

Supporting Information

Hierarchical Metastable γ -TaON Hollow Structures for Efficient Visible-Light Water Splitting

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EXPERIMENTAL SECTION

Synthesis

Ethanol, hydrogen peroxide and hydrofluoric acid (Caution! Hydrofluoric acid is highly corrosive and it must be handled carefully.) were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd (SCRB). Tantalum powders (99.9%) were supplied from Aladdin. Ammonia gas was supplied by Haipu Gas Co., Ltd. All materials were used as supplied. Deionized (DI) water was used in all experiments.

u-Ta₂O₅: Urchin-like tantalum oxide hierarchical nanostructures are prepared by a hydrothermal process. In a typical synthesis procedure, stoichiometric tantalum powder (black-color) was added to a certain amount of hydrofluoric acid and hydrogen peroxide aqueous solution, which was loaded into a Teflon-lined cylindrical autoclave. Then the sealed autoclave was heated at 240 °C for different times in a box furnace. After the autoclave was cooled to room temperature naturally, the final white-color precipitates were separated, washed with ethanol for three times and then dried in oven at 60 °C for 12 h to obtain the final products of tantalum oxide powders.

γ -TaON: *u*-Ta₂O₅ powder (0.5 g) was heated to 850 °C at 10 °C min⁻¹ and held for 5 h under the flow of ammonia gas (20 mL min⁻¹) through a conical flask containing 100 mL deionized water at 30 °C. The reaction was then allowed to cool to 25 °C whilst retaining the ammonia flow to give γ -TaON as a yellow powder.

γ/β -TaON: *u*-Ta₂O₅ powder (0.5 g) was heated to 850 °C at 10 °C min⁻¹ and held for 10 h under the flow of ammonia gas (20 mL min⁻¹) through a conical flask containing 100 mL deionized water at 30 °C. The reaction was then allowed to cool to 25 °C whilst retaining the ammonia flow.

β -TaON: *u*-Ta₂O₅ powder (0.5 g) was heated to 850 °C at 10 °C min⁻¹ and held for 15 h under the flow of ammonia gas (20 mL min⁻¹) through a conical flask containing 100 mL deionized water at 30 °C. The reaction was then allowed to cool to 25 °C whilst retaining the ammonia flow.

u-Ta₃N₅: *u*-Ta₂O₅ powder (0.5 g) was heated to 850 °C at 10 °C min⁻¹ and held for 10 h under the flow of ammonia gas (40 mL min⁻¹). The reaction was then allowed to cool to 25 °C whilst retaining the ammonia flow to give *u*-Ta₃N₅ as a red powder.

c-TaON: Ta₂O₅ powder (0.5 g, SCRB) was heated to 850 °C at 10 °C min⁻¹ and held for 10 h under the flow of ammonia gas (20 mL min⁻¹) through a conical flask containing 100 mL deionized water at 30 °C. The reaction was then allowed to cool to 25 °C whilst retaining the ammonia flow to give *c*-TaON as a yellow-green powder.

c-Ta₃N₅: Ta₂O₅ powder (0.5 g, SCRB) was heated to 850 °C at 10 °C min⁻¹ and held for 10 h under the flow of ammonia gas (40 mL min⁻¹). The reaction was then allowed to cool to 25 °C whilst retaining the ammonia flow to give *c*-Ta₃N₅ as a red powder.

Calculations

The optimized γ -tantalum oxynitride and β -tantalum oxynitride model was calculated and the ground-state energy band by using the standard CASTEP package. The CASTEP code is a plane-wave pseudopotential total energy calculation method that is based on the density functional theory (DFT). In our calculational study, the electronic wave functions were expanded in a plane-wave basis set up to a 340 eV cutoff. The ultrasoft pseudopotential and 3×3×3 k-point for samples were chosen in the calculation. During geometry optimization, the parameters were set as follows: the self-consistent field (SCF) tolerance was 1×10⁻⁶ eV atom⁻¹, maximum force was 0.03 eV Å⁻¹, maximum stress was

0.05 GPa, and maximum displacement was 10^{-3} Å. In addition, the empty bands, which are important in the calculations, especially for the optical properties, were increased to 20. The electronic exchange-correlation energy was treated within the framework of the generalized gradient approximation (GGA) and the local density approximation (LDA). The calculations of the energy band and density of states (DOS) were executed. Scissors of 2.0 eV and smearing of 0.5 eV were employed for the results analysis.

Characterization

The obtained products were characterized with powder X-ray diffraction (XRD, MAC Science Co. Ltd Japan) using Cu K α ($\lambda = 0.1546$ nm) and XRD patterns were obtained for 10-90° 2 θ by step scanning with a step size of 0.02°. The crystal phases of the samples used in Rietveld refinement were characterized by XRD with a scanning range between 20° and 90° in the step of 0.02°(2 θ) and a counting time of 10s for each step. The morphology and size of the resultant powders were characterized by a Zeiss Ultra 55 field-emission scanning electron microscope (SEM) associated with X-ray energy-dispersive spectrometer (EDX). Transmission electron microscopy (TEM) images and the corresponding selected area electron diffraction (SAED) patterns were captured on the transmission electron microscopy (TEM, JEM-2010) at an acceleration voltage of 200 kV. The optical properties of the samples were analyzed by UV-vis diffuse reflectance spectroscopy (UV-vis DRS) using a UV-vis spectrophotometer (UV-2550, Shimadzu). Fine BaSO₄ powder is used as a standard for baseline and the spectra are recorded in a range 190-900 nm. The chemical states of the sample were determined by X-ray photoelectron spectroscopy (XPS) in a VG Multilab 2009 system (UK) with a monochromatic Al K α source and charge neutralizer. The surface area of the samples was

measured by TriStar 3000-BET/BJH surface area. The as-prepared sample was degassed at 200 °C prior to nitrogen adsorption measurements. The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3. A desorption isotherm was used to determine the pore size distribution via the Barret–Joyner–Halender (BJH) method. The photoluminescence (PL) and PL excitation (PLE) spectra were measured at room temperature with Jobin Yvon-Spex Fluoromax-4 spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source. The excitation wavelength was 400 nm, the scanning speed was 1200 nm/min, and the width of excitation slit and emission slit were both 2.0 nm.

Photocatalytic Tests

Photocatalytic hydrogen production was carried out in an air free closed gas circulation system reaction cell made of quartz. The total cylindrical volume of the cell was 250 mL. An optically polished piece of quartz glass was fused on top of the cell to minimize light scattering. Hydrogen evolution was detected using a gas chromatograph (Beijing, GC-3240, TCD, Ar carrier), which was connected to a gas-circulation line. Argon with a flowrate of 100 mL min⁻¹ was used as a carrier gas, and was passed through the quartz glass cell. The Ru and Pt cocatalyst was loaded on photocatalysts by impregnation from an (NH₄)₂RuCl₆ and H₂PtCl₆ aqueous solution followed by a hydrogen reduction treatment at 200 °C for 5 h. In a typical photocatalytic experiment, 0.3 g of catalyst was dispersed in an 200 mL mixed solution of methanol (20 mL) and DI water (180 mL). The reaction vessel was evacuated several times to completely remove the air from the reaction system, followed by the introduction of argon into the system. The reaction was initiated by irradiation with a 300 W xenon lamp fitted with a cut off filter ($\lambda > 420$ nm).

