

Enhanced photocatalytic activity of flower-like $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4:\text{Cr}$

Heterojunction composite with a long persistent luminescence

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1. Experimental Section

1.1 Materials and reagents

All reagents were used as received without further purification, Ga₂O₃ (99.99%), Zn(NO₃)₂·6H₂O (99.99%), Cr(NO₃)₃·9H₂O (99.95%), InCl₃·4H₂O (99.9%), ethylene glycol and Sodium dodecyl sulfonate were purchased from Aladdin (Shanghai, China). urea, concentrated nitric acid and aqueous ammonia (15 wt.%) was purchased from Shanghai Chemical Reagent. Ultrapure (ULPHW) water was used to prepare all solutions and in the photocatalytic tests.

1.2 Preparation of the In₂O₃/ZnGa₂O₄:Cr composite

The In₂O₃/ZnGa₂O₄:Cr composites were prepared using a two-step hydrothermal method^[1]. First, flower-like In₂O₃ microspheres were synthesized. A typical synthesis process is described as follows: 0.391 g of InCl₃·4H₂O was dissolved in 80 mL of ULPHW. Then, 1.09 g of C₁₂H₂₅NaO₄S and 0.4 g of CH₄N₂O were added to the transparent solution and stirred for 60 min at room temperature. Thereafter, the mixture solution was transferred to a 100-mL Teflon-lined stainless steel autoclave in an ambient environment and heated at 120 °C for 12 h. After the autoclave was cooled to room temperature, the white precipitates formed were separated by centrifugation, washed with distilled water and absolute ethanol several times, and dried in air at 80 °C for 8 h. Finally, the dried precipitates were annealed in air at 500 °C for 2 h with a heating rate of 10°C/min, and pure flower-like In₂O₃ microspheres were obtained.

Subsequently, 100 mg of In₂O₃ was ultrasonically dispersed in 10 mL of C₂H₆O₂ for 30 min. The mixed solution was stirred at room temperature for 30 min. Then, it was added to 1.99 mL of Ga³⁺ (0.2 molL⁻¹), 1 mL of Zn²⁺ (0.4 molL⁻¹), 0.4 mL of Cr³⁺ (0.01 molL⁻¹) and stirred for 30 min. The pH of the mixture was then adjusted to 9 using aqueous NH₃ (15 wt%) and stirred at room temperature for 30 min. The resulting mixture was transferred to a 20-mL Teflon-lined stainless steel autoclave in an ambient environment and heated at 170°C for 24 h. The purified products were separated by centrifugation, washed with distilled water and ethanol, and dried in a vacuum oven at 60°C for 12 h. Finally, the sample was annealed at

700°C in N protection for 3 h with a heating rate of 5°C/min.

1.3 Sample characterization

The crystal structure of the obtained samples was characterized by XRD on a Bruker D8 Focus Advance X-ray diffractometer with Cu-K α radiation ($\lambda = 0.15406$ nm, receiving slit, 0.2 mm, scintillation counter, 40 mA, 40 kV) with scattering angles of 10–80° at a step of 0.03. Micro structures were determined by JEOL SU8220 field-emission scanning electron microscopy (FESEM) which was equipped with an energy-dispersive spectroscopy (EDS) spectrometer to analyze the chemical composition and JEOL JEM-2100 high-resolution transmission electron microscopy (HRTEM) at an accelerating voltage of 200 kV. The X-Ray photoelectron spectra (XPS) were recorded on a Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer, and the binding energy (BE) calibration of the spectra has been referred to the carbon 1s peak, located at BE = 284.8 eV. The excitation and emission spectra and the long-lasting luminescence decay curves were obtained at room temperature using a F-4500 fluorescence spectrophotometer (Hitachi, Japan). The NIR afterglow decay images of ZGSO: Cr were obtained by a Lumazone FA LUMO Imaging System (PI, Roper Technologies, Inc. America) equipped with a cooled CCD camera with an exposure time of 10–600 s. The UV-Vis diffuse reflectance spectra were obtained on a spectrophotometer (Shimadzu UV-2600, Japan) ranging from 200 to 800 nm.

