQDs@TNF.

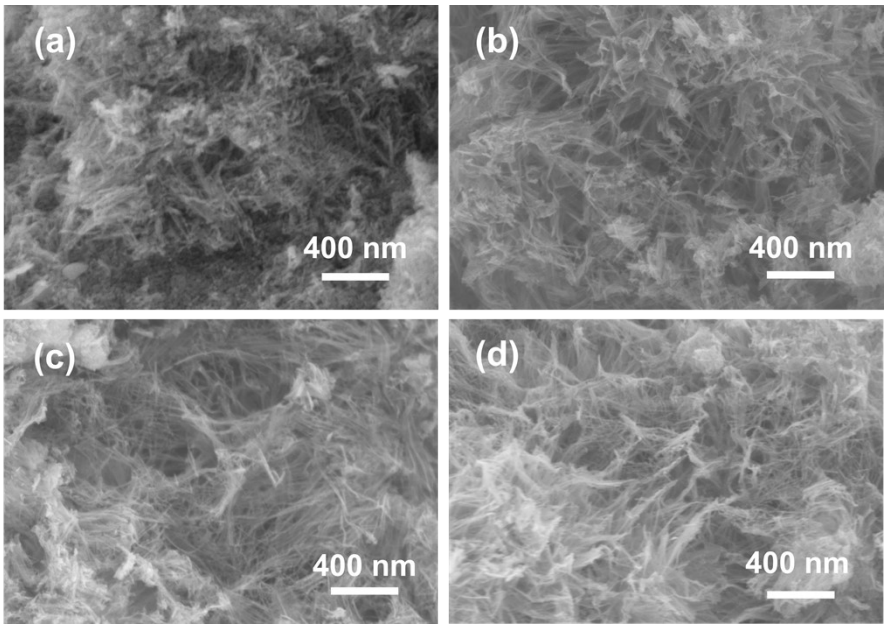

Fig. S2. The SEM images of (a) TNF, (b) 1%C@TNF, (c) 2%C@TNF and (d) 4%C@TNF.

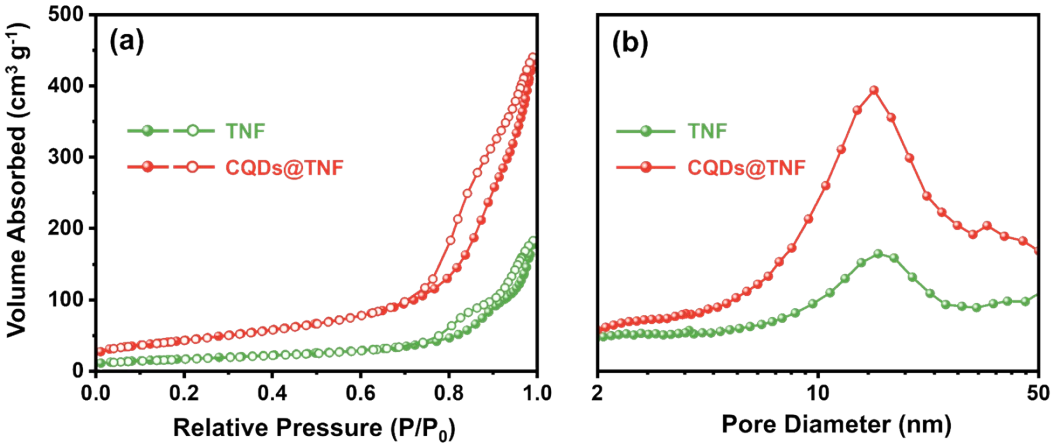

Fig. S3. (a) Nitrogen adsorption/desorption curves and (b) the corresponding pore size distribution of TNF and CQDs@TNF.