The whole system, including the photocatalyst, was flushed with Ar at 100 mL min⁻¹ for 1 h to remove any trace of air (including nitrogen and oxygen) before any photocatalytic reaction was carried out. During the process, agitation of the solution ensured uniform irradiation of the suspensions. A 0.4 mL sample of the generated gas was collected intermittently through the septum, and hydrogen content was analyzed by a gas chromatograph. All glassware was rigorously cleaned and carefully rinsed with distilled water prior to use. Quantum efficiency (QE) was measured under identical photocatalytic reaction conditions with irradiation light at $\lambda = 420$ nm by using a 300 W xenon lamp and combined band pass and cut-off filters. The number of incident photons was also calibrated with a Si photodiode (FZ-A, HANDY). The QE was calculated according to the following equation:

$$\begin{aligned} \text{QE (\%)} &= \frac{\text{The rate of reacted electrons}}{\text{The rate of incident photons}} \times 100 \\ &= \frac{\text{The rate of evolved H}_2 \text{ molecules} \times 2}{\text{The rate of incident photons}} \times 100 \end{aligned} \quad (1)$$

Photoelectrochemical Measurements

The photoelectrodes were prepared by dip-coating route. 10 mg as-synthesized architecture particles were suspended in 2 mL ethanol and dissolved 5 mg polyethylene glycol (PEG, Aladdin M_w=20,000) as a binder material to produce a slurry, which was then dip-coated onto a 1 × 2 cm FTO glass electrode. The film was dried at room temperature and calcined at 400 °C for 1 h under N₂ flow (rate = 20 mL min⁻¹) to remove the binder. The deposition of cocatalyst Co₃O₄ onto photoanode was carried out by an impregnation method as the previous work.¹ The colloidal Co(OH)_x solution was firstly prepared by the addition of NaOH into an cobalt nitrate aqueous solution. The electrode

was then immersed into the as prepared $\text{Co}(\text{OH})_x$ colloidal solution for 1 h, washed with distilled water and then calcined at 300 °C for 10 minutes in air. The electrochemical cell used a standard three-electrode configuration with a Pt gauze counter electrode and a standard saturated calomel electrodes (SCE). The photocurrents were measured using a Solartron 1287 potentiostat. Mott–Schottky analyses were performed with a Solartron 1255B frequency response analyzer under control by ZPLOT software. The solution contained 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte. A 300 W Xe lamp was utilized as a light source.

Additional Results

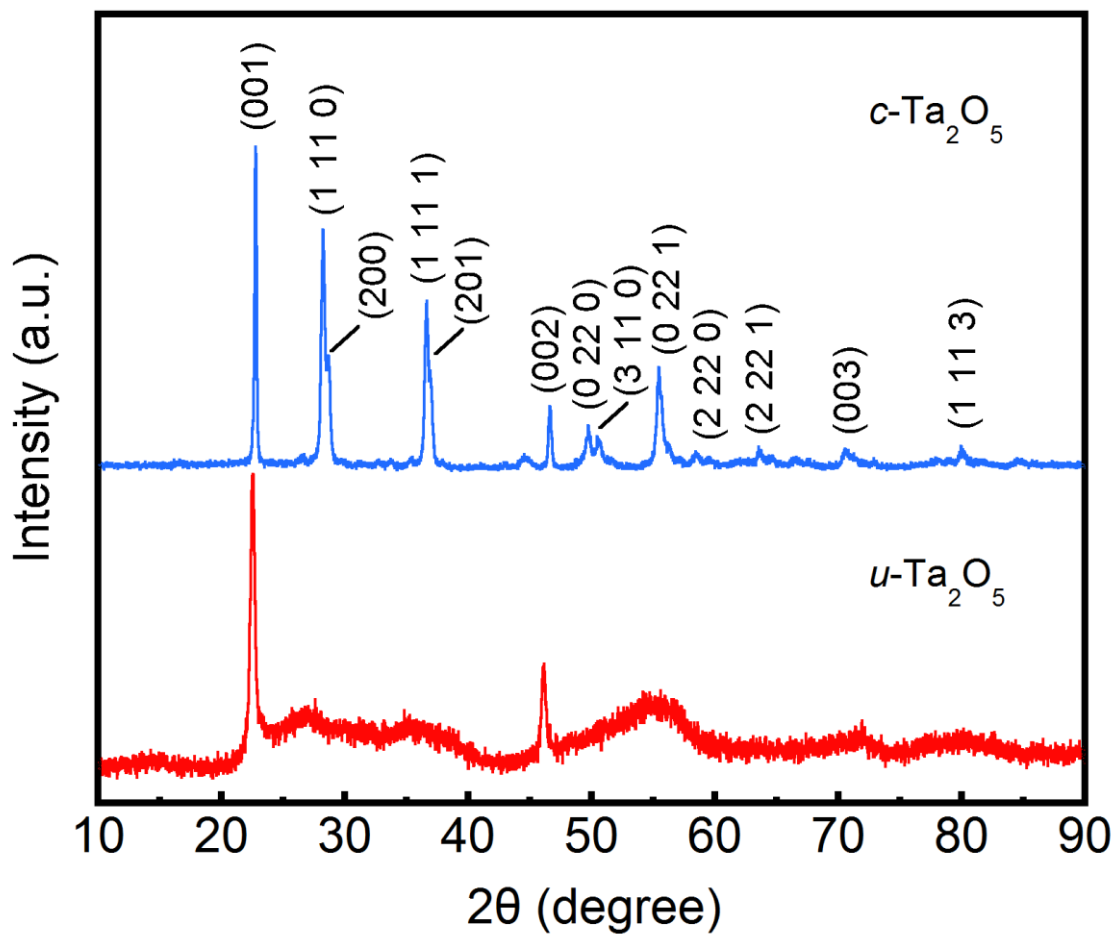


Fig. S1. XRD of hollow urchin-like and commercial Ta_2O_5 powders.

