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(Supporting information)

Synthesizing Zr-based oxynitride with low defect by CaH_2-assisted nitridation for photocatalytic Z-scheme overall water splitting

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Experimental section

Synthesis of Zr_2ON_2, Hf_2ON_2, $SrTaO_2N$, Ta_3N_5 using CaH_2 as nitridation agent

The oxynitride Zr_2ON_2 (Hf_2ON_2, Ta_3N_5) was prepared by a CaH_2 assisted nitridation method, the detail process follows the steps as: chemicals ZrO_2 (99.99%, aladdin), Ta_2O_5 (99.9%, aladdin), HfO_2 (99.9%, aladdin) and CaH_2 (99.5%, Macklin) were fully grinded in a weight ratio of 1:1 and then the mixed powder was collected in a clean alumina boat. The mixed powder was nitrided with a gas flow of NH_3 (200 $mL\cdot min^{-1}$) at around 1073 K for less than 10 hours. The nitridation process was conducted using a quartz tube with a diameter of 34 mm, with a heating rate of 5 K/min, while a high-purity ammonia gas flow was maintained throughout the procedure. Each time the nitrided oxide-precursor amount was fixed to be 0.15 g. The nitrided sample was cooled naturally to room temperature and the CaH_2 was removed by thoroughly washing with 0.1 M hydrochloric acid solution and pure water for several times to obtain a pure sample.

In comparison, the Zr_2ON_2 was synthesized with the conventional nitridation method and labeled as ZON. The ZrO_2 was used as the nitridation precursor and it was directly placed in a porcelain boat, and then nitrided with a gas flow of NH_3 (500 $mL \cdot min^{-1}$) at 1323 K for 40 h. Similarly, the HfO_2 was directly nitrided with a gas flow of NH_3 (500 $mL \cdot min^{-1}$) at 1323 K for 50 h to synthesize Hf_2ON_2, and Ta_2O_5 and $Sr_2Ta_2O_7$ were directly nitrided with a gas flow of NH_3 (200 $mL \cdot min^{-1}$) at 1173 K for 15 h to synthesize Ta_3N_5 and $SrTaO_2N$, respectively.

Photoelectrochemical measurements

The electrodes were prepared by electrophoretic deposition in an acetone solution (50 mL) containing Zr_2ON_2 powder (50 mg) and iodine (20 mg). Two parallel FTO electrodes were immersed in the solution with a 10~15 mm separation, and 40 V bias was applied for 10 s, and then the 0 V bias continues for 5 s, repeating 10 times to obtain a uniformly coated electrode sheet. The deposited electrodes were calcined with N_2 flow at 623 K for 1 h to remove absorbed iodine and then the deposition area was controlled to be around 0.25 cm^2 with insulating glue. Measurements were carried out using a conventional Pyrex electrochemical cell, with a platinum wire as a counter electrode and an Ag/AgCl reference electrode under potentiostat control (HSV-100, Hokuto Denko, Japan). An aqueous solution containing 0.5 M Na_2SO_4 was used as the electrolyte with pH = 8.5 (adjusted with NaOH aqueous solution). A 300 W xenon lamp with a wavelength of 420~800 nm was used as the light source. The potential scan range for the linear voltammetric scan is from -0.6 V (vs. Ag/AgCl) to 0.63 V (vs. Ag/AgCl), with a scan rate of 10 mV/s. The frequency and amplitude of AC potential were 1~3 kHz and 0.01 V, respectively. The OCVD measurement was conducted in a 1.0 M NaOH aqueous solution with a pH value of 13.6, and a 300 W xenon lamp was used as the light source. All the potentials were recorded with respect to the reversible hydrogen electrode (RHE).

Photocatalytic reaction test

The hydrogen evolution cocatalyst Pt was loaded by the traditional impregnation method using H_2PtCl_6 (Alfa 99%) as a Pt precursor. Typically, 0.15 g of photocatalyst powder and calculated amounts of H_2PtCl_6 (0.5 wt %) were mixed and ultrasound for 5 minutes. Then, dried at 353 K under vigorous stirring at the same time. Before the photocatalytic activity test, the sample was reduced in a 200 ml·min^{-1} H_2/Ar (5% H_2) mixture at 473K for 1 h.