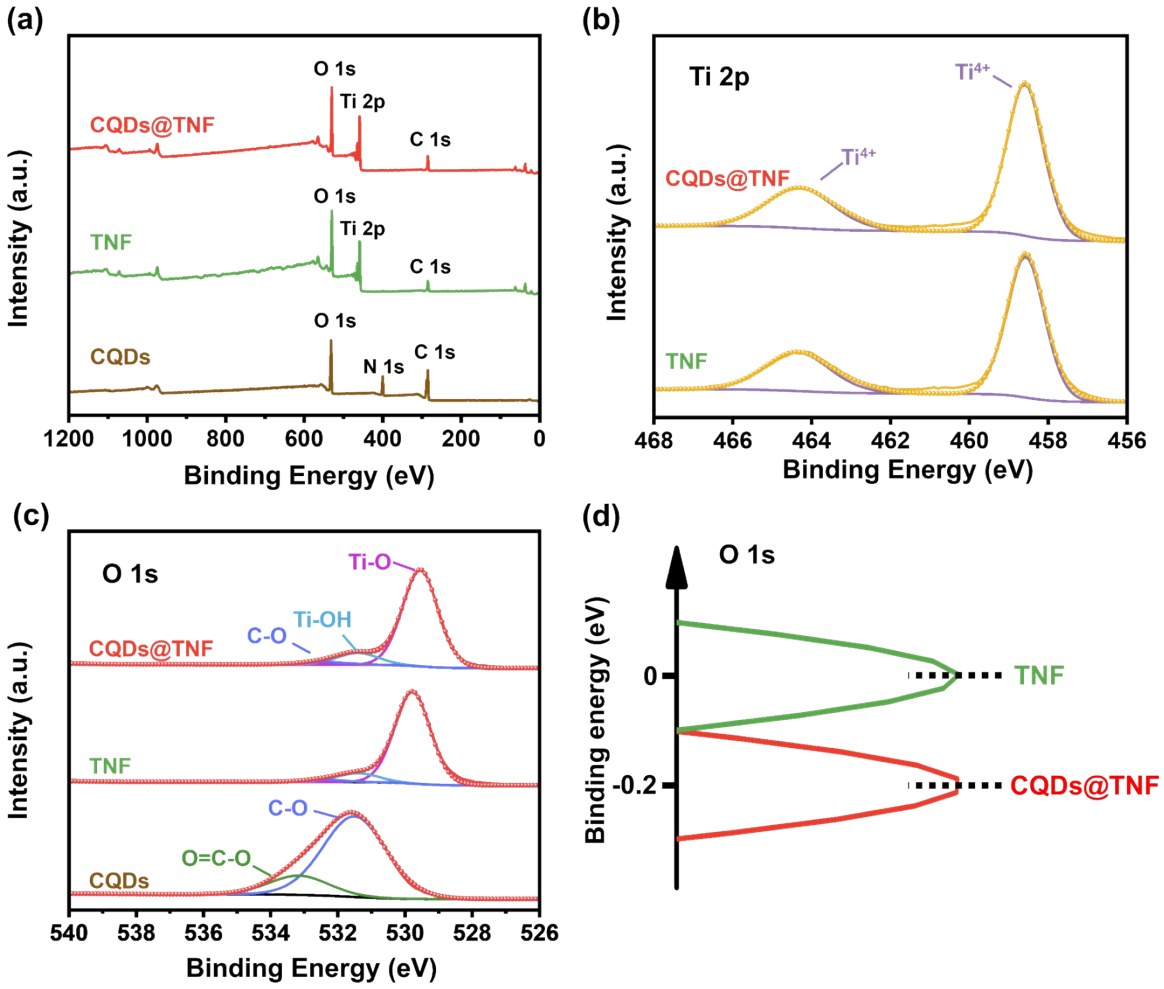

Fig. S4. (a) Survey XPS spectra of CQDs, TNF and CQDs@TNF. (b) Ti 2p XPS spectra of TNF and CQDs@TNF. (c) O 1s XPS spectra of CQDs, TNF and CQDs@TNF. (d) Chemical shift of O 1s XPS spectra of TNF and CQDs@TNF.

