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Spatial Engineering of Photo-active Sites on g-C_3N_4 for Efficient Solar Hydrogen Generation

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As shown in Fig. S1, the Fe 2p and Zn 2p XPS spectra of the $ZnFe_2O_4$ modified g-C_3N_4 photocatalysts were analyzed. For Fe 2p XPS spetra, the peaks at 711.2 eV should be attributed to Fe^{3+} $2p_{3/2}$ according to the previous reports.[1] No satellite peaks associated with $2p_{3/2}$ of Fe around 717 eV in Fe_3O_4 were detected, indicating that Fe existed only in Fe^{3+}. For Zn 2p XPS spectra, the peak at 1021.3 eV is ascribed to Zn^{2+} atom occupying tetrahedral site in zinc ferrite.[1] The increasing intensity of Fe 2p and Zn 2p peaks should be due to the increased content of $ZnFe_2O_4$. As demonstrated from the XPS quantitative analysis (Table S1), the Zn/Fe weight ratios for ZFO-X were nearly 1:1.7, and the $ZnFe_2O_4$ weight ratio for ZFO-X (X = 10, 25, 50, 100, 200) samples were calculated to be 0.12 wt%, 0.18 wt%, 0.30 wt%, 0.52 wt%, 0.82 wt%, respectively, which confirmed the successful preparation of $ZnFe_2O_4$ on g-C_3N_4. The concentration of $ZnFe_2O_4$ precursor solution was about 0.02 g-Fe/mL, corresponding to 43 mg-$ZnFe_2O_4$/mL, if the precursors were completely converted. Taking ZFO-200 (Raw materials: 3.0 g of melamine and 200 μL of $ZnFe_2O_4$ precursor solution) for example, in the precursor, weight ratio of $ZnFe_2O_4$/(melamie+$ZnFe_2O_4$) was 0.29 wt%. While for ZFO-200 photocatalysts, the weight ratio of $ZnFe_2O_4$/(g-C_3N_4+$ZnFe_2O_4$) increased to 0.82 wt%. This is because that 3.0 g of melamine could be converted to about 1.2 g of g-C_3N_4 in our experiment, in another word, the productive percent of melamine to g-C_3N_4 was about 40%, while the conversion percent of $ZnFe_2O_4$ precursor to $ZnFe_2O_4$ was about 100%.

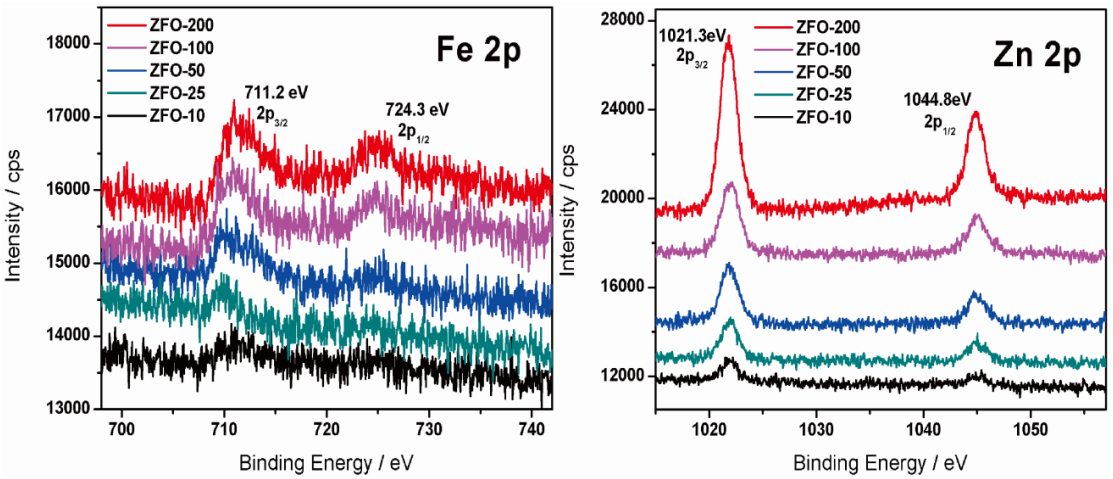

Fig. S1. XPS spectra of Fe 2p and Zn 2p for the $ZnFe_2O_4$-modified g-C_3N_4 photocatalysts.

