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Effect of Indium Doping on Hydrogen Evolution Performance of g-C_3N_4 Based Photocatalysts

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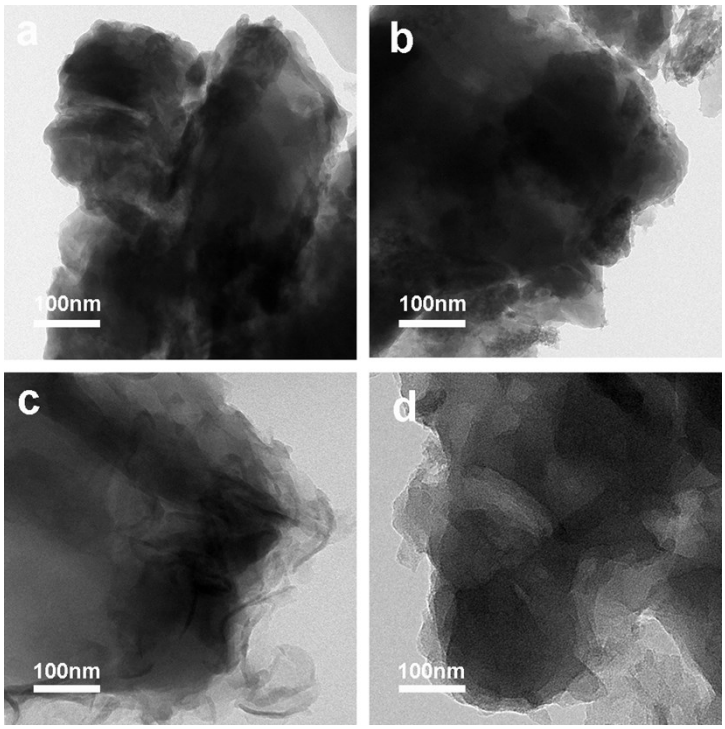

Fig. S1 TEM images of the (a) pristine g-C_3N_4 and In-g-C_3N_4 photocatalysts doped with (b) 0.52 wt.%, (c) 1.15 wt.% and (d) 2.21 wt.% indium. All the samples presented the similar sheet-like structure, meaning the doping of indium had little effect on layered structure of the g-C_3N_4.

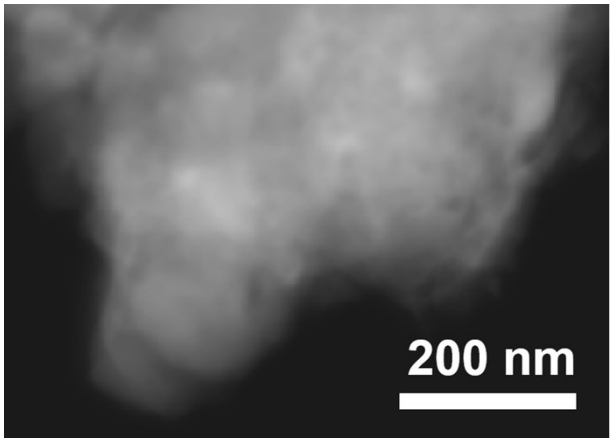

Fig. S2 High-annular dark-field scanning transmission electron microscopy (STEM) image of the In-g-C_3N_4 photocatalyst doped with 2.18 wt.% indium, corresponding to the elemental mapping images shown in Fig. 1b–e.

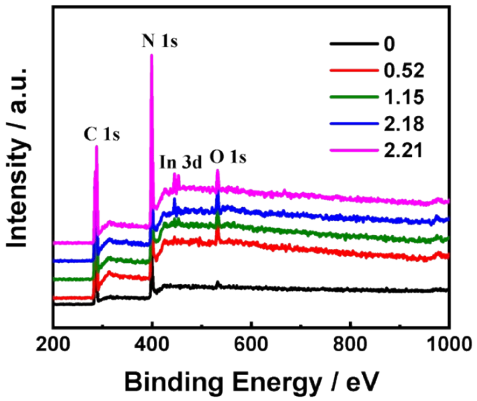

Fig. S3 Survey XPS spectra of the pristine g-C_3N_4 and In-g-C_3N_4 photocatalysts doped by 0.52, 1.15, 2.18 and 2.21 wt.% indium. Intensity of the C1s and N1s peaks kept less changed, while that of In and O gradually increased with the increased amount of In doped. The atomic ratio of O to C (O/C) increased from 3.09% to 6.76%, 7.63%, 10.34% and 12.7% when the amount of indium doped increased from 0 to 0.52, 1.15, 2.18 and 2.21 wt.%, attributed to the increased surface areas of the photocatalyst with the increased amount of In doped (see Fig. S6).

