

Supplementary Information

Integration of Nonlinear Two-photon Excited Fluorescence and Photocatalysis Boosts Overall Water Splitting Performance

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1. Experimental section

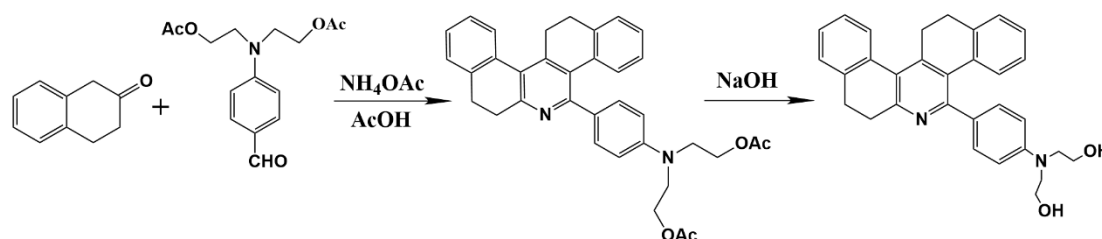
1.1 Materials and synthesis

Zinc oxide (ZnO, 99%, Kanto Chemicals Co., Ltd.), Gallium oxide (Ga_2O_3 , 99.99%, High Purity Chemicals Co., Ltd.), Ammonium chlorochromate ($(\text{NH}_4)_3\text{RhCl}_6$, Rh 27.5%, Shanghai Macklin Biochemical Co., Ltd.), potassium chromate (K_2CrO_4 , 99.9%, Shanghai Macklin Biochemical Co., Ltd.). The general chemicals are obtained from Aladdin industrial corporation and are purified by standard methods.

1.1.1 Synthesis of $(\text{ZnO})_{1-x}(\text{GaN})_x$ solid solution

A mixture of 1.3693 g of ZnO and 0.6307 g of Ga_2O_3 powder (with an atomic ratio of Zn to Ga of 2.5:1) was heated at 1023 K for 10 h under an NH_3 stream.¹ The obtained pristine $(\text{ZnO})_{1-x}(\text{GaN})_x$ was dispersed in 50 mL of Ultrapure water containing $(\text{NH}_4)_3\text{RhCl}_6$ and K_2CrO_4 (1 wt% Rh and 1.5 wt% Cr relative to the $(\text{ZnO})_{1-x}(\text{GaN})_x$ powder). Then the photo-deposition was carried out under a 300 W Xe lamp ($\lambda \geq 420$ nm) for 5 h. The $\text{Rh}_{2-\gamma}\text{Cr}_\gamma\text{O}_3/(\text{ZnO})_{1-x}(\text{GaN})_x$ composite was obtained after filtration and drying. Subsequent references to the $(\text{ZnO})_{1-x}(\text{GaN})_x$ solid solution herein refer to the $(\text{ZnO})_{1-x}(\text{GaN})_x$ solid powder that has been photo-deposited with the co-catalyst $\text{Rh}_{2-\gamma}\text{Cr}_\gamma\text{O}_3$, if not otherwise specified.

1.1.2 Synthesis of DSC fluorescent solute



81.60 g (0.45 mol) of 2-hydroxyethyl aniline was weighed and dissolved in 108 mL of pyridine. Subsequently, 127.50 mL (1.35 mol) of acetic anhydride was added, and the mixture was refluxed at 383 K for 6 h. After cooling, the mixture was poured into ice water and washed with water more than 10 times until the upper layer solution turned pale gray. The solution was subsequently extracted with dichloromethane, evaporated to dryness, and the resulting residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate (20:1) to yield a

white solid. Under ice bath conditions, 23.70 g (0.15 mol) of phosphorus oxychloride was weighed and added dropwise to 5.60 g (0.07 mol) of dimethylformamide to form a frozen salt. Add 50 mL of trichloromethane solution containing 8.00 g (0.03 mol) of raw material to the frozen salt, slowly raise the temperature to 338 K, and reflux for 6 h. Then, pour the product into crushed ice, adjust the pH to weak alkaline with a sodium hydroxide solution, extract with dichloromethane, separate the lower organic layer, evaporate to dryness to obtain the product, disperse in ethanol to obtain a white solid, and name it as M. Add 3.85 g (50 mmol) of ammonium acetate to a round bottom flask, followed by 1.47 g (5 mmol) of compound M, 1.49 g (10 mmol) of 2-tetrahydronaphthalene ketone, and 30 mL of acetic acid. Stir at room temperature for 24 h. Then, filter to obtain a solid, pour the filtrate into a large amount of water to obtain a milky white solid, filter and dry, purify with a 5:1 mixture of petroleum ether and ethyl acetate using column chromatography to obtain a milky white solid, designated as DSA. Add 0.50 g (0.90 mmol) of DSA to a round bottom flask, dissolve it in 100 mL of ethanol, add a 10% aqueous solution of sodium hydroxide, stir at room temperature for 24 h, adjust the pH to neutral with a diluted hydrochloric acid solution, filter to obtain a solid, wash with plenty of water, extract with dichloromethane, and evaporate to dryness to obtain the fluorescent solute DSC.