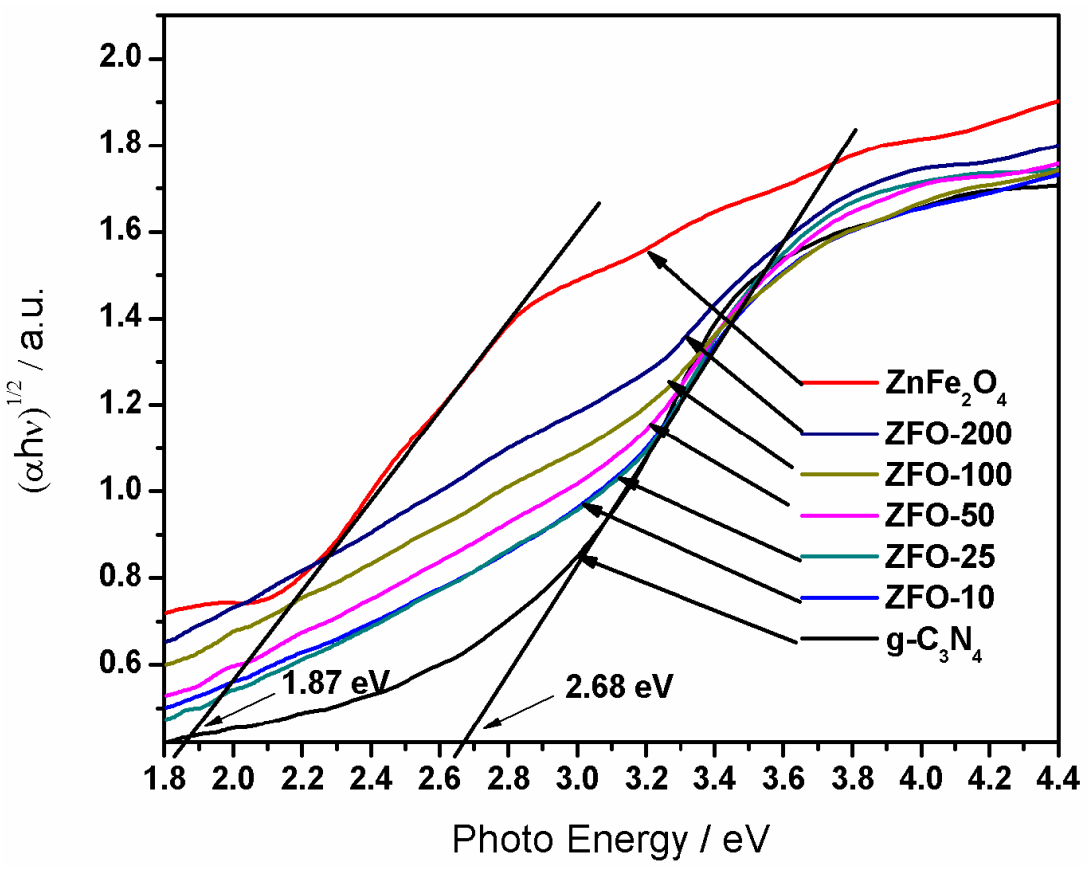

Fig. S2. The Tauc plot transformation for all the as-prepared photocatalysts.