The oxygen evolution co-catalyst CoO_x was loaded via an impregnation-calcination method. The procedure involved: thoroughly dispersing 0.15 g of Zr_2ON_2 powder in 5 mL of $Co(NO_3)_3$ aqueous solution containing 15 mg Co, followed by stirring to dryness in a 353 K water bath. The dried powder was collected and calcined in a tube furnace under NH_3 flow (200 mL·min^{-1}) at 973 K for 1 h, then subsequently calcined in a muffle furnace under air atmosphere at 473 K for 1 h.

Meanwhile, PtO_x was deposited onto WO_3 to act as a cocatalyst for the reduction of IO_3^-, following methods outlined in previous studies[1]. Initially, 500 mg of WO_3 was immersed in a 0.5 wt.% H_2PtCl_6 solution (based on metal content). After ultrasonic treatment for 5 minutes, the mixture was dried with continuous stirring in an 80 °C water bath. The resulting powder was then transferred to an alumina crucible and calcined at 550 °C for 30 minutes. Upon cooling, a Cs_2CO_3 solution, prepared to achieve a Cs^+/WO_3 molar ratio of 1%, was added to the powder. After drying, the sample was calcined at 500 °C for 10 minutes. Finally, the powder underwent ultrasonic dispersion in 1 M H_2SO_4 for 1 hour, followed by washing, drying, and collection.

The photocatalytic H_2 evolution or O_2 evolution activities were measured in an air-free top irradiation type quartz reactor connected to a closed gas circulation system. In a typical photocatalytic reaction, 0.15 g of the pure photocatalyst was suspended in a 150 ml aqueous solution containing 30 ml formic (methanol) acid or 4 mmol $AgNO_3$ as the sacrificial agent. Before the light irradiation, the solution was evacuated several times to ensure the complete removal of air and then irradiated from the top side with a 300 W Xenon lamp (Hoya, L-42; $\lambda > 420$ nm) using a filtration mirror. A flow of cooling water was used to maintain the reactant solution at 288 K. The amounts of the evolved gas were determined by gas chromatography (Agilent; GC-2014, MS5A column, TCD, Ar carrier). The photocatalytic hydrogen evolution experiments were performed in a similar setup except using HCOOH aqueous solution (20 vol%) as a sacrificial agent, each experiment was vacuumed for 20 min.

For each Z-scheme OWS test, 100 mg of the hydrogen evolution photocatalyst and 50 mg of the oxygen evolution photocatalyst were uniformly dispersed in 150 mL of 1 mM KI solution via ultrasonication. Before each photocatalytic run, the air was completely removed by pumping for 30 min to create an inert atmosphere. A 300 W Xenon lamp was employed as the light source and a filter was used to eliminate ultraviolet (UV) radiation ($\lambda < 420$ nm) unless otherwise specified.

Characterizations

The crystal structures and phase purities of the as-prepared powder samples were examined with X-ray powder diffraction (XRD) on a SmartLab Focus diffractometer with Cu K_α ($\lambda = 1.5406$ Å) as incident radiations. To collect the detailed XRD signals for refinement, the step size and collection time were 0.01° and 0.1 s, respectively. The General Structure Analysis System (GSAS) software package was adopted to perform Rietveld refinements [2]. The content of Ca^{2+} was determined with inductively coupled plasma-optical emission spectrometry (ICP-OES, avio550). The morphologies of the powder samples were observed with a field emission scanning electron microscope (JSM-7900F). The surface element-distributions and the binding energies of their core level electrons were examined by the X-Ray photoelectron spectrometer (XPS, Thermo Esclab 250Xi, monochromatic Al Kα X-ray source). The C1s peak (284.8 eV) was referenced to normalize the measured binding energies for each sample and the background of the spectra was assumed to be Shirley type. UV-Vis diffuse reflectance spectra (DRS) were recorded on a UV-Vis spectrophotometer (SHIMADZU UV-2600) equipped with a $BaSO_4$ integrating sphere. The time-resolved photoluminescence (TRPL) spectra were carried out using a PL scan-imaging microscope (FLS1000) coupled with a time-correlated single-photon counting (TCSPC) module at 370 nm laser excitation at room temperature and the TRPL signals were fitted with a biexponential function. The Surface Photovoltage (SPV) was measured using a custom-built setup (Bruker Dimension V SPM system), with a Pt/Ir alloy-coated tip serving as the probe. The surface potential is defined as the difference in work function between the sample surface and the tip. A 500 W Xe lamp was used, and modulation was achieved through a grating.