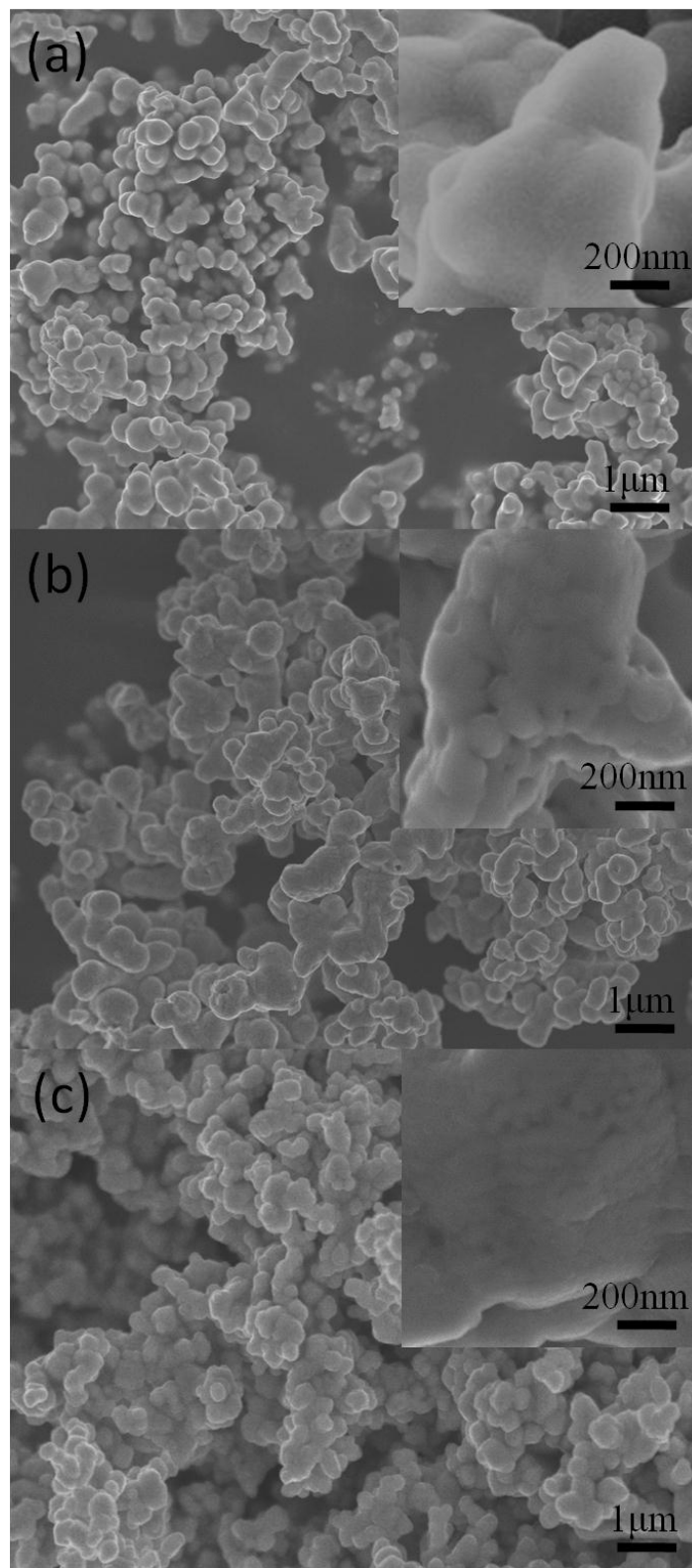


Fig. S2. SEM images of $c\text{-Ta}_2\text{O}_5$ (a), $c\text{-TaON}$ (b) and $c\text{-Ta}_3\text{N}_5$ (c).

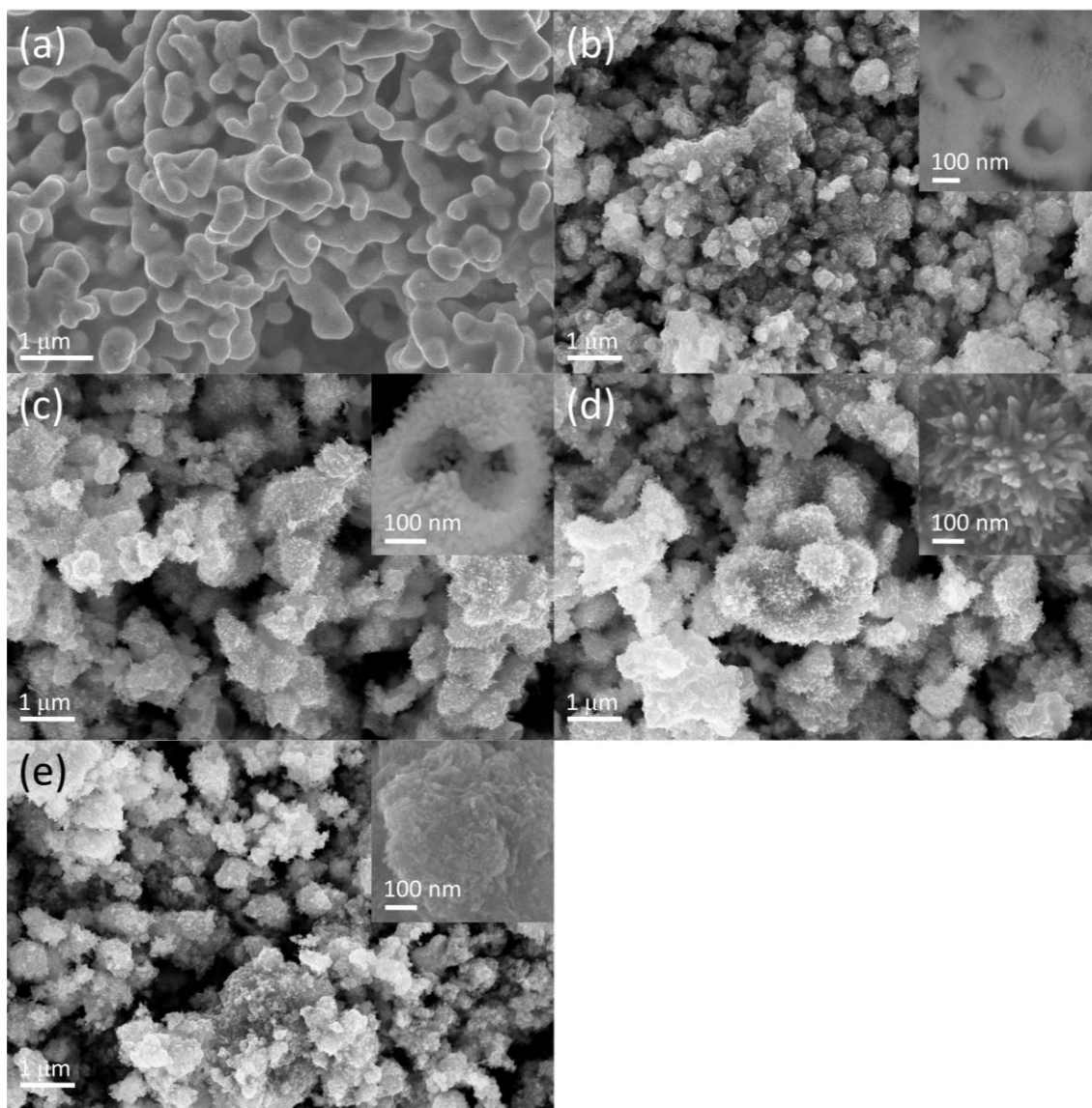


Fig. S3. SEM images of precursor Ta powder and *u*-Ta₂O₅ with different hydrothermal time (b) 3 h, (c) 6 h, (d) 12 h and (e) 24 h.