1.2 Materials Characterization

The X-ray diffraction (XRD) measurements of materials were carried out by a diffractometer operating (Smartlab 9 kW, Cu $K\alpha$ radiation) at 40 kV and 200 mA, in a 2θ range of 10-80° with a step width of 0.01°. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were recorded using a shimadzu UV-2600i UV-visible/NIR spectrophotometer in diffuse absorption mode with Ba_2SO_4 as a white standard reference. Fourier transform infrared spectroscopy (FT-IR) was collected on Thermo Scientific Nicolet iS50R spectrometer. Scanning electron microscopy (SEM) images were obtained by Regulus 8230. Fluorescence spectra are measured using Hitachi F-7000 fluorescence spectrophotometer. The nuclear magnetic resonance (NMR) spectra are measured on a Bruker AVANCE instrument using the dimethylsulfoxide- d_6 (DMSO- d_6) as solvents (400 MHz for 1H NMR). ESI Mass Spectrometer are recorded using LCQ Fleet.

1.3 Photocatalytic Experiment

The overall water splitting performances of samples were evaluated in a 200 mL closed quartz vial under the top irradiation photocatalytic reaction system (MC-SPB10, Beijing Merry Change Technology Co., Ltd.). Generally, 50 mg of the sample was suspended in 50 mL of ultrapure water. Subsequently, the solution was exposed to a 300 W Xe lamp (MC-PF300C, Beijing Merry Change Technology Co., Ltd.) equipped with a cut-off filter ($\lambda \geq 420$ nm or $\lambda \geq 550$ nm), and the temperature of the reaction solution was maintained at 281 K using a circulating cooling water system. Before irradiation, the system was evacuated for 30 min to completely remove the dissolved oxygen. The gases produced during the photocatalytic reaction were analyzed via gas chromatography (GC-5190, Anhui Chromatography Co., Ltd.) equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column.

1.4 Two-photon excited fluorescence (2PEF) spectroscopy

To avoid the possibility excited state absorption, a femtosecond laser pulse is used to record the two-photon cross-sections of the compounds and using Ti: Sapphire system (680–1080 nm, 80 MHz, 140 fs) as the light source. Their 2PEF is compared with that of fluorescein to obtain a 2PA cross section (σ), the formula is as follows:

$$\sigma_s = \frac{\sigma_r \times F_s \times C_r \times n_r}{F_r \times \phi_s \times C_s \times n_s}$$

The subscripts “s” and “r” represent sample and reference (here, fluorescein in a NaOH solution is used as reference and samples and the concentration of the sample is 1.0×10^{-3} mol/L with a 1 cm standard quartz cell). The concentration of fluorescein and NaOH are both 1.0×10^{-3} mol/L. F is the 2PEF integral intensity of the solution emitted at the exciting wavelength. ϕ , n and C are the quantum yield of the fluorescence, the refractive index of the solvent, and the concentration of the solution, respectively. The values of σ_r at different wavelengths and F_r are taken from the literature. The formula for calculating the apparent quantum yield of the fluorescence (ϕ) is as follows:

$$\phi_s = \frac{Y_r \times F_s \times A_r}{F_r \times A_s}$$

The subscripts “s” and “r” represent the test substance and reference substance, respectively. A denotes absorbance, F denotes fluorescence integral area, and Y denotes quantum yield.

1.5 Two-photon absorption (2PA) spectroscopy

To study the third-order NLO properties of DSC its nonlinear 2PA coefficient (β) and the molecular 2PA cross-sections (σ) were obtained by an open-aperture Z-scan technique using a femtosecond laser pulse (680-1080 nm, 80 MHz). The pulse length was 140 fs, and the average laser power was 36 mW. The sample in DMSO (its thickness is 1 mm) was put in the light path, and all measurements were carried out at room temperature. The filled squares represent the experimental data, and the solid line is the theoretical curve modified from the following equations.

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{-q_0(z)^m}{(m+1)^{3/2}}; q_0(z) = \frac{\beta I_0 L_{eff}}{1+x^2}$$

where $x = z/z_0$, in which $z_0 = \pi\omega_0^2/\lambda$ is the diffraction length of the beam, where ω_0 is the spot size at the focus, λ is the wavelength of the beam, and z is the sample position. I_0 is the input intensity at the focus $z = 0$ and equals the input energy divided by $\pi\omega_0^2$. $L_{eff} = (1 - e^{-\alpha L})/\alpha$ is the effective length, in which α is the linear absorption coefficient and L is the sample length.