1.4 Photocatalytic activity test

We evaluated the photocatalytic performance of the as-prepared catalysts by measuring photo-degradation efficiency of Rh B with UV light irradiation using a mercury lamp (300W, diameter 1.8 cm, length 14.5 cm, illumination intensity 8.1346 w/cm²)^[2] at room temperature. The 20 mg of In₂O₃/ZnGa₂O₄:Cr sample was combined with 40 mL of a 10 mg/L aqueous RhB solution, and continuously stirred in darkness for 40 min to reach the adsorption-desorption equilibrium between the catalyst and the RhB. The suspension was then placed under UV light irradiation, and samples were taken, separated, and analyzed at regular time intervals (every 20 min) with a Shimadzu UV-2600 UV-vis spectrophotometer employed under the same

method.

Table S1. The current $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4:\text{Cr}$ composites comparison with other PLNPs literatures with the photo-degradation efficiency for RhB

Sample Name	Dyes	Light source	amount	efficiency	References
$\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4:\text{Cr}$	RhB	300W UV	20 mg	80min,98%	Current paper
$\text{Zn}_{0.85}\text{Ga}_2\text{O}_{3.85}$	RhB	500W UV	50 mg	100min,87%	[3]
$\text{CaAl}_2\text{O}_4:(\text{Eu},\text{Nd})/\text{TiO}_2-x\text{Ny}$	RhB	450W UV	0.16g	160min,97%	[4]
$\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$	RhB	500W UV	100 mg	100min,20%	[5]
$\text{ZnGa}_2\text{O}_4:\text{Cr}/\text{Bi}$	RhB	300W UV	20 mg	100min,98%	[6]
$\text{Ga}_{1.94}\text{O}_3:\text{Cr}_{0.01}, \text{In}_{0.05}$	RhB	300W UV	100 mg	100min,93%	[7]
$\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+}$	RhB	250W UV	100 mg	00min,30%	[8]

Table S2. The parameters of NIR afterglow decay curve fitting

τ_1/s	A_1	τ_2/s	A_2	τ_3/s	A_3	$\tau_{\text{av}}/\text{s}^{[a]}$
11.5	4798.92	260.53	826.15	11.53	6883.03	27.97

$$^{[a]}\tau_{\text{av}} = (A_1\tau_1 + A_2\tau_2 + A_3\tau_3) / (A_1 + A_2 + A_3)$$

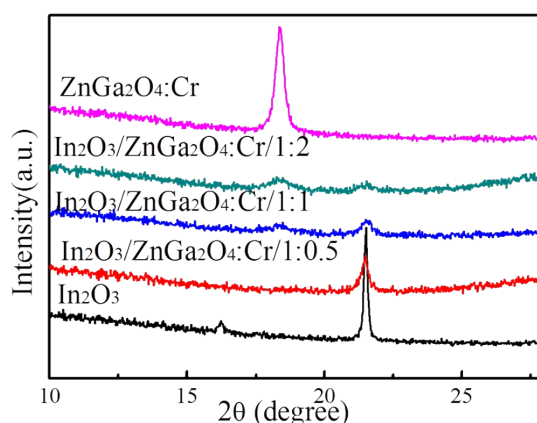


Fig. S1 XRD patterns of flower-like $\text{In}_2\text{O}_3 \cdot \text{ZnGa}_2\text{O}_4:\text{Cr}$ nanoparticles and $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4:\text{Cr}$ composites

