Supporting Information for

Enhanced carrier separation and increased electron density in 2D heteroatoms heavily N-doped $ZnIn_2S_4$ for hydrogen production

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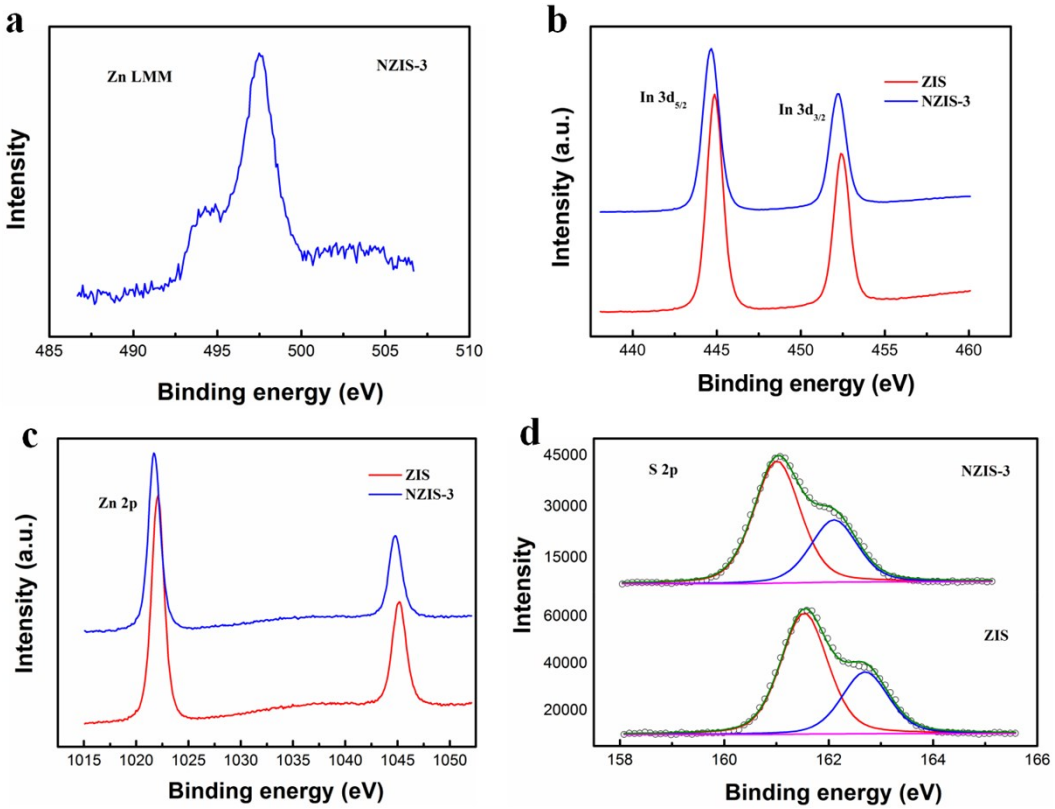

Figure 1 XPS analysis of ZIS and NZIS-3. (a) Zn LMM XPS spectra of NZIS-3, (b) In 3d, (c) Zn 2p and (d)S 2p.

