

Supporting Information

Enhancing photocatalytic hydrogen evolution from water splitting over CaTaO₂N via engineering surface of platinum cocatalyst

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Sample characterization

Powder X-ray diffraction (XRD) measurements were carried out on Rigaku RU-200b X-ray powder diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) executed at 45 kV and an emission voltage of 50 mA. Transmission Electron Microscope (TEM) images were obtained on the JEOL JEM-2100 (RH) machine with an operational accelerating voltage of 200 KV. X-ray Photoelectron Spectroscopy (XPS) data was operated on Thermo ESCALAB 250, USA XPS spectroscopy instrument using Al Ka X-ray radiation. The ultraviolet-visible (UV-Vis, DRS, UV-2450, Shimadzu Corp, Japan) absorption spectra were acquired on a UV-visible spectrometer equipped with an integrating sphere assembly. Photoluminescence spectra were measured using PL, FS-2500, Japan, fluorescence spectrometer equipped with the Xe lamp. The electrochemical impedance spectroscopy (EIS) response and Mott-Schottky (MS) plots were performed by an electrochemical workstation (CHI660E, China). The prepared photocatalytic material was coated onto the FTO glass electrode for the working electrode. Platinum foil was used for the counter electrode, and Ag/AgCl was prepared as the reference electrode in NaH₂PO₄/K₂HPO₄ (0.1 M) aqueous solution.

Calculation methods

The geometry optimization and electronic structure are calculated by density functional theory (DFT) with the simulation package code (VASP version 5.4.4). During the calculations, the projector augmented wave (PAW) method is used for the pseudopotential of inner electrons, while the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) is carried out for the exchange-correlation potentials. The value of kinetic cutoff energy is set to 520 eV for the valence electrons. The atomic positions will be suspended to relax in the configurations when the force and energy on each atom are smaller than $0.01 \text{ eV } \text{\AA}^{-1}$ and 10^{-7} eV , respectively. The $3 \times 3 \times 1$ gamma-centered k-mesh was chosen for the simulation of the surface Brillouin-zone. For CTON (IMP), the slab of the Pt (111) was expanded to $2 \times 2 \times 1$ supercell. For CTON (IMPD), two Pt atoms were placed on the top of the Pt (111) supercell with 3D geometry character to mimic the real system (denoted as Pt (111)-Pt2). The vacuum length for all the slabs was set to be 15 \AA . The H atom on Pt surface was simulated with H bonding to Pt atom in the Pt (111) and Pt (111)-Pt2, denoted as Pt (111)-H and Pt (111)-Pt2-H, respectively.

Photocatalytic water splitting testing

The Photocatalytic water splitting testing was conducted in a Pyrex top irradiation-type reaction vessel connected to a closed gas circulation system (CEL-SPH2N, AG, CEAULIGHT, Beijing). The selected sample, weighing 150 mg, was introduced into a 150 mL aqueous solution containing 10 vol% Methanol. The reactor was maintained at a reaction temperature of approximately 283 K through the circulation of cooling water. The mixed solution containing the photocatalyst was subjected to vacuum for 15 minutes and subsequently exposed to a 300w xenon lamp ($\lambda \geq 420 \text{ nm}$). The total amount of hydrogen evolution was determined using gas chromatography (GC 7920, Beijing) equipped with a thermal conductivity detector, while nitrogen was employed as the carrier gas. The reaction system was periodically evacuated for 30 minutes, and the hydrogen products generated during each 30-minute irradiation cycle were analyzed using CEL-SPH2N.

Apparent quantum yield (AQY)

The AQY was determined using a pyrex top-irradiation-type reaction vessel and a 300 W Xe lamp equipped with band-pass filters centered at 420 nm. The AQY of this study was calculated using the following equation:

$$\text{AQY (\%)} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} * 100$$

$$= \frac{\text{number of } H_2 \text{ molecules} * 2}{\text{number of incident photons}} * 100$$

Solar-to-hydrogen (STH) calculations

The water-splitting reaction was conducted under simulated solar irradiation. The equation below illustrates the efficiency of solar hydrogen production (STH):

$$\text{STH (\%)} = \frac{r(H_2) * \Delta G_r}{S * P} * 100$$

where $R(H_2)$, ΔG_r , S , and P denote the rate of hydrogen evolution overall water-splitting reaction, the Gibbs energy for the water splitting reaction at the standard condition (237 kJ mol⁻¹).