1.6 Apparent quantum yield (AQY) calculation methods.

To produce one H atom from an H^+ ion, one electron is required, while the production of one H_2 molecule requires two electrons through a one-step excitation process. To measure the AQY for H_2 production, we used a 300 W Xe lamp (MC-PF300C, Beijing Merry Change Technology Co., Ltd.) equipped with various bandpass filters ($\lambda=380\pm 15, 420\pm 20, 480\pm 20, 500\pm 30$) to obtain monochromatic light. The number of incident photons was determined with a fiber spectrometer (AvaSpecULS2048XL-EVO). The AQY was calculated using the Supplementary Equation:

$$N = \frac{S \times P \times \lambda \times t}{h \times c} \quad (1)$$

$$\begin{aligned} \text{AQY}(\%) &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \% \quad (2) \\ &= \frac{\text{number of evolved hydrogen molecules } (n_{H_2} \times N_A) \times 2}{\text{number of incident photons}} \times 100 \% \end{aligned}$$

where P is the intensity of irradiation light, S is the irradiation area, t is the photocatalytic reaction time, and λ is the wavelength of the monochromatic light, n_{H_2} is the amount of H_2 molecules, N_A is Avogadro's constant, h is the Planck constant, c is the speed of light.

1.7 STH Measurement and calculation.

1.7.1 STH Conversion Efficiency Measurement

The photocatalytic overall water splitting was conducted under an AM 1.5G solar simulator irradiation. The STH can be calculated by the Supplementary Equation (3)

$$\text{STH}(\%) = (R(\text{H}_2) \times \Delta G_r) / (P \times S) \times 100 \quad (3)$$

where $R(\text{H}_2)$, ΔG_r , P , and S are the rate of hydrogen evolution during the water splitting reaction, reaction Gibbs energy for water splitting (237 kJ mol⁻¹ at 288 K), intensity of the AM 1.5G solar irradiation (100 mW cm⁻²), and irradiation area (4 cm²), respectively. In this study, the calculated solar-to-hydrogen (STH) efficiency of the best-performing DSC-3 photocatalytic reaction system was found to be 0.09 %.

1.7.2 Calculation of the theoretical maximum STH value

Table S1 The theoretical maximum solar-to-hydrogen (STH) values corresponding to the bandgaps of certain photocatalysts before and after coupling with DSC solutions.

Photocatalyst	Band gap (eV)	Theoretical maximum STH	Photocatalyst-DSC theoretical maximum STH
TiO ₂	3.2	1.3 %	1.3 %
(ZnO) _{1-x} (GaN) _x	2.58	6.4 %	9.9 %
CdS	2.42	9.2 %	13.9 %

The STH value can be calculated from the product of the hydrogen production rate and an increase in the Gibbs free energy of 237 kJ mol⁻¹. The calculation formula is similar to Equation (3):

$$\text{STH} = \frac{\text{output energy}}{\text{Energy of incidence solar light}} = \frac{R_{\text{H}_2} \times \Delta G}{P_{\text{Sun}} \times S} \quad (4)$$

where P_{Sun} is the energy flux of sunlight and S is the area of the reactor. ASTM-G173 AM 1.5 global tilt is commonly used as the standard solar irradiation, with an energy flux of 100 mW·cm⁻² and a well-defined power spectrum.²

In this study, the theoretical maximum STH efficiency is calculated based on the following assumptions: (1) The apparent quantum yield of the nonlinear photocatalytic reaction system is 100 %. (2) Low-energy photons in the solar spectrum (700-850 nm) can be completely converted into high-energy photons (400-550 nm) through two-photon absorption and two-photon excited fluorescence by the DSC solution. (3) It is assumed that two water molecules split into two hydrogen molecules and one oxygen molecule in four-photon process.

The specific calculation approach is as follows: First, we determine the photocatalyst's absorption edge. Then, using the ASTM-G173 AM 1.5 global tilt spectrum, we calculate the total number of photons within the absorption edge per unit time and area. Assuming a four-photon conversion to two hydrogen molecules and an apparent quantum yield (AQY) of 100 %, we derive the maximum hydrogen production corresponding to the absorption edge from the number of photons. Finally, we can calculate the solar-to-hydrogen (STH) efficiency limit for photocatalysts at different wavelengths using the STH calculation formula mentioned above. For instance, the $(\text{ZnO})_{1-x}(\text{GaN})_x$ solid solution photocatalyst synthesized in this study demonstrates the ability to absorb photons within the 480 nm wavelength range. Analysis of the ASTM-G173 AM 1.5 global tilt spectrum yields a total photon flux of $3.2595 \times 10^{20} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ within this range, resulting in a hydrogen production rate of $0.27 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. The theoretical maximum solar-to-hydrogen (STH) efficiency is calculated to be 6.4 % using the relevant formula. Moreover, in the context of the proposed nonlinear photocatalytic reaction system, the DSC solution exhibits the capability to absorb photons within the 700-850 nm wavelength range. Considering the property of nonlinear two-photon absorption, which combines two low-energy photons into one high-energy photon, it can be inferred that the presence of DSC facilitates the utilization of photons within the 700-850 nm wavelength range by $(\text{ZnO})_{1-x}(\text{GaN})_x$. Taking into account the absorption edge of $(\text{ZnO})_{1-x}(\text{GaN})_x$, its Photocatalyst-DSC theoretical maximum STH is calculated to be 9.9 %.