Computational methods

All the density functional theory (DFT) calculations were performed in the Vienna ab initio simulation package (VASP)[3] with the frozen-core projector augmented wave (PAW) method. The Perdew-Burke-Ernzerhof (PBE) functional within the framework of the generalized gradient approximation (GGA) was utilized to describe the exchange-correlation interactions. The energy cutoff of the plane wave basis was set to be 500 eV and Brillouin zone integration was performed using a 3×3×3 Monkhorst–Pack k-point grid. The geometrical structure was fully optimized with the energy convergence criterion and the tolerance for force convergence was set to 1.0×10^{-5} eV and 0.01 eV/Å, respectively.

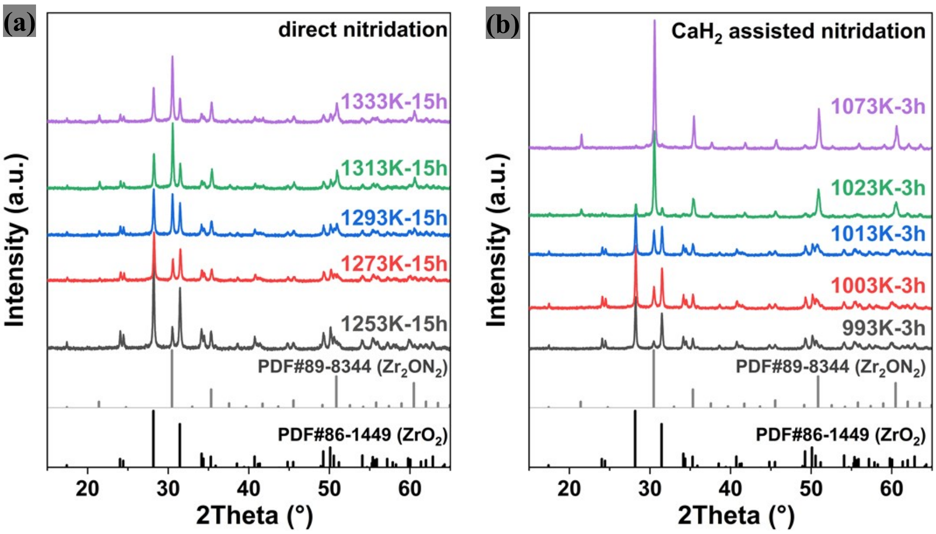


Fig. S1. (a) XRD patterns of the ZON samples that were directly nitrided at 1253~1333 K for 15 h; (b) XRD patterns of the ZON(CaH_2) samples that were nitrided using CaH_2 as the nitridation agent at 993~1073 K for 3 h.