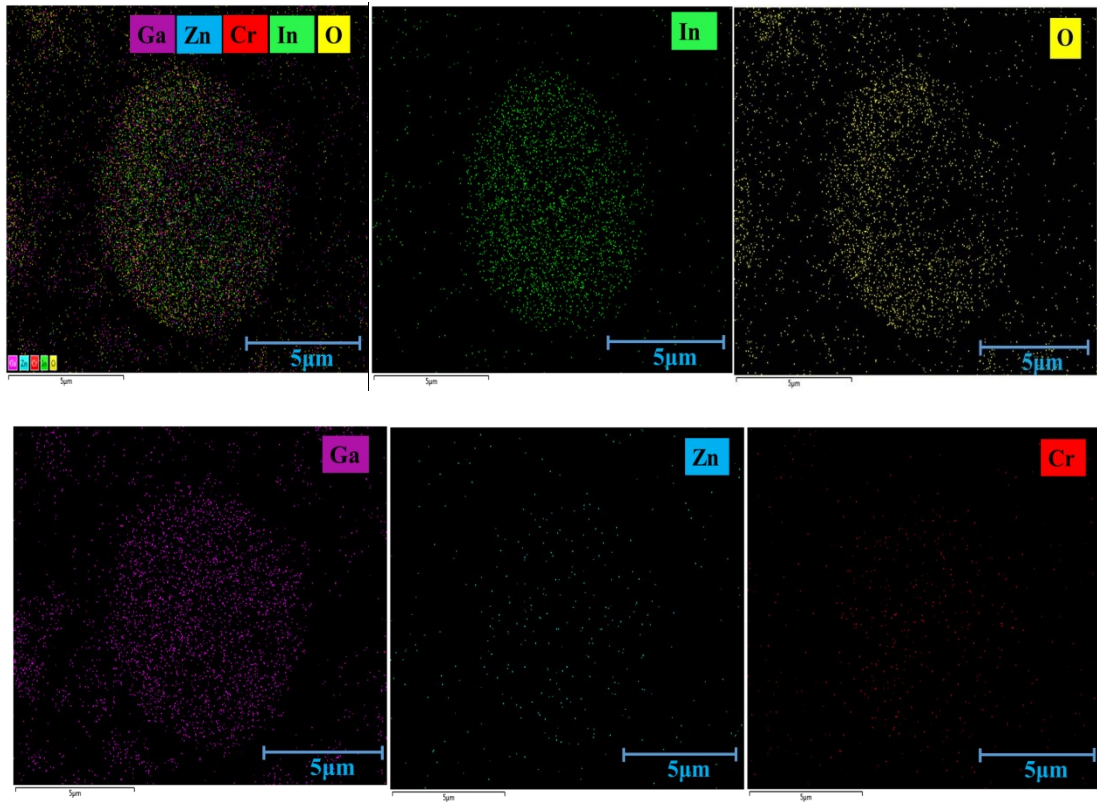
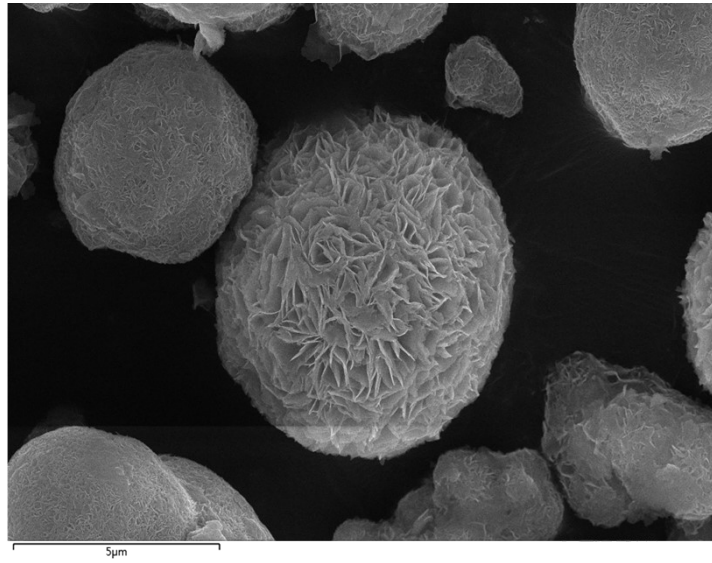