Supplementary Figures

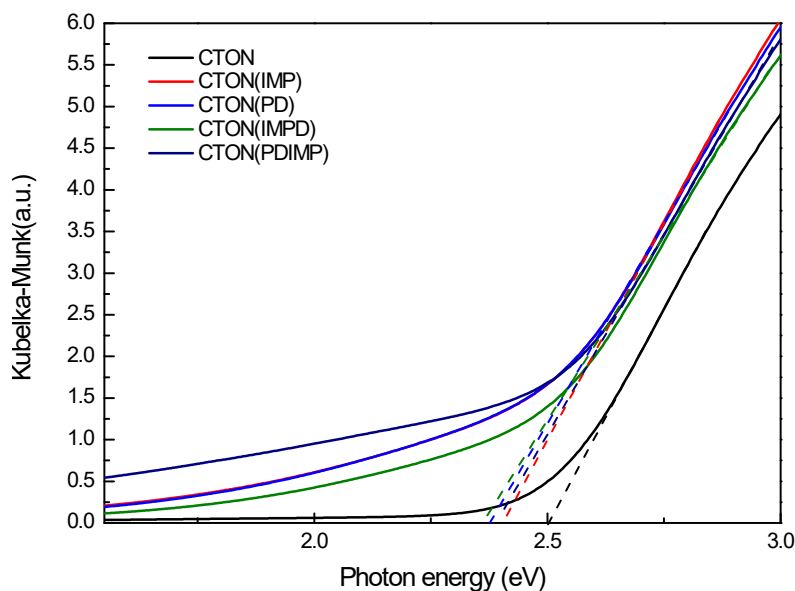


Fig.S1 Bandgaps of CTON, CTON (IMP), CTON (PD), CTON (IMPD) and CTON (PDIMP)

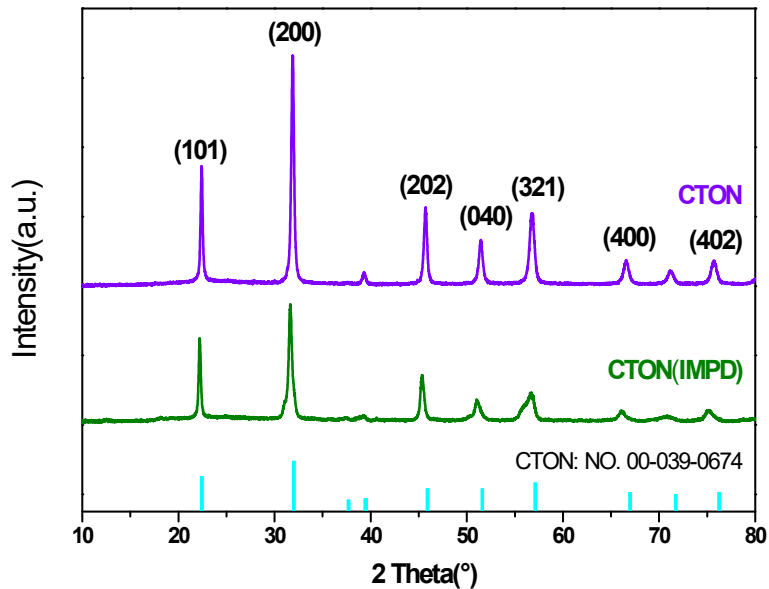


Fig.S2 XRD patterns for the CTON and CTON (IMPD) after reaction.