2. Supplementary Figures

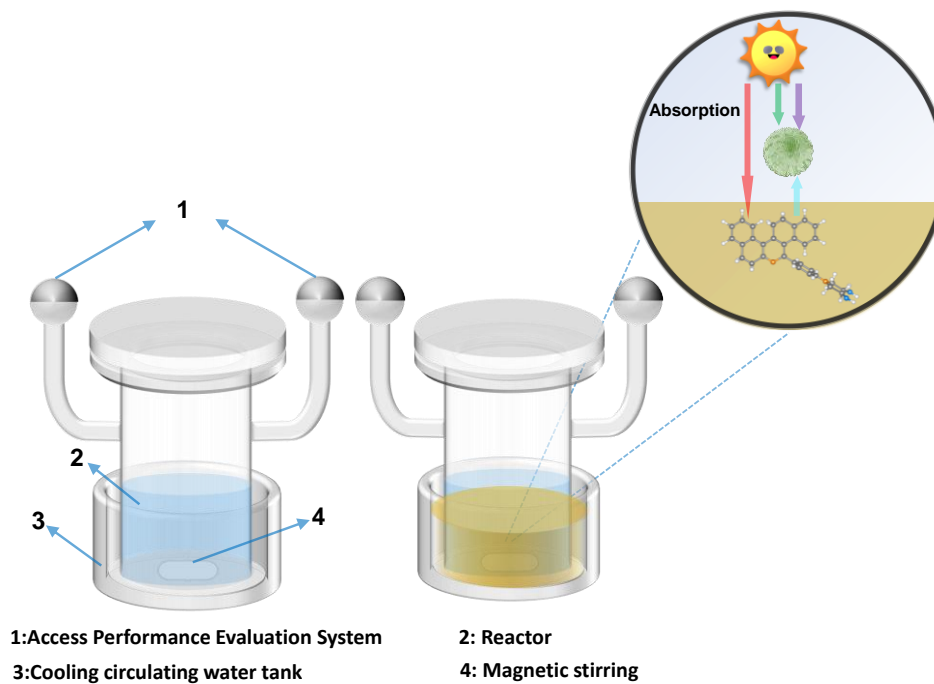


Fig.S1. The external non-contact performance evaluation system. The photocatalytic solution is placed in the reactor (2), while the DSC fluorescent solution is placed between the reactor (2) and the cooling circulation water tank (3).

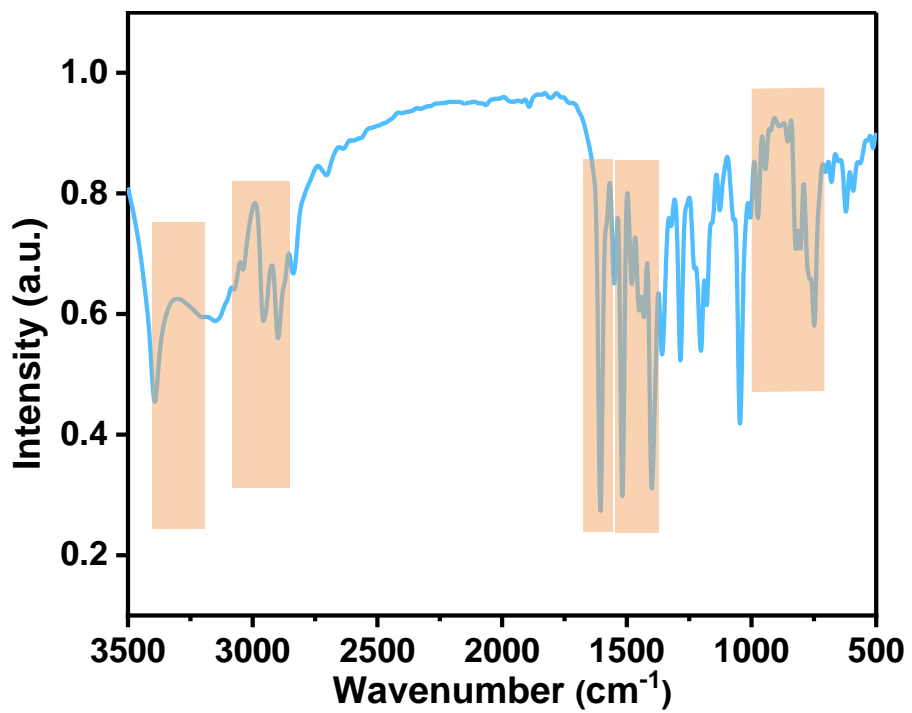
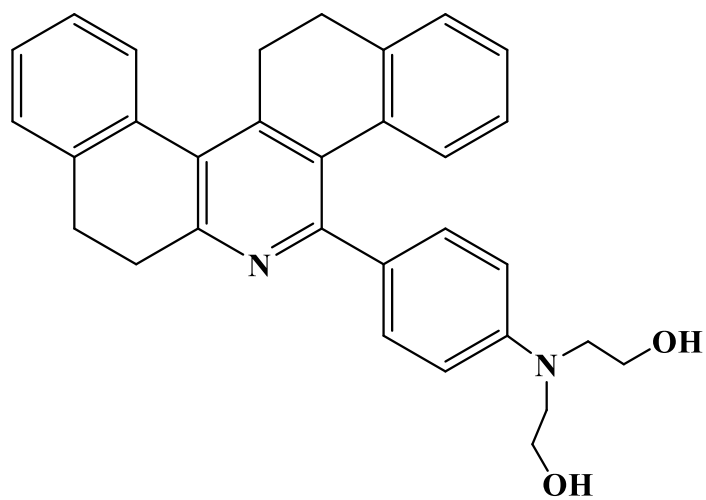