Fig. S2 EDS-mapping images of $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4:\text{Cr}/1:1$ composites

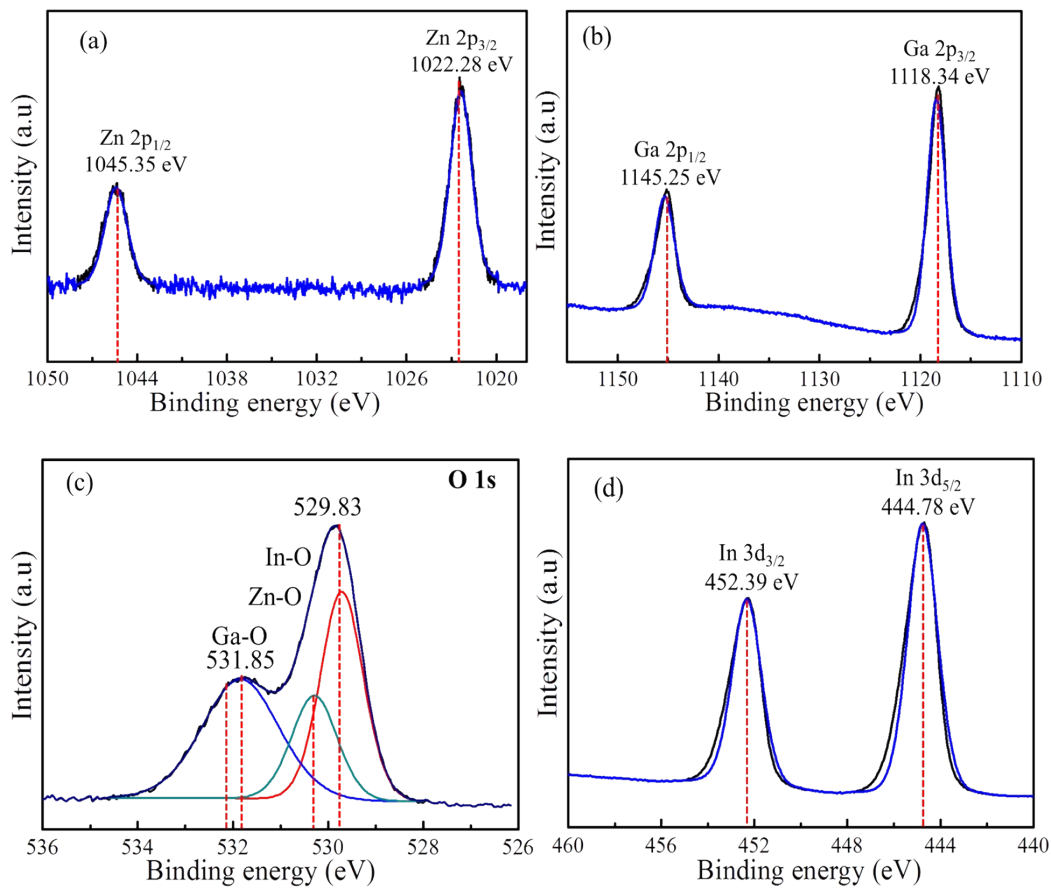


Fig. S3 (a-d) High-resolution XPS spectra of Ga 2p, Zn 2p, In 3d and O 1s for In_2O_3 /