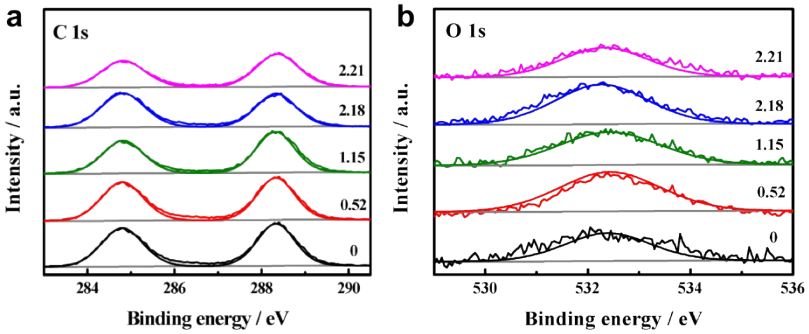

Fig. S4 High resolution XPS spectra (a) C 1s and (b) O 1s of the pristine g-C_3N_4 and In-g-C_3N_4 photocatalysts doped with 0.52, 1.15, 2.18 and 2.21 wt.% indium. The C 1s peaks at 288.4 and 284.8 eV in the pristine g-C_3N_4, assigned to the C-N-C and C-C groups, as well as the O 1s peak centered at 532.5 eV, ascribed to the adsorbed oxygen, experienced negligible shift upon the doping of indium, implying that there were no interactions between indium with the C and O atoms in the In-g-C_3N_4.

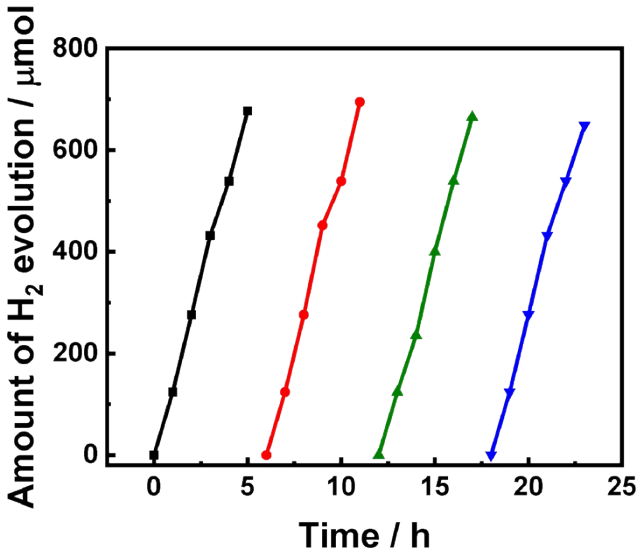

Fig. S5 Variations in H_2 evolution over the In-g-C_3N_4 photocatalyst doped with 2.18 wt.% indium during four cycles of the reactions. The almost unchanged H_2 evolution rate after the four cycles indicated the good stability of the photocatalyst.