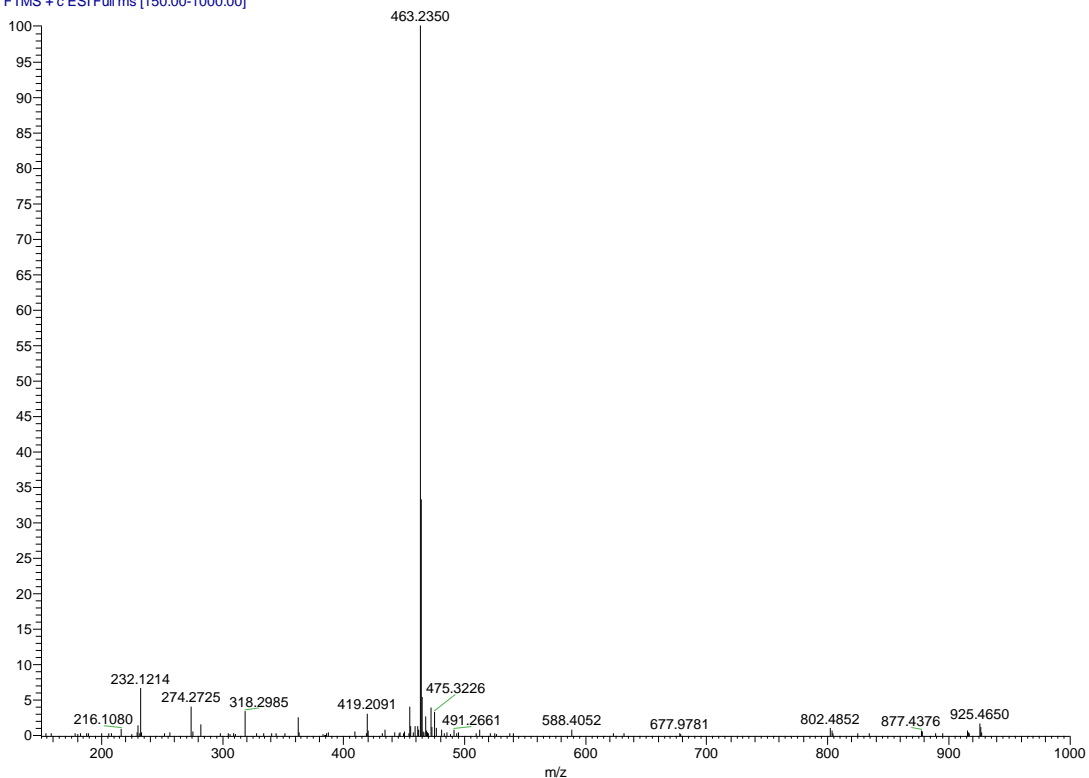
Fig.S2. The FT-IR spectrum of the DSC.



2,2'-((4-(7,8,13,14-tetrahydrodibenzo[*a,i*]phenanthridin-5-yl)phenyl)azanediyl)bis(ethan-1-ol)

Fig.S3. The structural formula of DSC.

DSC #6 RT: 0.08 AV: 1 SB: 1 0.03 NL: 3.86E6
T: FTMS + c ESI Full ms [150.00-1000.00]



DSC #6 RT: 0.08 AV: 1 SB: 1 0.03 NL: 3.86E6
T: FTMS + c ESI Full ms [150.00-1000.00]