ZnGa_2O_4 :Cr/1:1 composites

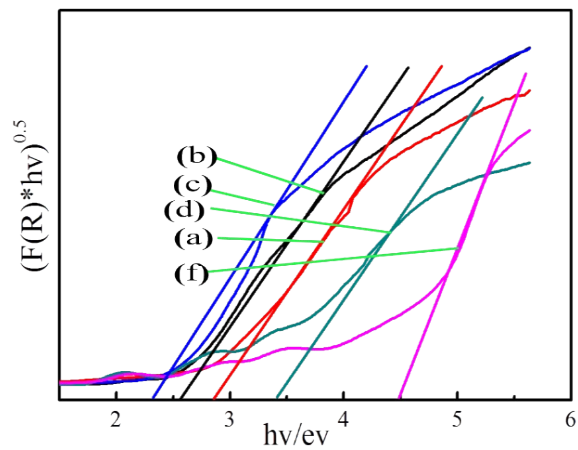


Fig. S4 Band gap of (a) In_2O_3 , (b) $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4$:Cr/1:0.5, (c) $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4$:Cr/1:1, (d) $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4$:Cr/1:2, (f) ZnGa_2O_4 :Cr

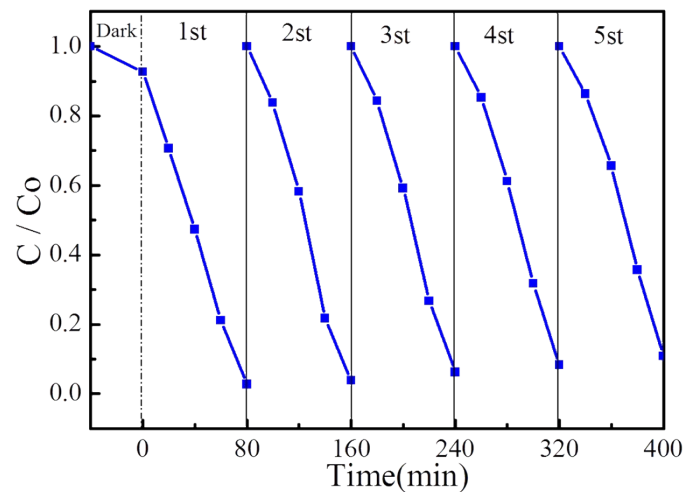


Fig. S5 Recycle tests of the In₂O₃/ZnGa₂O₄:Cr/1:1 for photo-degradation of RhB

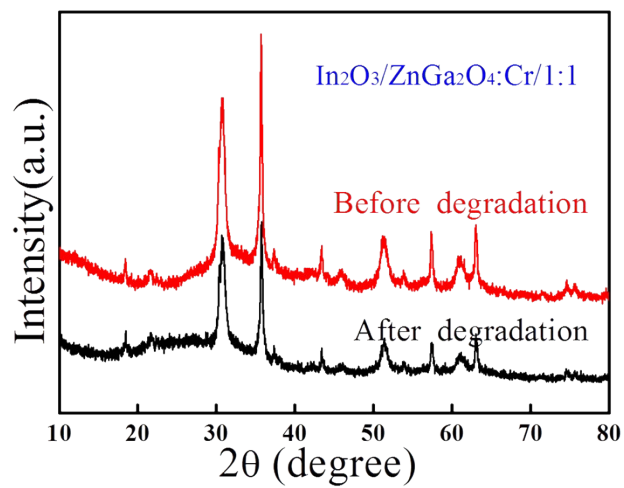


Fig. S6 XRD patterns of the In₂O₃/ZnGa₂O₄:Cr/1:1 before and after the photocatalytic recycles