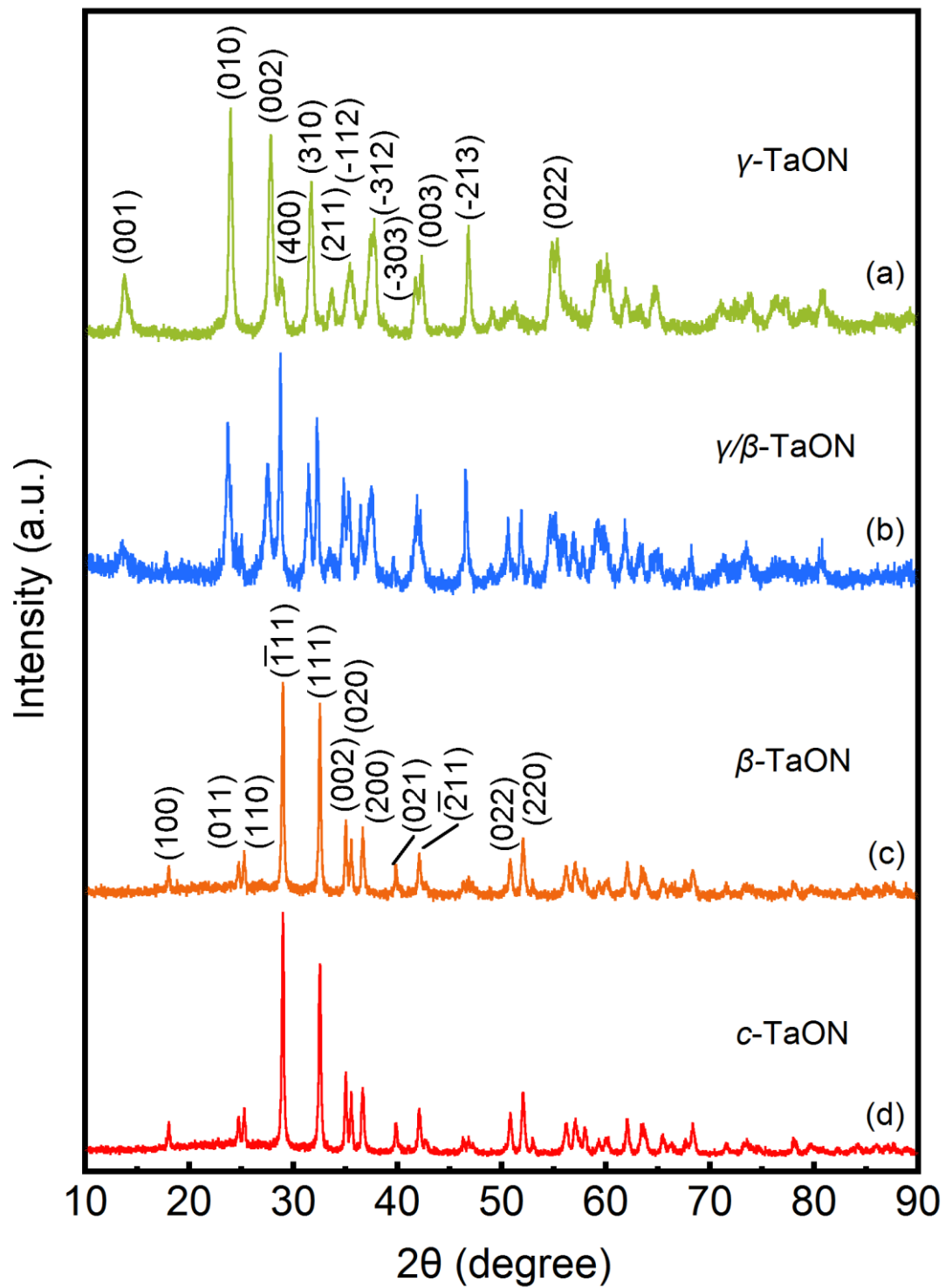


Fig. S4. XRD of hollow urchin-like and commercial TaON powders.

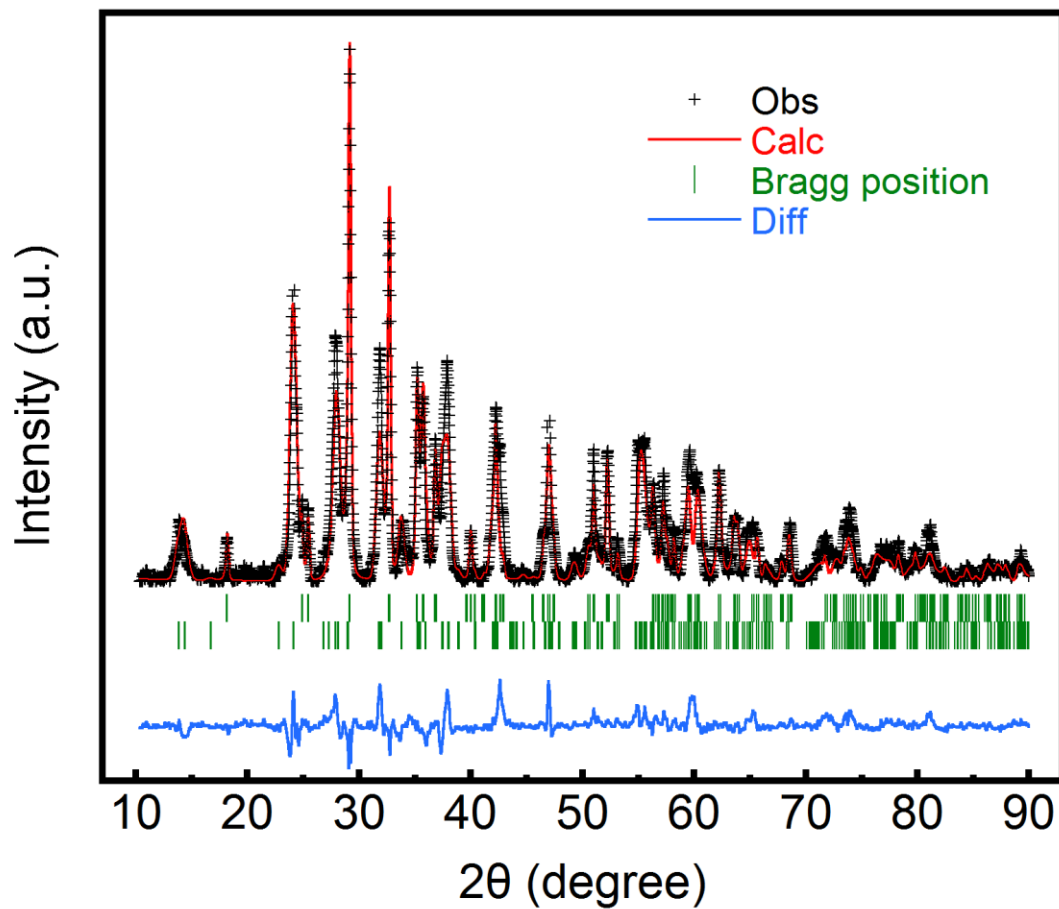


Fig. S5a. Rietveld refinement of XRD pattern of γ/β -TaON sample. (+) observed, (red solid line) calculated, (| symbols) Bragg position, (bottom, blue solid line) difference of phase.