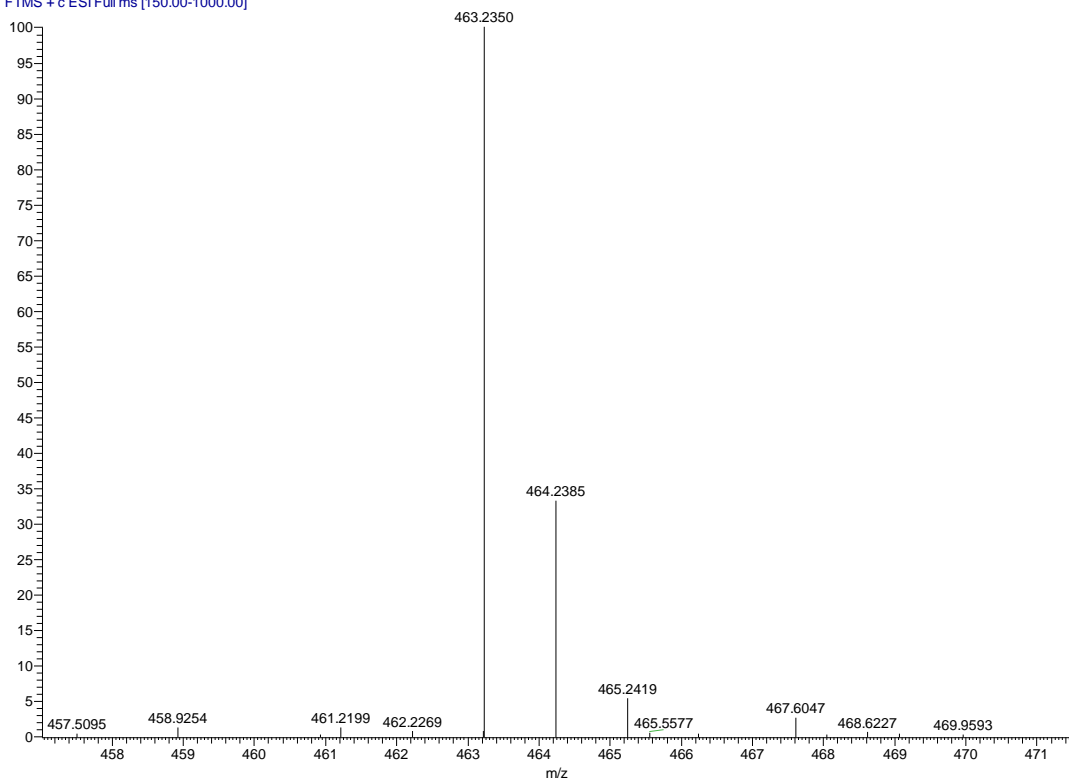


Fig. S4. ESI-Mass spectrum of DSC.

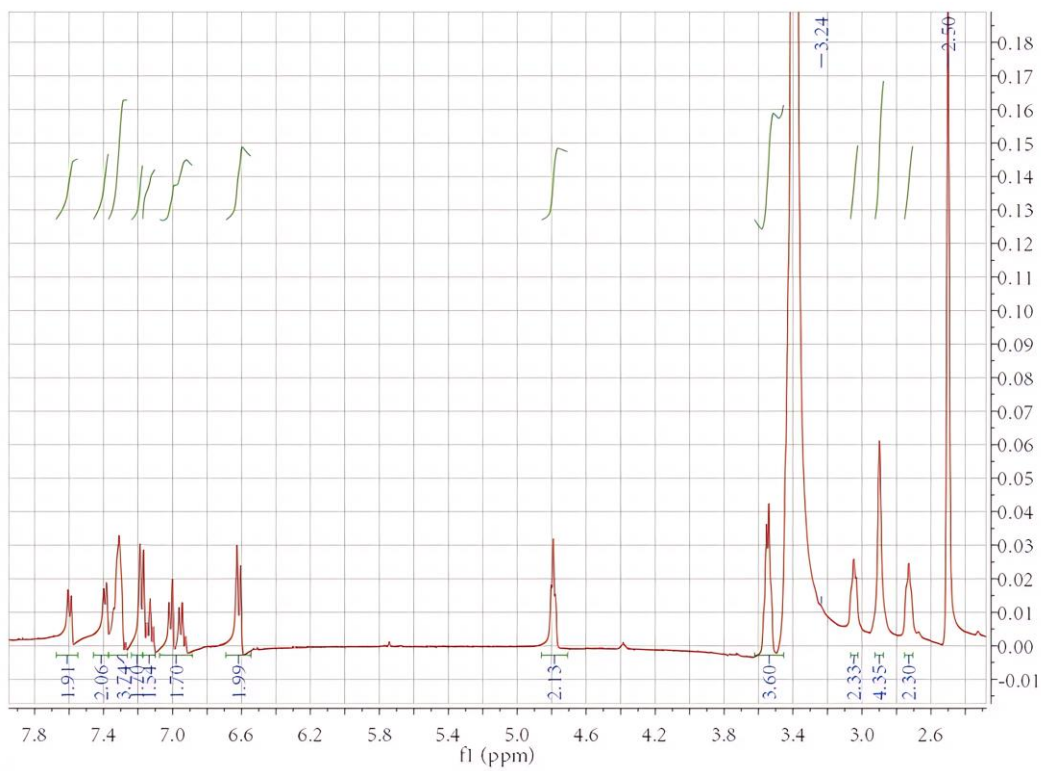


Fig. S5. ¹H NMR spectrum (400 MHz, d₆-DMSO, room temperature) of DSC.