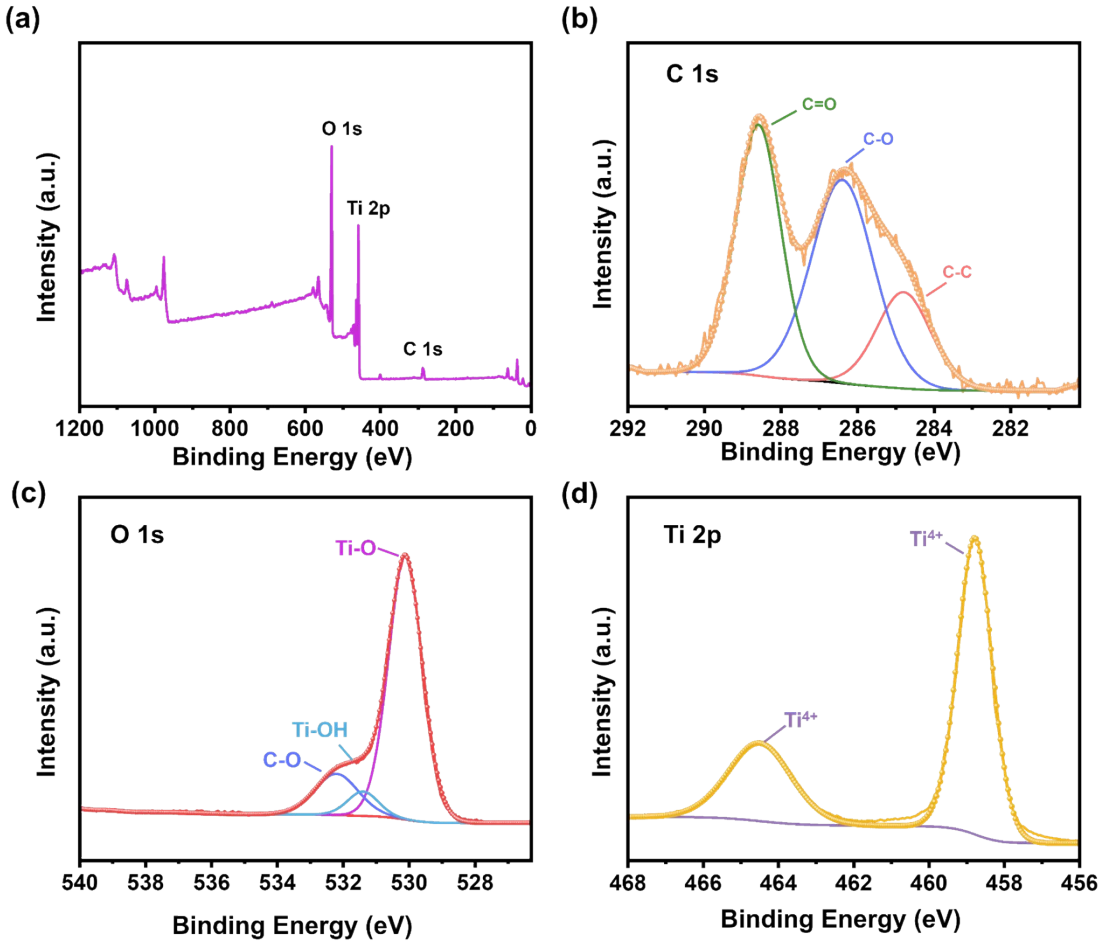

Fig. S5. (a) Survey XPS spectra, (b) C 1s XPS spectra, (c) O 1s XPS spectra and (d) Ti 2p XPS spectra of CQDs/TNF.