Phase 1

Table 1: Structural Parameters of γ -TaON after Rietveld Refinement^a

Atom	site	occupancy: <i>g</i>	atomic coordinates		
			<i>x</i>	<i>y</i>	<i>z</i>
Ta (1)	4 <i>i</i>	1.0	0.3083(3)	0	0.1942(6)
Ta (2)	4 <i>i</i>	1.0	0.5993(1)	0	0.2071(4)
O (1)	4 <i>i</i>	1.0	0.378(24)	0	0.473(01)
O (2)	4 <i>i</i>	1.0	0.152(34)	0	0.192(18)
N (1)	4 <i>i</i>	1.0	0.468(83)	0	0.333(51)
N (2)	4 <i>i</i>	1.0	0.781(64)	0	0.344(86)

^aUnit cell: Monoclinic $C2/m$, $a = 12.9224(25) \text{ \AA}$, $b = 3.8662(75) \text{ \AA}$, $c = 6.7089(17) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 107.425(13)^\circ$, $\gamma = 90^\circ$, $V = 355.8(8) \text{ \AA}^3$. Weight percent = 61% $R_{wp} = 0.0886$, $R_p = 0.0651$, $R_F = 0.0293$.

Phase 2

Table 2: Structural Parameters of β -TaON after Rietveld Refinement^a

Atom	site	occupancy: <i>g</i>	atomic coordinates		
			<i>x</i>	<i>y</i>	<i>z</i>
Ta (1)	4 <i>e</i>	1.0	0.2861(7)	0.0426(0)	0.2148(6)
O (1)	4 <i>e</i>	1.0	0.066(21)	0.327(29)	0.344(38)
N (1)	4 <i>e</i>	1.0	0.444(76)	0.755(75)	0.480(81)

^aUnit cell: Monoclinic $P2_1/c$, $a = 4.9592(05) \text{ \AA}$, $b = 5.0267(63) \text{ \AA}$, $c = 5.1773(77) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 99.645(97)^\circ$, $\gamma = 90^\circ$, $V = 126.4(3) \text{ \AA}^3$. Weight percent = 39% $R_{wp} = 0.0886$, $R_p = 0.0651$, $R_F = 0.0293$.

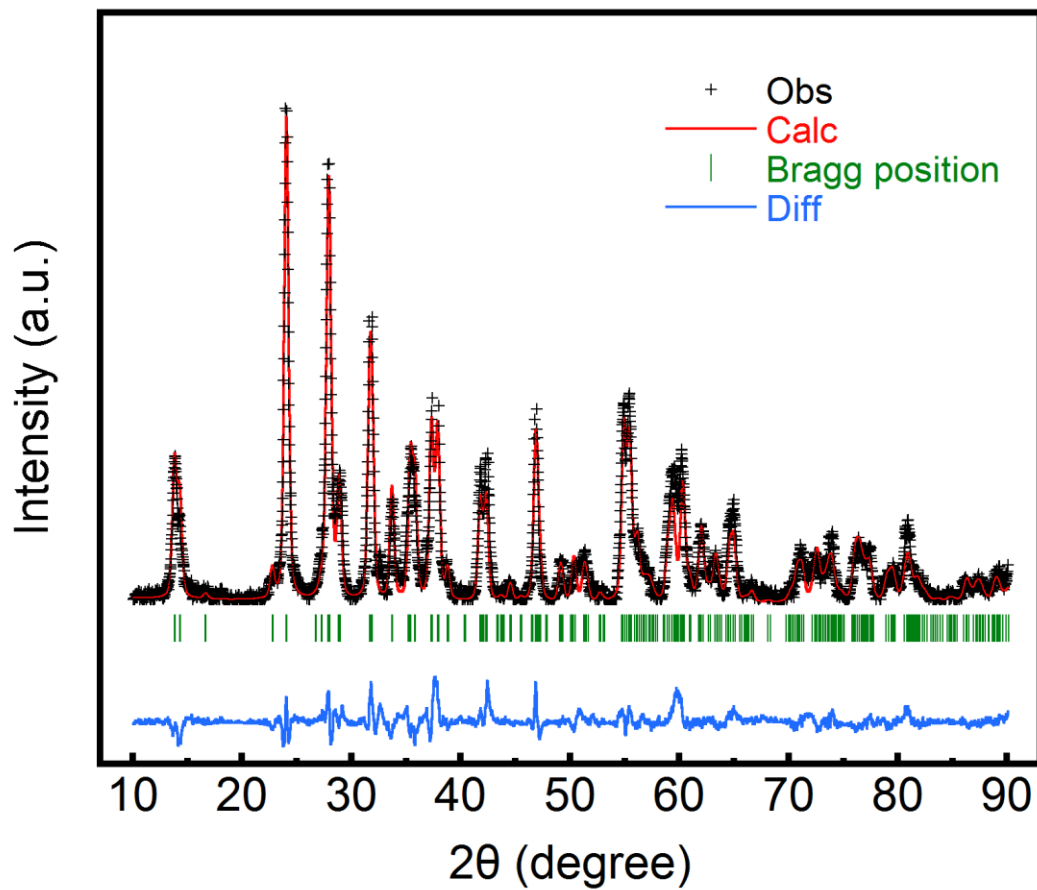


Fig. S5b. Rietveld refinement of XRD pattern of γ -TaON sample. (+) observed, (red solid line) calculated, (| symbols) Bragg position, (bottom, blue solid line) difference of phase.

Table 3: Structural Parameters of γ -TaON after Rietveld Refinement^a

Atom	site	occupancy: <i>g</i>	atomic coordinates		
			<i>x</i>	<i>y</i>	<i>z</i>
Ta (1)	4 <i>i</i>	1.0	0.3090(7)	0	0.1966(5)
Ta (2)	4 <i>i</i>	1.0	0.6000(5)	0	0.2095(3)
O (1)	4 <i>i</i>	1.0	0.369(71)	0	0.471(28)
O (2)	4 <i>i</i>	1.0	0.143(81)	0	0.190(45)
N (1)	4 <i>i</i>	1.0	0.470(56)	0	0.174(07)
N (2)	4 <i>i</i>	1.0	0.781(64)	0	0.185(42)

^aUnit cell: Monoclinic $C2/m$, $a = 12.9726(81) \text{ \AA}$, $b = 3.8753(14) \text{ \AA}$, $c = 6.7110(69) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 107.431(67)^\circ$, $\gamma = 90^\circ$, $V = 321.8(92) \text{ \AA}^3$. $R_{wp} = 0.0742$, $R_p = 0.0535$, $R_F = 0.0198$.

Full-profile structure refinement of XRD data was performed using the Rietveld program Fullprof² with the previously reported crystal structures of γ -TaON³ and β -TaON⁴ as starting models.