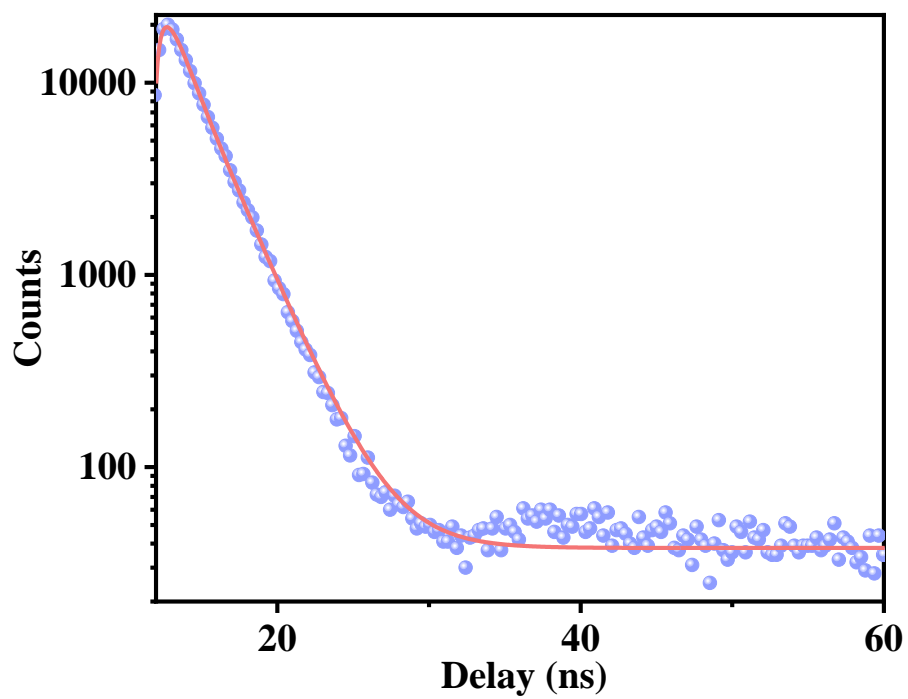


Fig. S6. Fluorescence spectra of the DSC fluorescence solution.

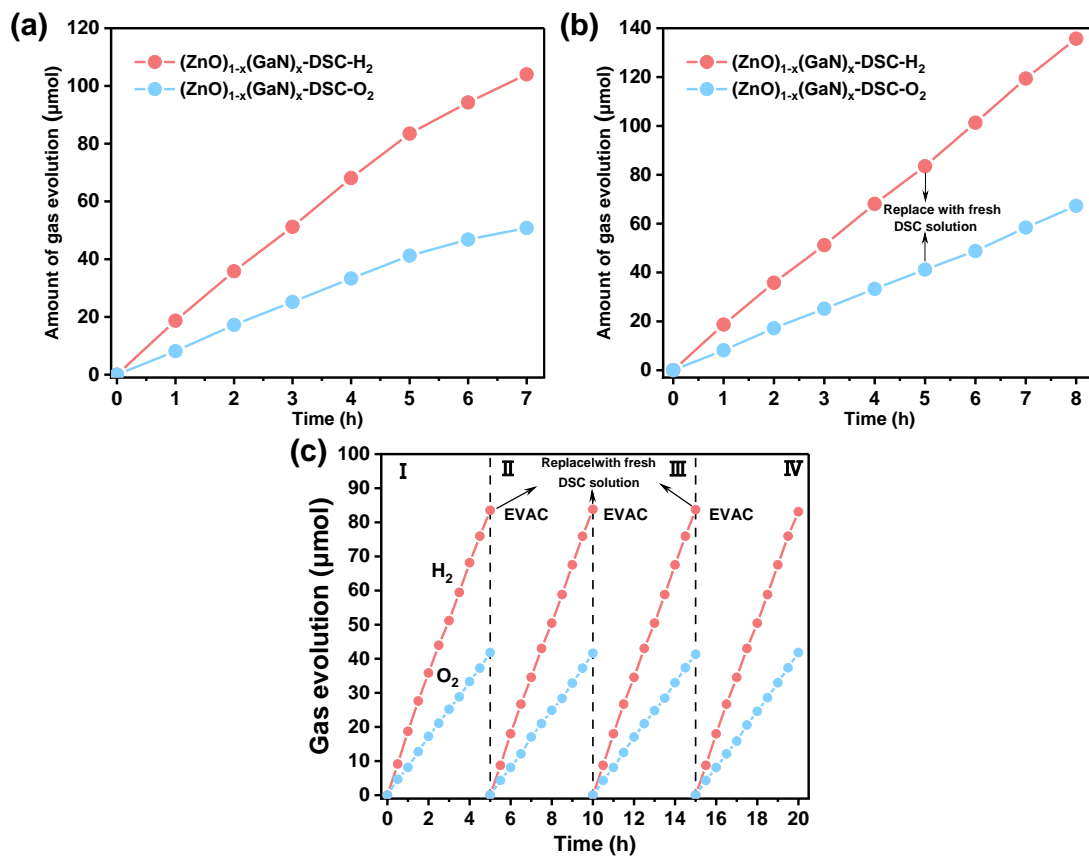


Fig. S7. Typical time course of photocatalytic overall water splitting performance of DSC solution coupling with $(\text{ZnO})_{1-x}(\text{GaN})_x$ under visible light ($\lambda \geq 420 \text{ nm}$). (a) Do not replace DSC fluorescence solution, (b) Replace fresh DSC fluorescence solution at 5 hours and (c) Cycle test chart for replacing fresh DSC fluorescence solution every 5 hours. Reaction condition: amount of $(\text{ZnO})_{1-x}(\text{GaN})_x$ catalyst, 100 mg; cocatalysts, $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ (1 wt% Rh, 1.5 wt% Cr); solution, 50 mL of ultrapure water.