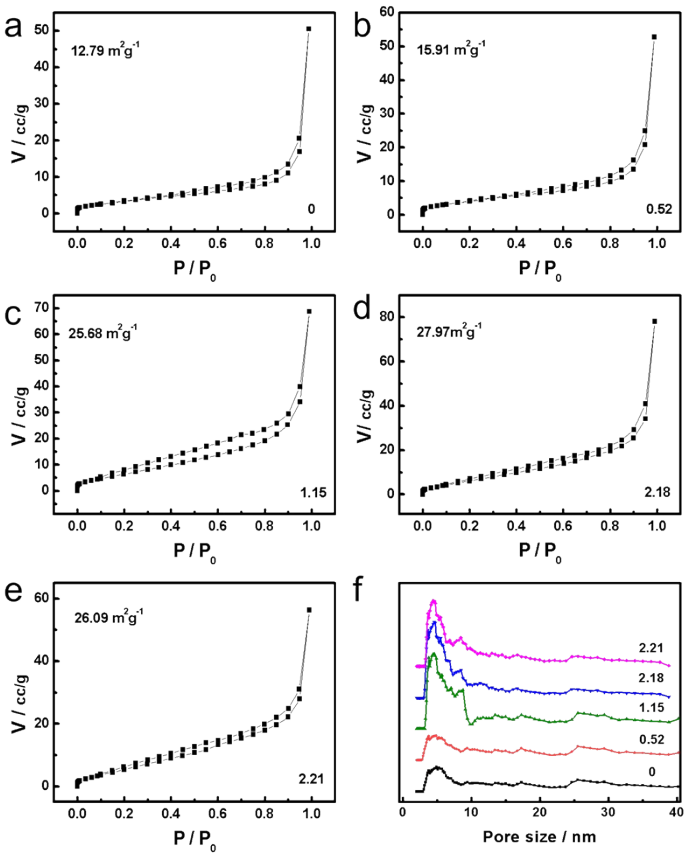

Fig. S6 Nitrogen adsorption-desorption isotherms of the In-g-C_3N_4 photocatalysts doped with (a) 0 wt.%, (b) 0.52 wt.%, (c) 1.15 wt.%, (d) 2.18 wt.% and (e) 2.21 wt.% indium and (f) the corresponding size distribution curves. Surface areas of the In-g-C_3N_4 photocatalysts were determined to be 12.79, 15.91, 25.68, 27.97 and 26.09 m^2g^{-1}, and their pore volumes were 0.07, 0.08, 0.11, 0.11 and 0.08 cm^3g^{-1} when the amounts of indium doped were 0, 0.52, 1.15, 2.18 and 2.21 wt.%. According to the derived pore size distribution plots (Fig. S5f), sizes of the mesopores in the pristine g-C_3N_4 were primarily distributed in the range of 3–5 nm, while additional mesopores with sizes in the range of 8–9 nm were identified for the In doped photocatalysts. The In-g-C_3N_4 photocatalysts doped with 1.15 and 2.18 wt.% indium presented comparable surface areas (25.68 and 27.97 $m^2 \cdot g^{-1}$) and the same pore volume (0.11 $cm^3 \cdot g^{-1}$) but very different H_2 evolution rates (0.39 and 1.35 $mmol \cdot h^{-1} \cdot g^{-1}$), suggesting that the differences in surface area and thus the amount of surface active sites are not the primary reason responsible for the improved photocatalytic activity.

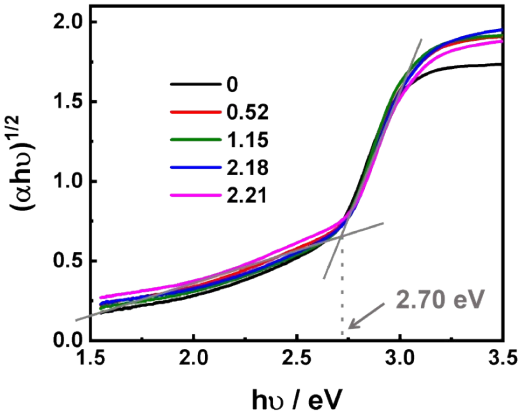

Fig. S7 Tauc plots of the In-g-C_3N_4 photocatalysts doped with 0, 0.52, 1.15, 2.18 and 2.21 wt.% indium derived from the UV-Vis spectra shown in Fig. 3b. The value reckoned from the X intercept at the tangent of Tauc plots (2.70 eV) corresponding to the band gap value (Eg) of the semiconducting g-C_3N_4, which kept almost unchanged with the increased amount of indium doped, meaning the indium doping had little effect on band structure of g-C_3N_4.