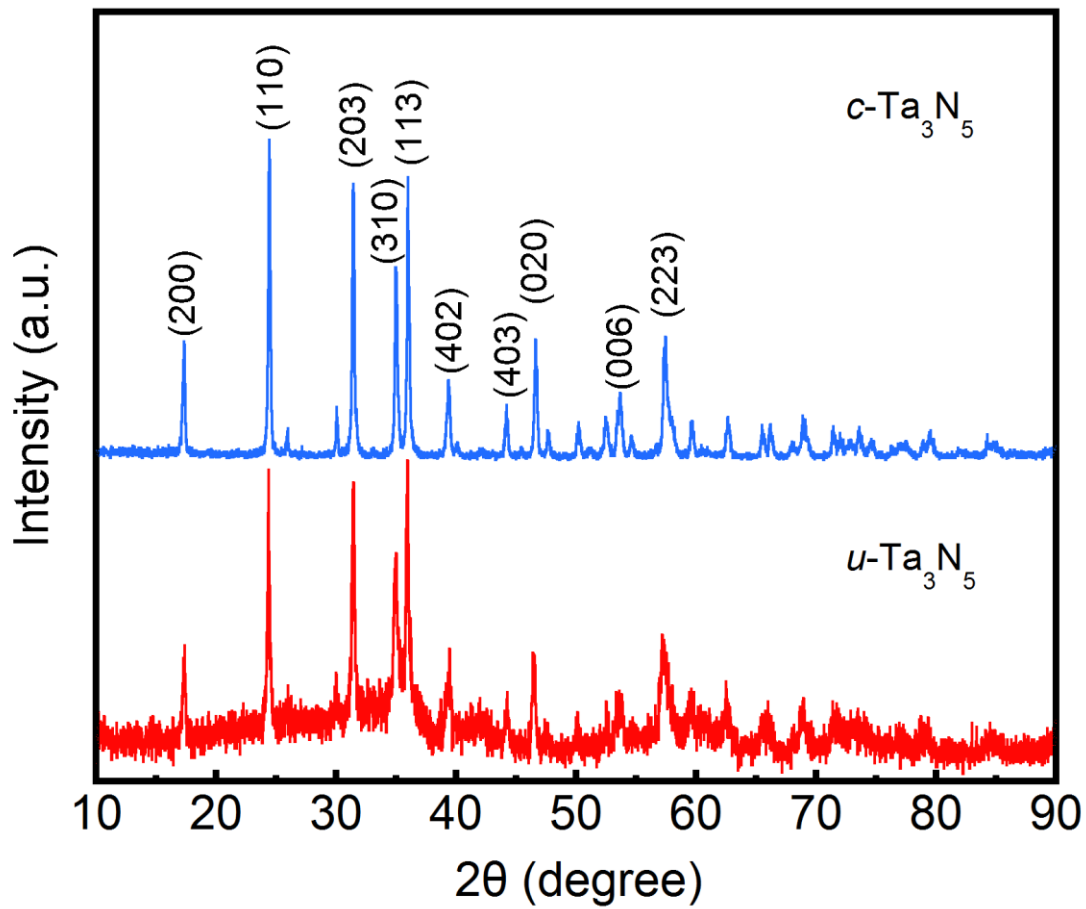


Fig. S6. XRD of hollow urchin-like and commercial Ta_3N_5 powders.

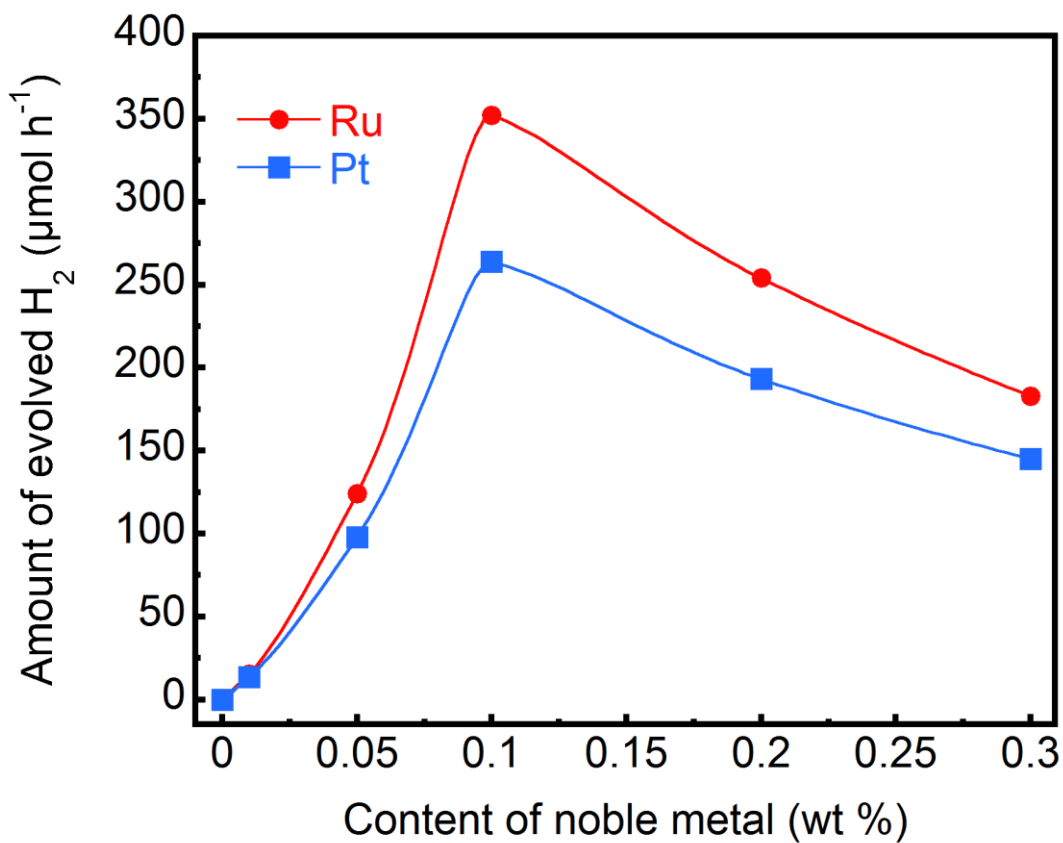


Fig. S7. Rate of H₂ evolution on Pt and Ru modified γ/β -TaON sample plotted against cocatalyst content. Reaction conditions: catalyst, 0.3 g; reactant solution, 10:1 water:methanol solution, 200 mL; light source, xenon lamp (300 W) with cut-off filter ($\lambda > 420$ nm); reaction vessel, top-irradiation type; 1 h irradiation.