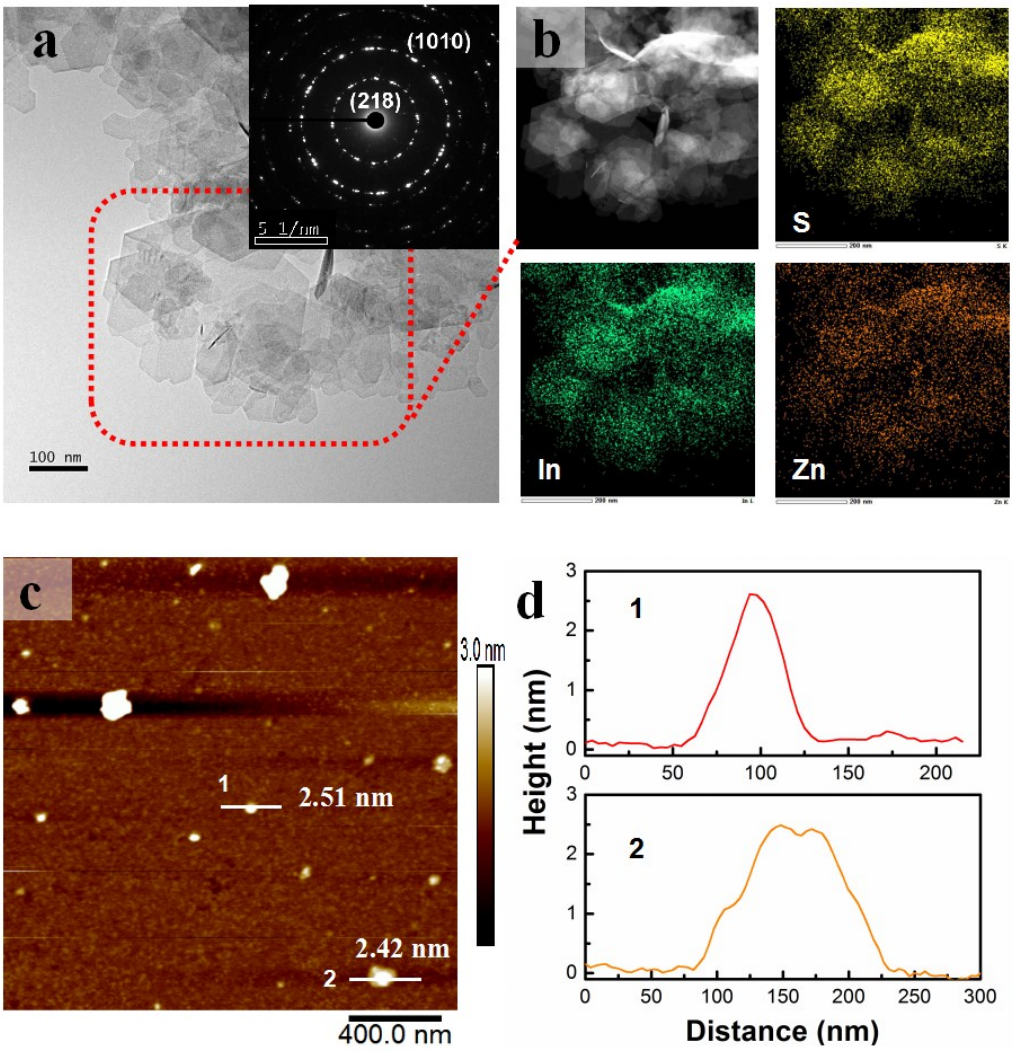

Figure 2 (a) TEM image, the inset of SAED image, (b) Elemental mapping of S, In and Zn image of the region outlined in red in (a), (c)AFM image and (d) The corresponding height profiles of ZIS.