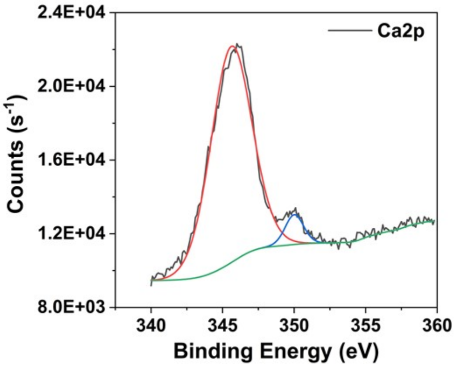
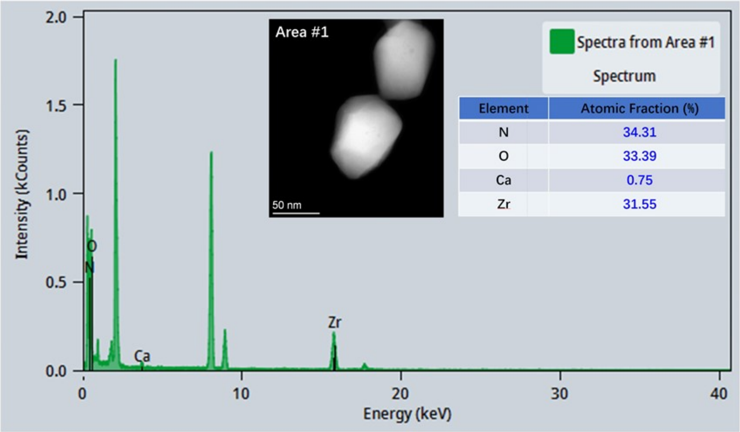


Fig. S2. The Ca2p XPS signal of ZON(CaH_2) that was nitrided under 1073 K for 5h.



Element	Atomic Fraction (%)
N	34.31
O	33.39
Ca	0.75
Zr	31.55

Fig. S3. The quantified total element-signal from the EDS mapping of the selected area #1 in ZON(CaH_2).

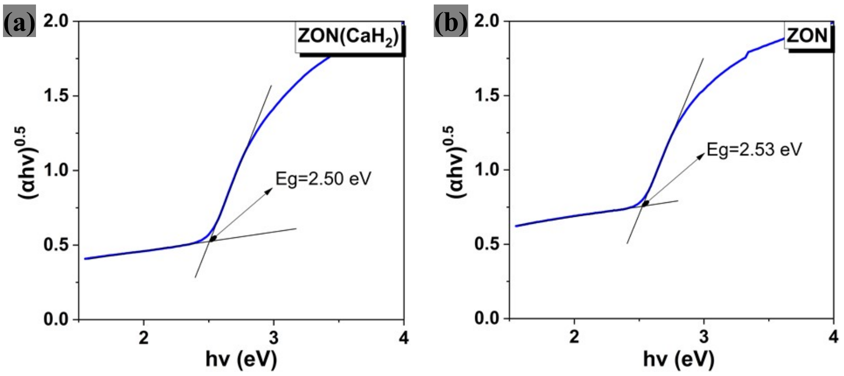


Fig. S4. The Tauc-plot of (a) ZON(CaH_2) and (b) ZON. (The bandgap of ZON(CaH_2) and ZON were revealed to be 2.50 eV and 2.53 eV, respectively)

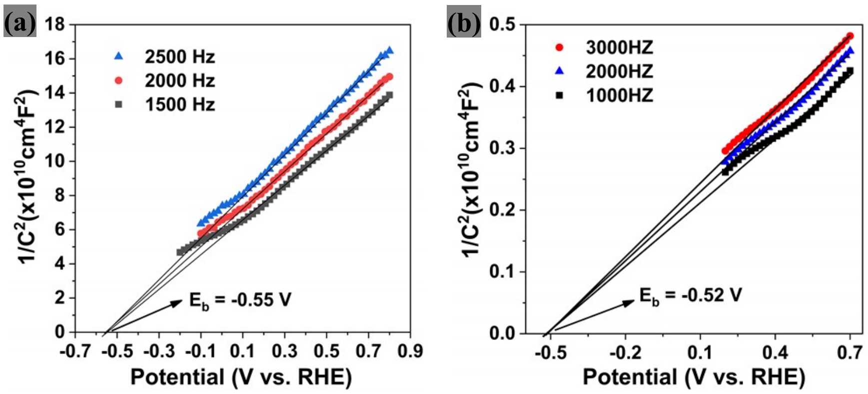


Fig. S5. Mott-Schottky plot of (a) ZON(CaH$_2$) and (b) ZON. (The flat band potential of ZON(CaH$_2$) and ZON were determined to be -0.55 V and -0.52 V (vs. RHE), respectively)