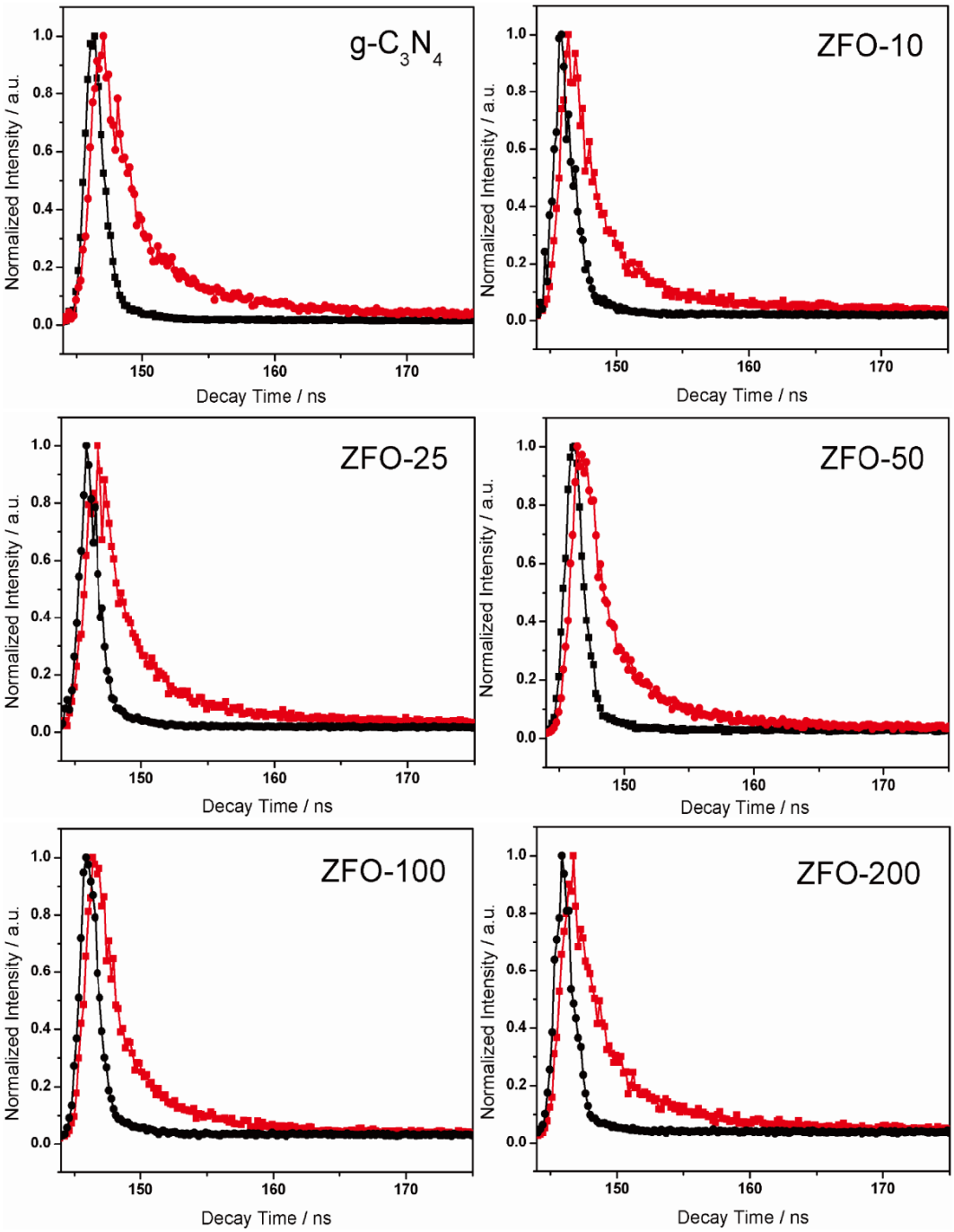

Fig. S3. Fluorescence emission decay curves for all the as-prepared $ZnFe_2O_4$-modified g-C_3N_4 photocatalysts at room temperature. Observation wavelength for all the samples was at 470 nm and the excitation wavelength was at 337 nm. (●) decay curve, (■) Instrument response function (IRF) curve. Solid lines represent the kinetic fit using tri-exponential decay analysis.

As shown in Fig. S4, the almost unchanged Fe 2p and Zn 2p XPS spectra of ZFO-100 after 5-cycle photocatalytic test evidenced that the chemical states of Fe^{3+} and Zn^{2+} were not changed. Moreover, before and after photocatalytic reaction, the Zn contents in ZFO-100 were measured to be 0.14 wt% and 0.13 wt%, while Fe content to be 0.24wt% and 0.25 wt%, which indicated that the content of $ZnFe_2O_4$ did not change. Both the unchanged chemical

states of Fe^{3+}/Zn^{2+} and $ZnFe_2O_4$ content means the good stability of $ZnFe_2O_4$-modified g-C_3N_4 photocatalysts.