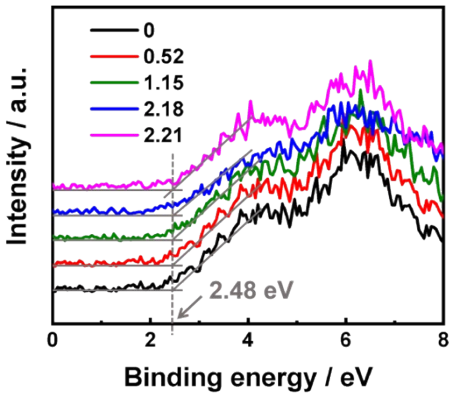

Fig. S8 Valence band XPS (VB-XPS) spectra of the In-g-C_3N_4 photocatalysts doped with 0, 0.52, 1.15, 2.18 and 2.21 wt.% indium. The valence band maximum (VBM) potential (2.48 eV) of the In-g-C_3N_4 photocatalysts kept less changed with the amount of indium doped. Combined with the appropriate Eg value (ca. 2.70 eV), the conductance band minimum (CBM) of In-g-C_3N_4 photocatalysts were calculated as -0.22 eV. Notably, In-g-C_3N_4 photocatalysts exhibited comparable energy band structure, which further elucidated that the doping of indium had little effect on forbidden band width and reducing ability of the g-C_3N_4.

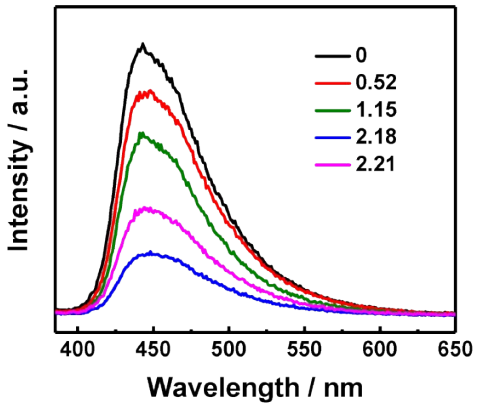

Fig. S9 Photoluminescence spectra of the In-g-C_3N_4 photocatalysts with 0, 0.52, 1.15, 2.18 and 2.21 wt.% of doped indium. Intensity of the emission peak of g-C_3N_4 at 447 nm decreased upon the doping of indium, indicating the doping of indium was effective to suppress the recombination of the photogenerated electron-hole pairs. The g-C_3N_4 doped with 2.18 wt.% indium presented the lowest PL emission intensity, implying optimized separation efficiency of the photogenerated charge carriers, which was in consistent with the SPV result in Fig. 4c.

Table S1 Comparison in visible light (λ > 420 nm) photocatalytic activities of the In^{3+} doped g-C_3N_4 with the typical transition or alkali metal ions doped g-C_3N_4.

Catalyst	Doped ions	H_2 evolution rate ($mmol \cdot h^{-1} \cdot g^{-1}$)	Ref.
g-C_3N_4	--	0.08	
g-C_3N_4	In^{3+} (2.18 wt.%)	1.35	This work
g-C_3N_4	Co^{2+}(0.46 wt.%)	0.45	Ref. 11 in the text
g-C_3N_4	Zn^{2+}(13.65 wt.%)	0.30	Ref. 12 in the text
g-C_3N_4	Mn^{2+}(2.93 wt.%)	0.13	Ref. 14 in the text
g-C_3N_4	Ni^{2+}(20.55 wt.%)	0.16	Ref. 15 in the text
g-C_3N_4	Li^{+}(0.83 wt.%)	<0.20	Ref. 19 in the text
g-C_3N_4	Na^{+}(1.20 wt.%)	0.37	Ref. 16 in the text
g-C_3N_4	K^{+}(2.30 wt.%)	0.24	Ref. 19 in the text

Table S2 Transient emission decays of the In-g-C_3N_4 photocatalysts doped with different amount of indium.

Samples	Parameters	Lifetime (ns)	Relative percentage (%)	Ave. τ/ns
g-C_3N_4	τ_1	13.37	41.33	4.632
	τ_2	2.26	41.50	
	τ_3	90.56	17.16	
In-g-C_3N_4 (0.52 wt.%)	τ_1	11.73	40.82	4.041
	τ_2	82.08	17.69	
	τ_3	1.97	41.49	
In-g-C_3N_4 (1.15 wt.%)	τ_1	1.88	43.08	3.740
	τ_2	10.84	40.01	
	τ_3	75.35	16.91	
In-g-C_3N_4 (2.18 wt.%)	τ_1	1.95	50.14	3.411
	τ_2	10.42	37.12	
	τ_3	82.02	12.74	
In-g-C_3N_4 (2.21 wt.%)	τ_1	12.15	40.00	4.045
	τ_2	81.81	16.79	
	τ_3	2.03	43.20	