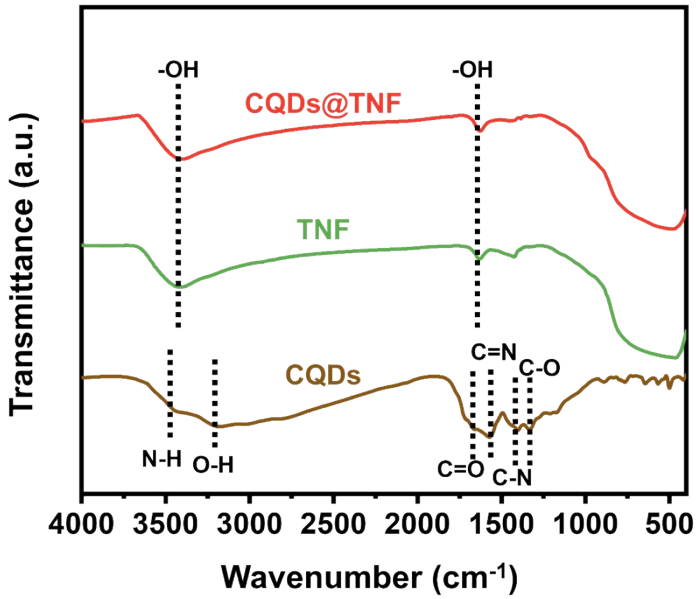

Fig. S6. FT-IR spectra of CQDs, TNF and CQDs@TNF.

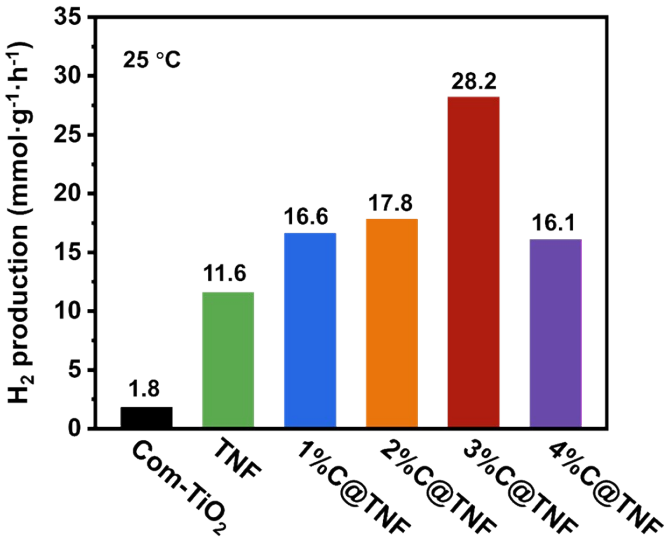

Fig. S7. Photocatalytic H_2 production activity of Com-TiO_2, TNF, 1%C@TNF, 2%C@TNF, 3%C@TNF, 4%C@TNF in seawater at 25 °C.

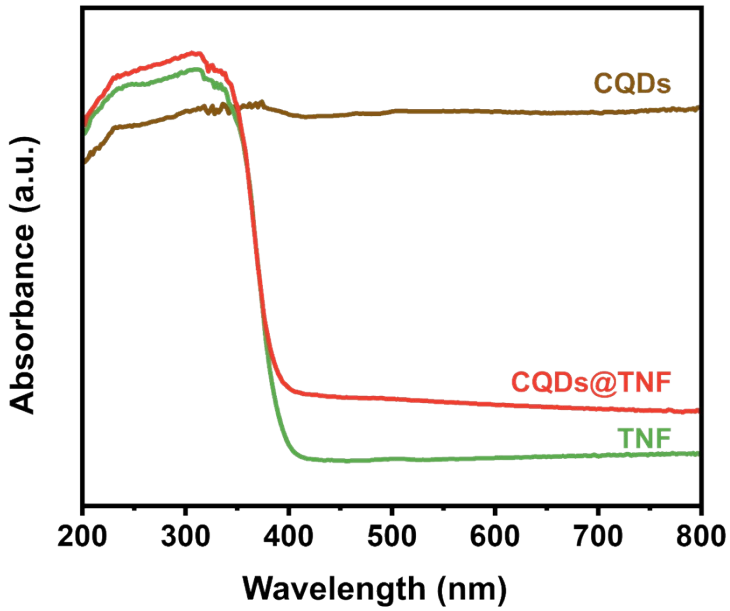

Fig. S8. UV-vis spectra of CQDs, TNF and CQDs@TNF.