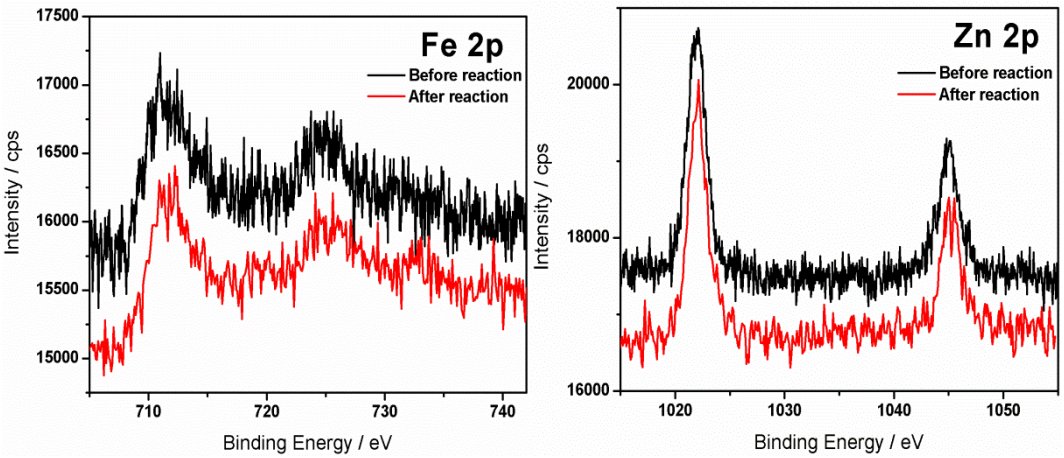

Fig. S4. Fe 2p and Zn 2p XPS spectra for as-prepared and used ZFO-100 photocatalyst.

Table S1. XPS quantitative analysis for the as-prepared photocatalysts. (*) ZFO weight ratios were calculated according to the Fe weight ratio; (#) The theoretical ratio of $ZnFe_2O_4$/(melamie+$ZnFe_2O_4$) in precursor.

Samples	Actual ratio of the element in the photocatalysts (wt%)						
	Zn (wt%)	Fe (wt%)	O (wt%)	C (wt%)	N (wt%)	ZFO (wt%)*	ZFO initial ratio (wt%)#
ZFO-10	0.033	0.056	1.25	48.54	50.12	0.12	0.025
ZFO-25	0.052	0.084	2.16	49.56	48.144	0.18	0.038
ZFO-50	0.083	0.14	2.42	49.23	48.127	0.30	0.075
ZFO-100	0.14	0.24	3.27	48.44	47.91	0.52	0.15
ZFO-200	0.22	0.38	4.05	49.68	45.67	0.82	0.29

Table S2. The average carrier lifetimes (τ_{avg}) for all the as-prepared $ZnFe_2O_4$-modified g-C_3N_4 photocatalysts.

Samples	τ_1	A_1	τ_2	A_2	τ_3	A_3	χ	τ_{avg}
g-C_3N_4	7.889	0.04386	0.08794	0.7164	1.52	0.2398	1.078	4.252393
ZFO-10	0.1867	0.5189	1.223	0.3734	5.101	0.1077	0.9311	3.063644
ZFO-25	4.569	0.06436	1.137	0.8201	4.576	0.1156	0.9033	2.748164
ZFO-50	5.314	0.08506	0.6832	0.7519	2.092	0.163	0.9294	2.652705
ZFO-100	1.109	0.3148	0.3352	0.5989	4.881	0.08638	1.009	2.586132
ZFO-200	1.645	0.06351	4.669	0.01778	0.06107	0.9187	0.9188	2.310741

Reference

1. S. Bera, A. A. M. Prince, S. Velmurugan, P. S. Raghavan, R. Gopalan, G. Panneerselvam, S. V. Narasimhan. *J. Mater. Sci.*, 2001, **36,** 5379-5384.