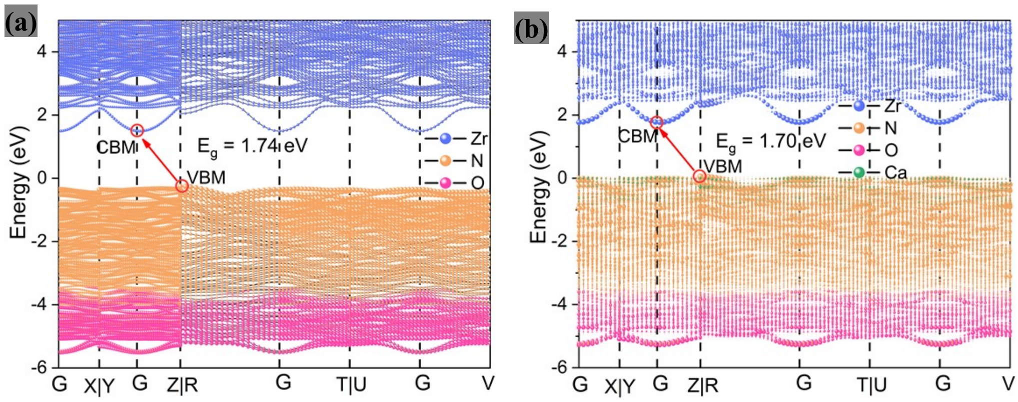


Fig. S6. The calculated band structure of (a) ZON and (b) ZON(CaH_2).

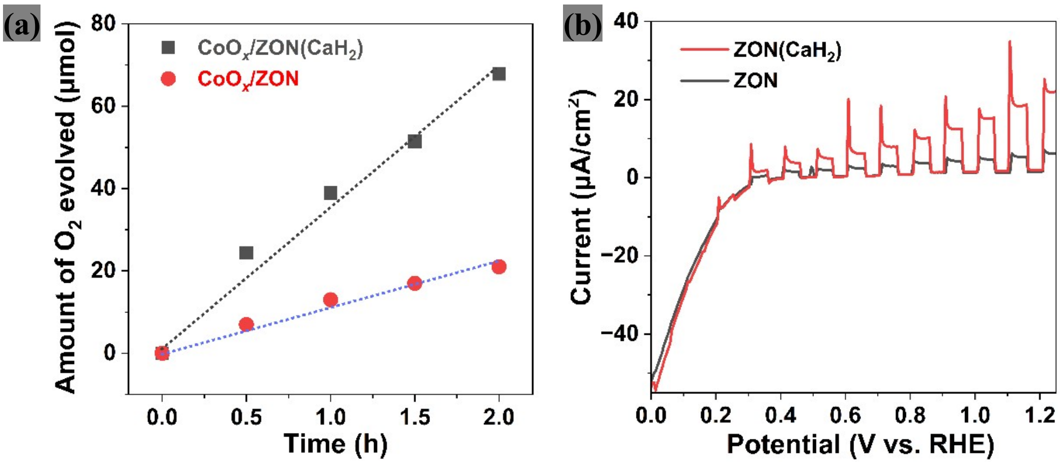


Fig. S7. (a) Time-dependent cumulative oxygen production curves of ZON (CaH_2) and ZON loaded with 1% CoO_x during photocatalytic oxygen evolution performance tests. (Test conditions: 150 mg photocatalyst, 4 mmol $AgNO_3$; 300 W Xe lamp, $\lambda \geq 420$ nm); (b) J-E curves of ZON (CaH_2)-based and ZON-based photoanodes, showing the magnitude of photocurrent response during the chopper process.