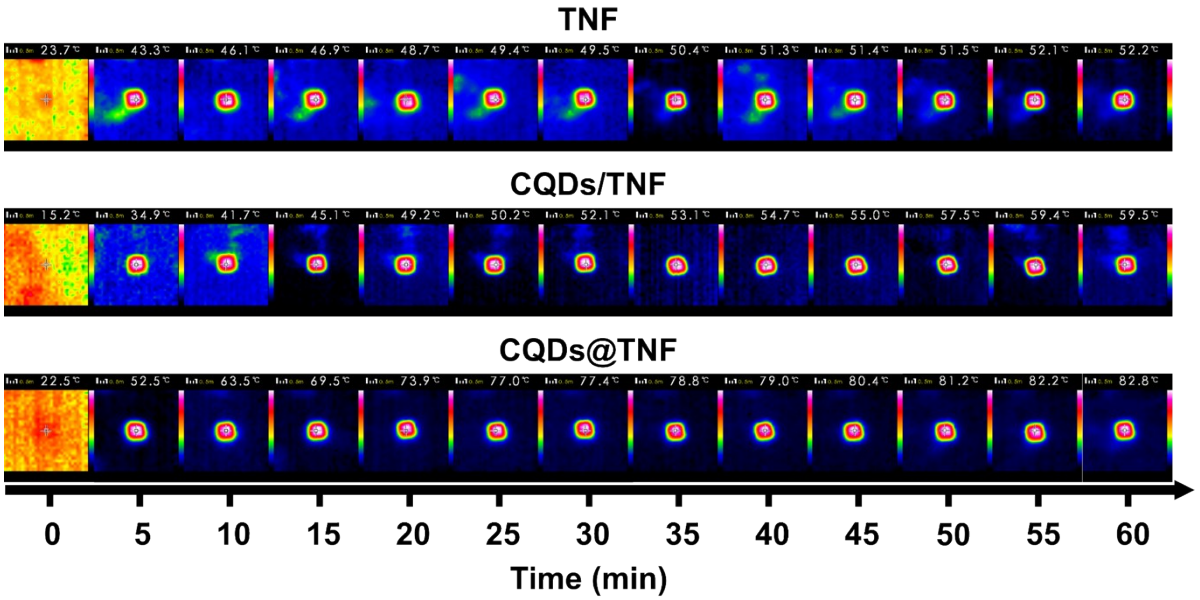

Fig. S9. Photothermal mapping images of TNF, CQDs/TNF and CQDs@TNF under infrared light irradiation.

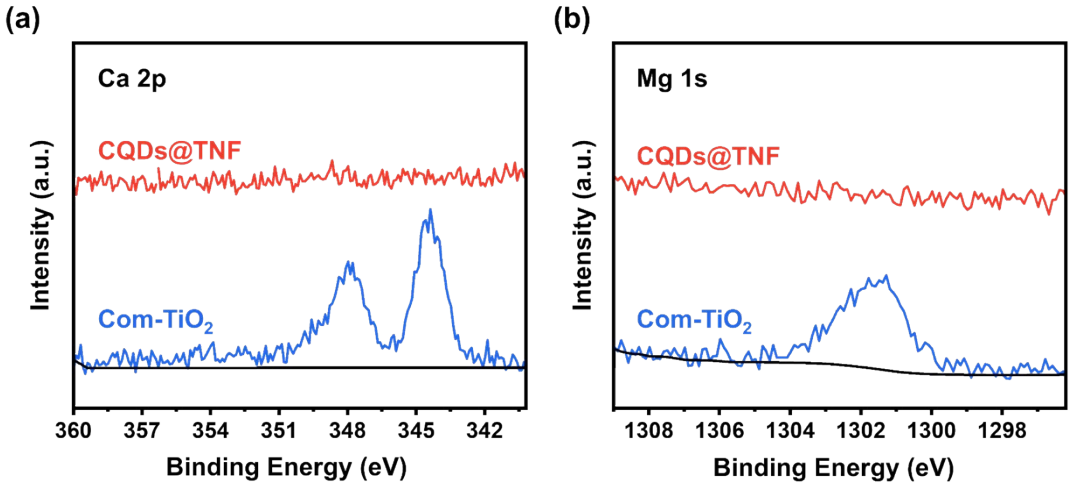

Fig. S10. (a) Ca 2p XPS spectra and (b) Mg 1s XPS spectra of CQDs@TNF and Com-TiO_2 after the photocatalytic hydrogen production reaction.

References

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