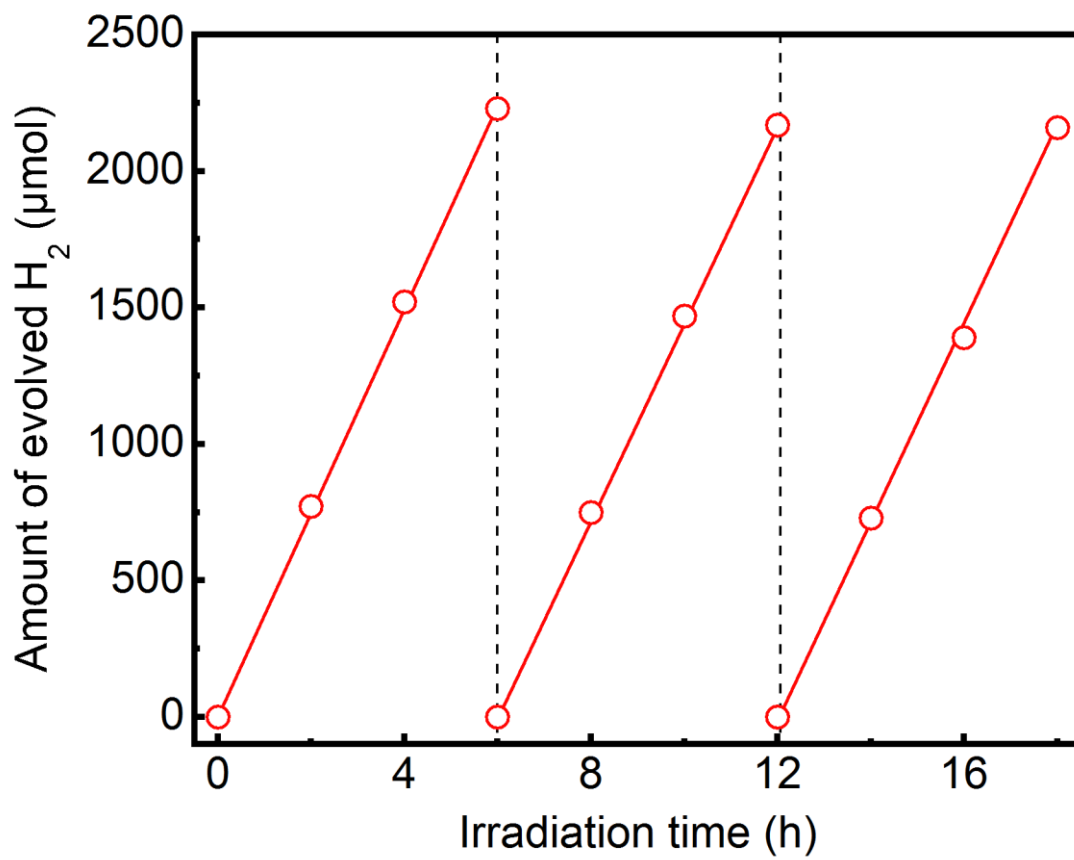


Fig. S8. Cycling measurements of hydrogen gas generation through direct photocatalytic water splitting with γ -TaON under visible-light ($\lambda > 420$ nm).

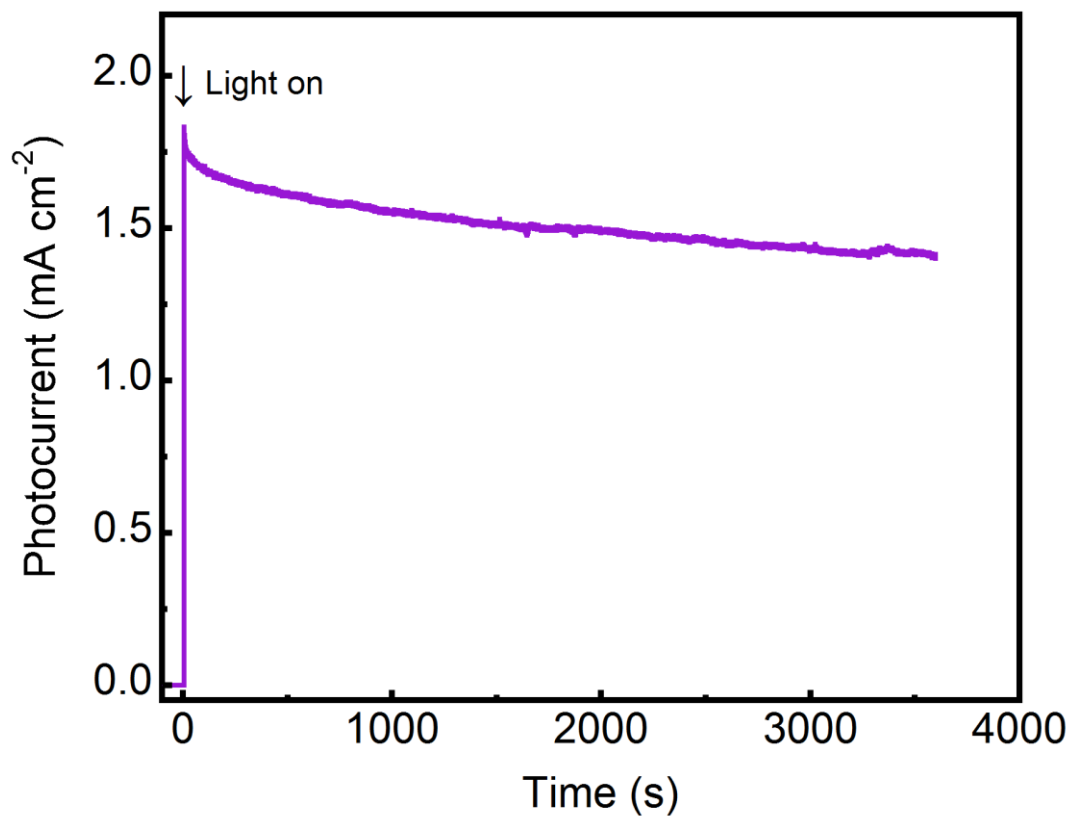


Fig. S9. Photocurrent decay curves measured at 1.0 V vs. SCE under visible light irradiation ($\lambda > 420$ nm) for γ - TaON with the Co_3O_4 as the cocatalyst in 0.5 M Na_2SO_4 solution.

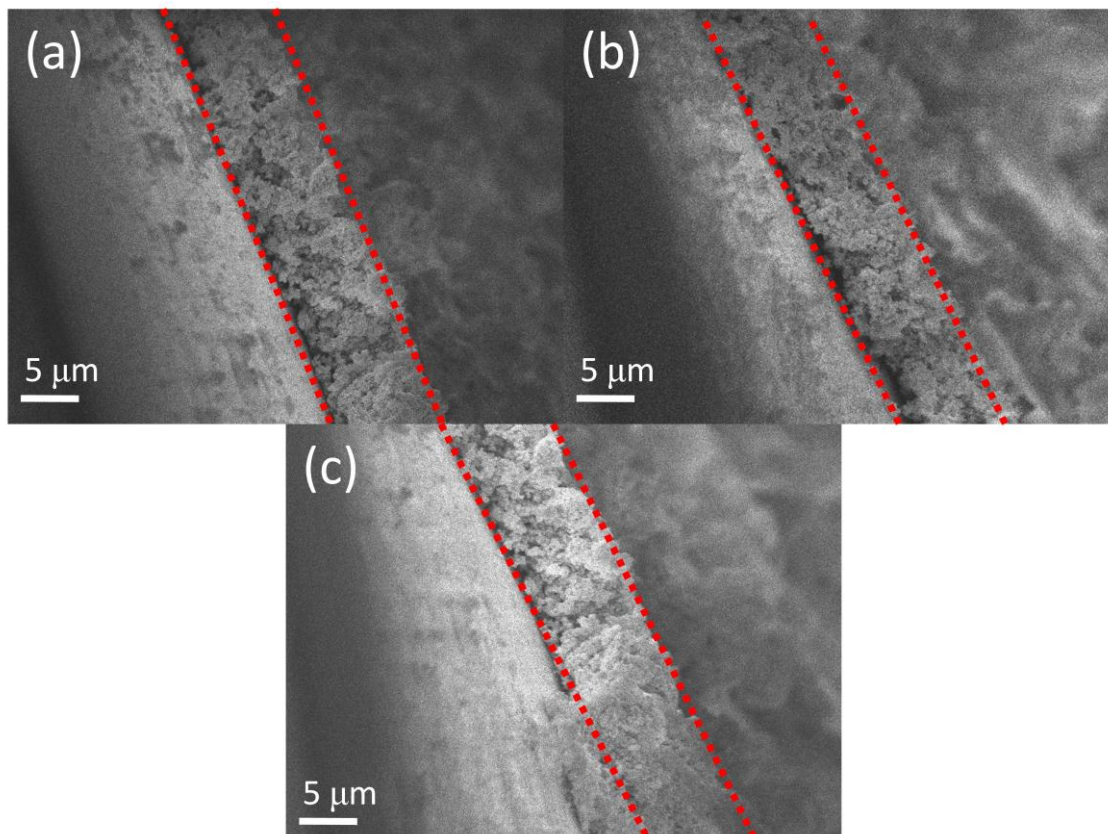


Fig. S10. SEM images of γ -, γ/β -, β -TaON photoanode films.