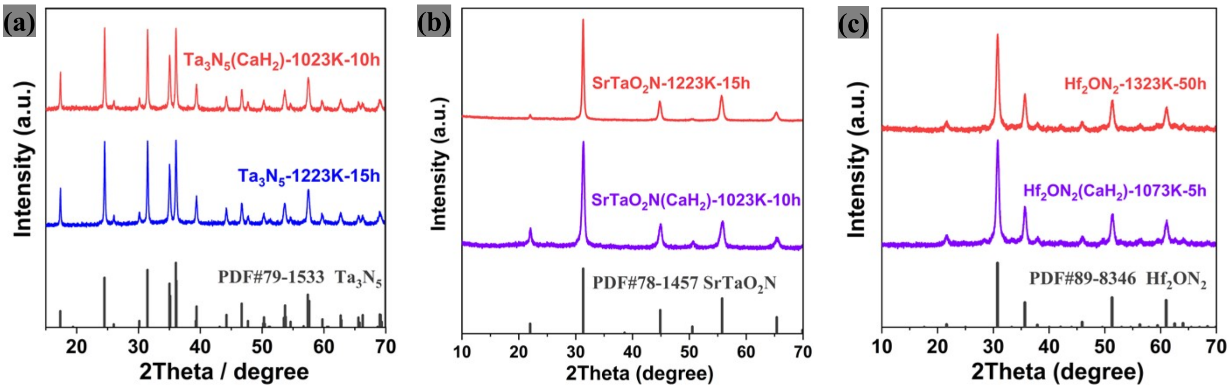


Fig. S8. XRD patterns of the CaH_2 assisted nitridation samples compared with their counterparts that was prepared by the direct nitridation method (a) Ta_3N_5; (b) $SrTaO_2N$; (c) Hf_2ON_2.

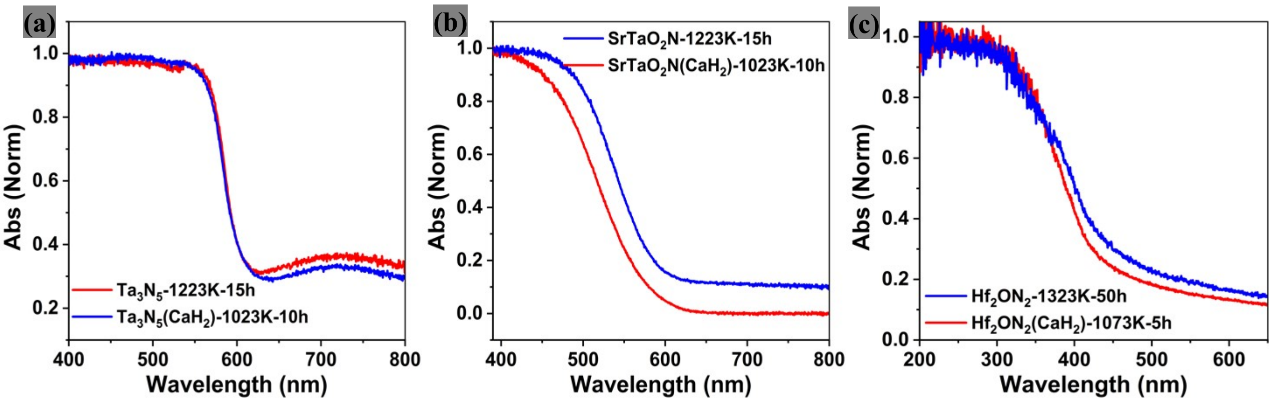


Fig. S9. UV-vis DRS spectra of the CaH_2 assisted nitridation samples compared with their counterparts that was prepared by the direct nitridation method (a) Ta_3N_5; (b) $SrTaO_2N$; (c) Hf_2ON_2.

Table S1. The XRD refinement results of ZON(CaH_2) and ZON samples that were nitrided with varied temperatures.