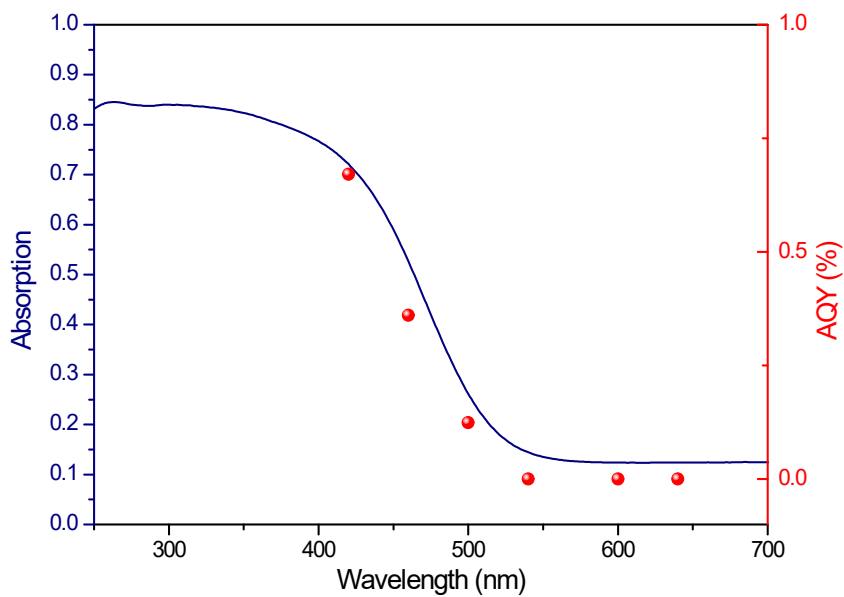


Fig.S3 Apparent quantum yield as a function of the incident light wavelength during visible-light-driven H₂ production over CTON (IMPD).

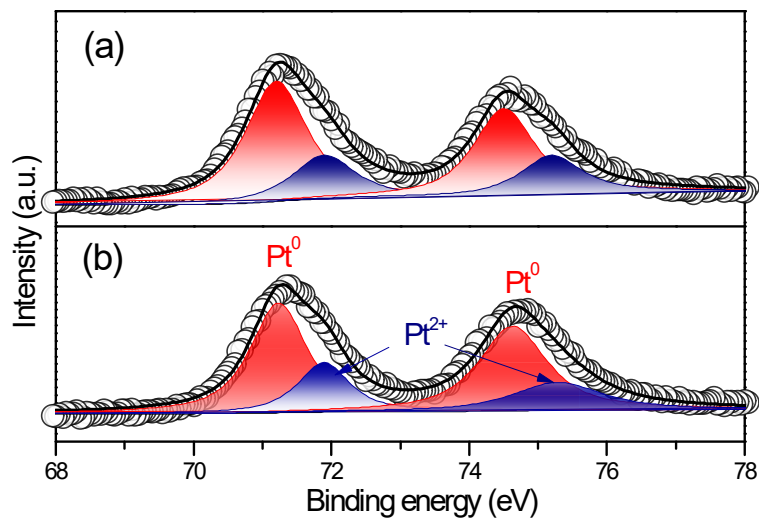


Fig.S4 Pt 4f XPS spectra of CTON (IMPD) (a) before and (b) after reactions.

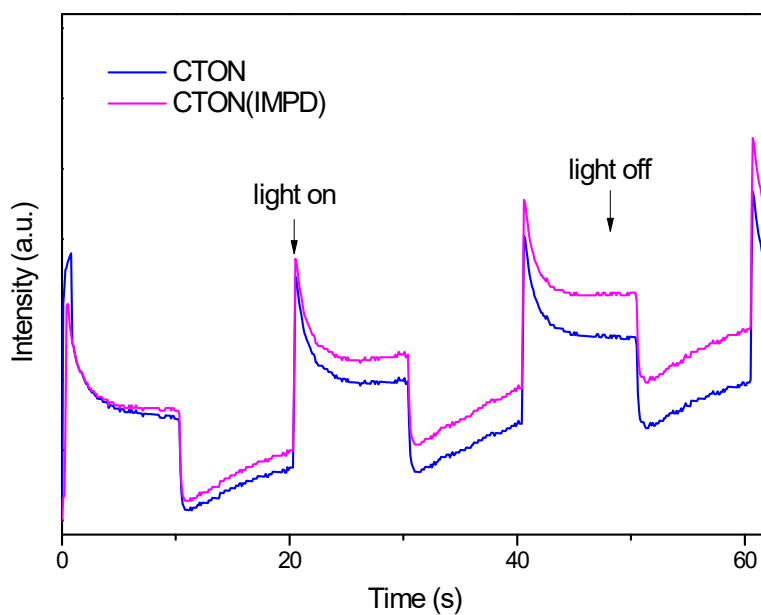


Fig.S5 Photocurrent responses of CTON, CTON (IMPD) under visible light radiation.

Supplementary Table

Table.S1 The compositions of Pt in CTON (PD), CTON (IMP), CTON (IMPD) and CTON (PDIMP).

Pt	Photocatalyst			
	CTON (PD)	CTON (IMP)	CTON (IMPD)	CTON (PDIMP)
Weight ratio^a (%)	0.98	1.01	1.08	0.94

^a Determined by ICP-OES analysis.