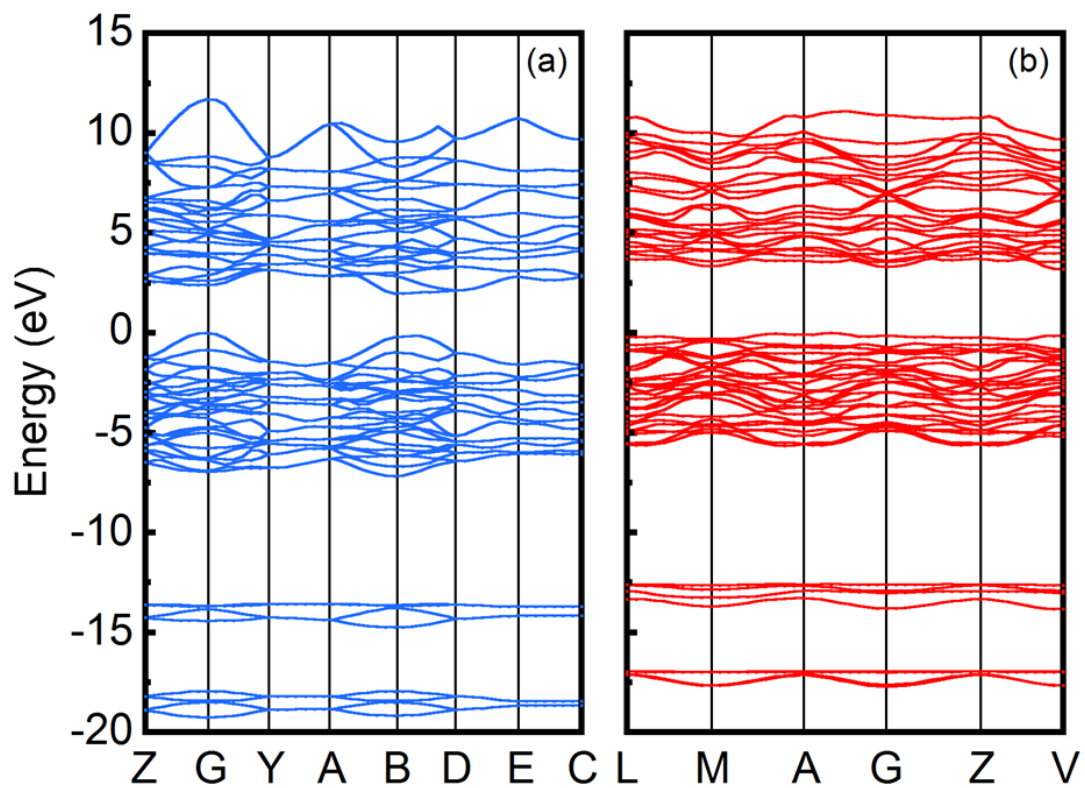


Fig. S11. The calculated energy band of β -TaON (a) and γ -TaON (b).

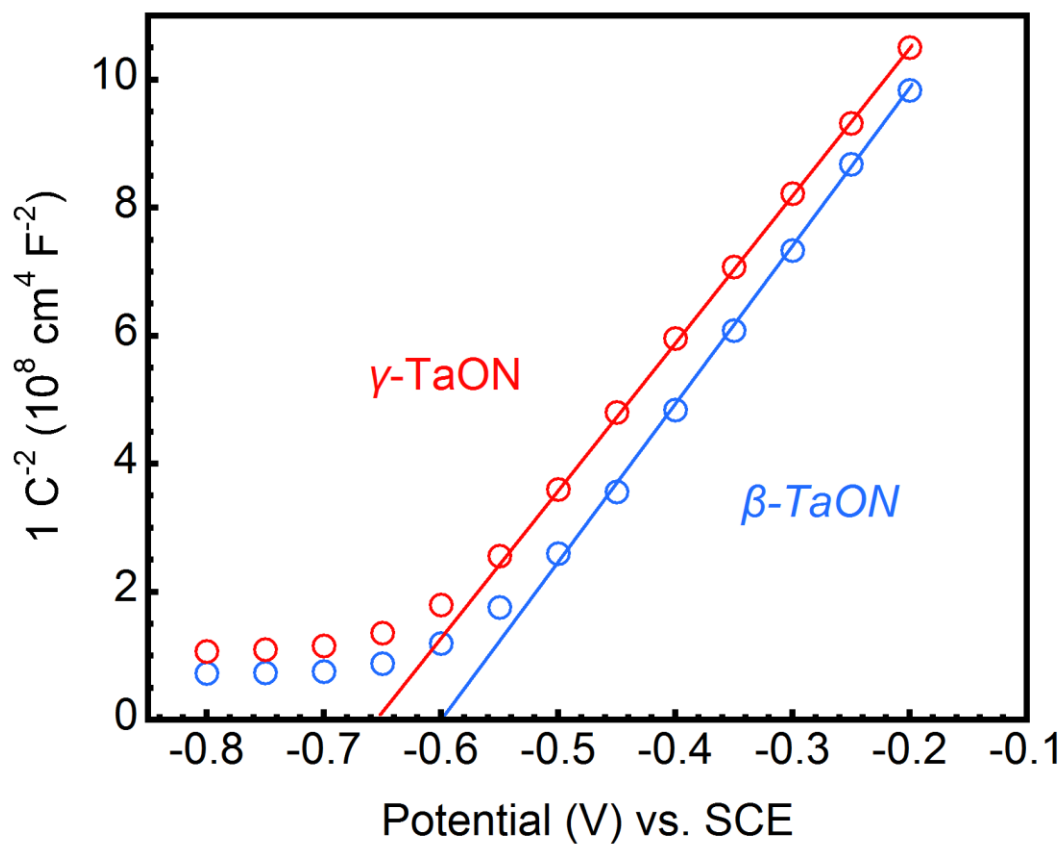


Fig. S12. Mott-Schottky plots for γ -TaON and β -TaON in 0.5 M Na_2SO_4 , the ac amplitude is 10 mV and the frequency is 1000Hz.

Reference:

- (1) Liao, M.; Feng, J.; Luo, W.; Wang, Z.; Zhang, J.; Li, Z.; Yu, T.; Zou, Z. *Adv. Funct. Mater.* **2012**, *22*, 3066-3074.
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- (4) Yashima, M.; Lee, Y.; Domen, K. *Chem. Mater.* **2007**, *19*, 588-593.