Sample		**Refined weight fraction of ZrO_2 (%)**	**Refined weight fraction of Zr_2ON_2 (%)**	**Goodness-of-fit factor after XRD refinement**		
				x^2	***wR*p**	***R*p**
ZON-	1253K-15h	90.4	9.6	3.8	0.08	0.06
	1273K-15h	84.3	15.7	2.6	0.09	0.07
	1293K-15h	71.2	28.8	2.3	0.08	0.06
	1313K-15h	54.1	45.9	2.0	0.08	0.06
	1333K-15h	45.6	54.4	1.8	0.07	0.05
	1323K-40h	0	100	2.0	0.05	0.04
ZON(CaH_2)	993K-3h	88.0	12.0	1.8	0.07	0.05
	1003K-3h	83.3	16.7	1.9	0.07	0.05
	1013K-3h	75.1	24.9	1.3	0.06	0.05
	1023K-3h	69.8	30.2	2.6	0.08	0.06
	1073K-3h	6.9	93.1	1.5	0.06	0.05
	1073K-5h	0	100	1.8	0.07	0.06

Table S2. Z-scheme OWS performance of typical oxynitride-based HEP at their initial reporting-stage.

HEP (cocatalyst)	**OEP (cocatalyst)**	**Overall water splitting reaction**			**Ref.**
		Reaction condition	**Activity (μmol/h)**		
			H_2	**O_2**	
$Zr_2ON_2(CaH_2)$ *(0.5 wt% Pt)*	WO_3 (*0.5 wt% PtO_x*)	1 mM KI aqueous solution under visible light (300 W Xe lamp), 100 mg of HEP and 50 mg of OEP	~2.1	~1.1	**This work**
$YTaON_2$ *(0.75 wt% Pt)*	WO_3 (*0.5 wt% PtO_x*)	1 mM KI aqueous solution under visible light (300 W Xe lamp), 100 mg of HEP and 50 mg of OEP	~0.3	~0.15	[4]
$BaTaO_2N$ *(0.3 wt% Pt)*	WO_3 (*0.5 wt% PtO_x*)	5 mM NaI aqueous solution under visible light (300 W Xe lamp), 100 mg of HEP and 100 mg OEP	~7.0	~3.5	[5]
$BaZrO_3$–$BaTaO_2N$ (*0.3 wt% Pt*)	WO_3 (*0.5 wt% PtO_x*)	1 mM NaI aqueous solution under visible light (300 W Xe lamp), 50 mg of HEP and 100 mg of OEP	~6.0	~3.0	[6]
$Ta_3N_5/BaTaO_2N$ (*0.5 wt% Pt*)	WO_3 (*0.45 wt% PtO_x*)	1 mM NaI aqueous solution under visible light (300 W Xe lamp), 50 mg of HEP and 50 mg of OEP	~2.0	~1.0	[7]
TaON *(0.3 wt% Pt)*	TaON *(0.3 wt% RuO_2)*	1 mM NaI aqueous solution under visible light (300 W Xe lamp), 50 mg of HEP and 50 mg of OEP	~1.5	~0.8	[8]
$YTaO_{4-x}N_y$ *(0.75 wt% Pt)*	WO_3 (*0.5 wt% PtO_x*)	1 mM KI aqueous solution under visible light (300 W Xe lamp), 100 mg of HEP and 50 mg of OEP	~1.1	~0.6	[9]

Table S3. Fitting parameters of PL decay spectra of ZON(CaH_2) and ZON.

Sample	**τ_1 (ns)**	**A_1 (%)**	**τ_2 (ns)**	**A_2 (%)**	**τ_3 (ns)**	**A_3 (%)**	**y_0**	$\bar{\tau}$
ZON(CaH_2)	6.50±0.34	0.7	95.00±3.41	80.2	633.54±17.91	19.1	3.64±0.13	**189.70±5.94**
ZON	2.96±0.15	1.1	73.28±2.32	84.0	549.77±12.5	16.9	4.21±0.13	**154.50±4.06**

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