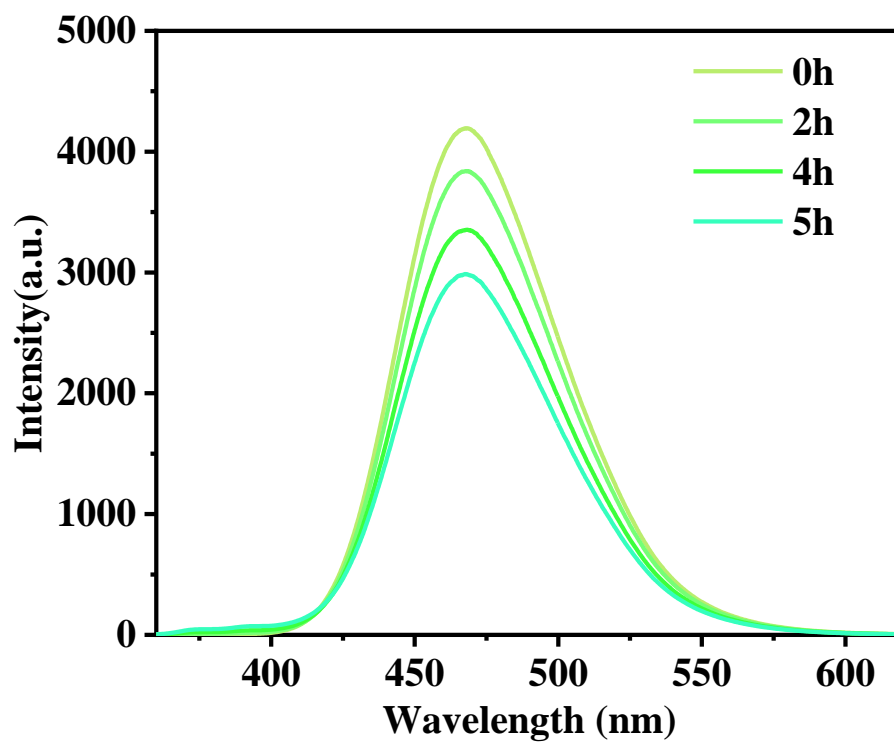


Fig. S8. Fluorescence intensity of the DSC fluorescence solution during the reaction by mixing photocatalytic water splitting solution and DSC solution.

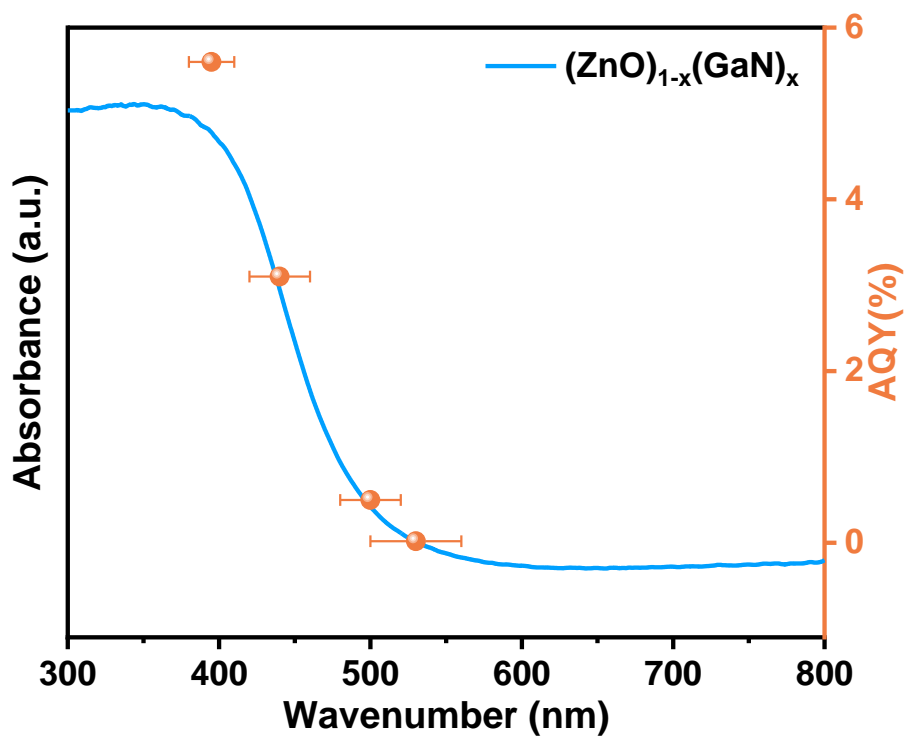


Fig. S9. Wavelength dependence of the apparent quantum yields (AQYs) for $(\text{ZnO})_{1-x}(\text{GaN})_x$. Reaction condition: amount of $(\text{ZnO})_{1-x}(\text{GaN})_x$ catalyst, 100 mg; cocatalysts, $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ (1 wt% Rh, 1.5 wt% Cr); solution, 50 mL of ultrapure water.

References

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- 2 Z. Chen, T. F. Jaramillo, T. G. Deutsch, A. Kleiman-Shwarscstein, A. J. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, E. W. McFarland, K. Domen, E. L. Miller, J. A. Turner and H. N. Dinh, *J. Mater. Res.*, 2010, **25**, 3–16.