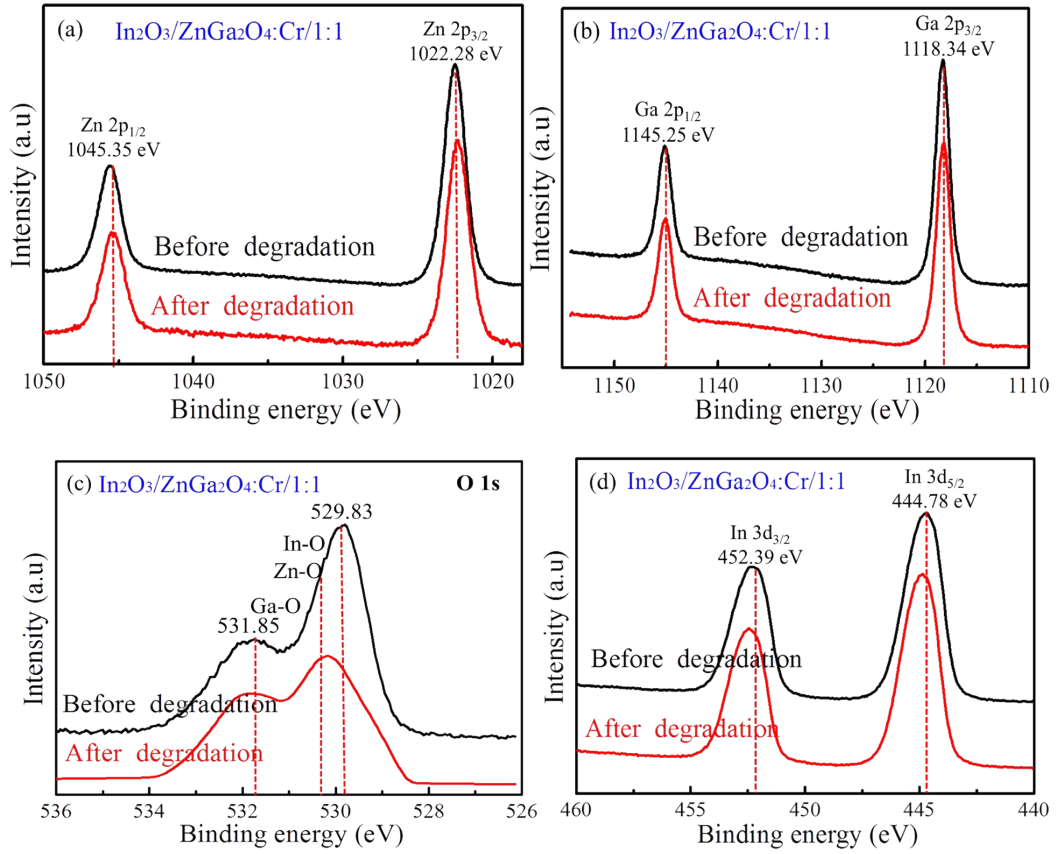


Fig. S7 (a-d) High-resolution XPS spectra of Ga 2p , Zn 2p, In 3d and O 1s for $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4:\text{Cr}/1:1$ composites

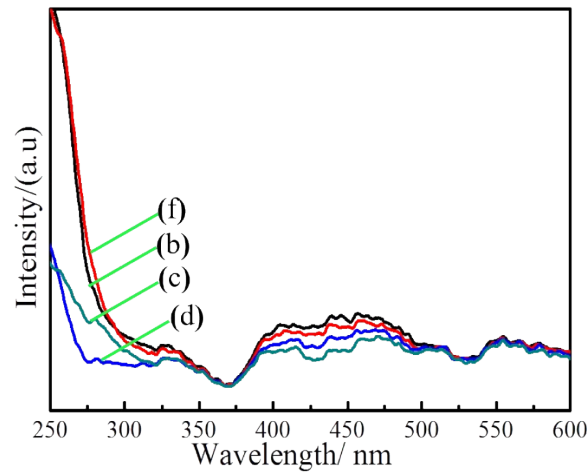


Fig. S8 Phosphorescence excitation spectra of (b) $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4:\text{Cr}/1:0.5$, (c) $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4:\text{Cr}/1:1$, (d) $\text{In}_2\text{O}_3/\text{ZnGa}_2\text{O}_4:\text{Cr}/1:2$, (f) $\text{ZnGa}_2\text{O}_4:\text{Cr}$ (obtained by monitoring 698 nm emission).

4. References

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