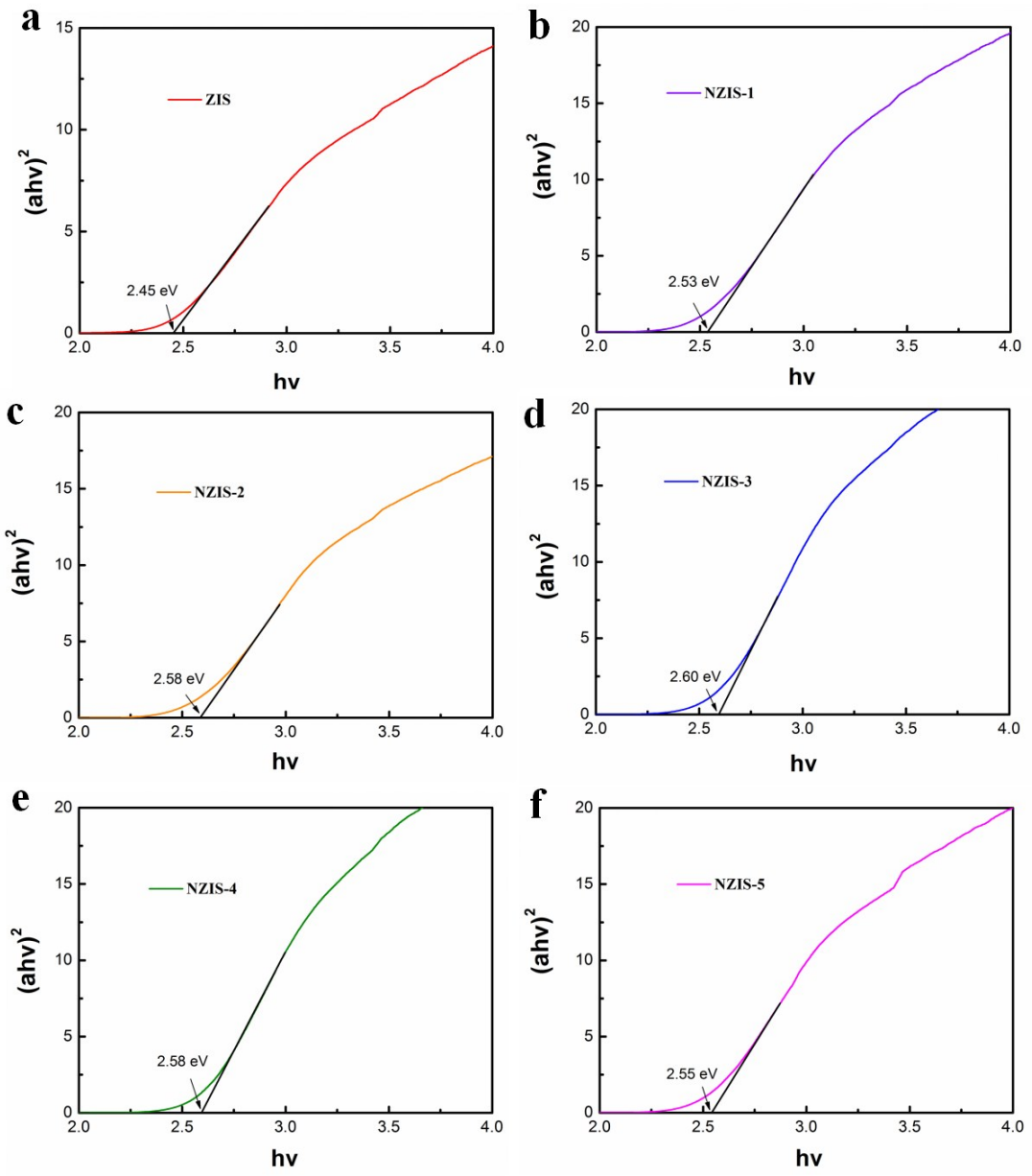

Figure 3 $(\alpha h\nu)^2$ versus $(h\nu)$ plots of (a) ZIS, (b)NZIS-1, (c)NZIS-2, (d)NZIS-3, (e)NZIS-4 and (f)NZIS-5.

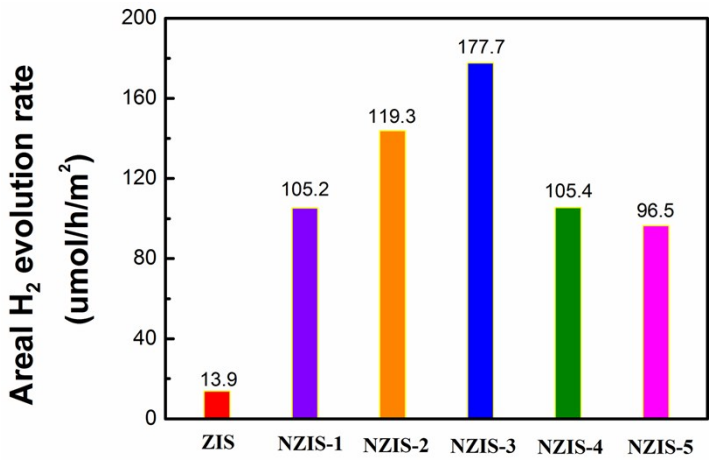

Figure 4 The areal H_2 evolution of all the as-prepared photocatalysts.

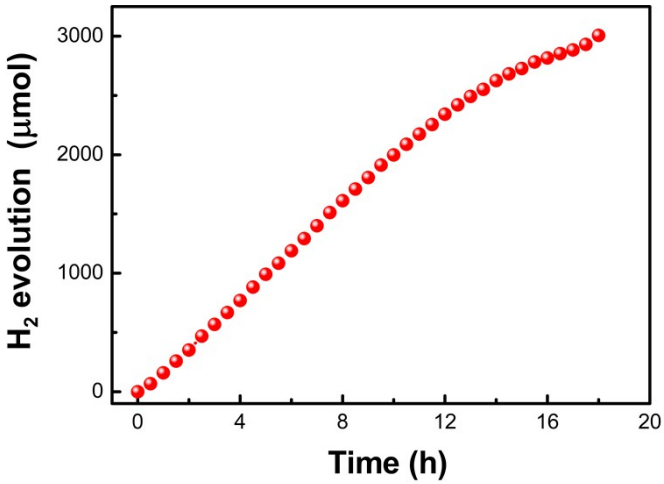

Figure 5 Photocatalytic H_2 generation of NZIS-3 for a long time.

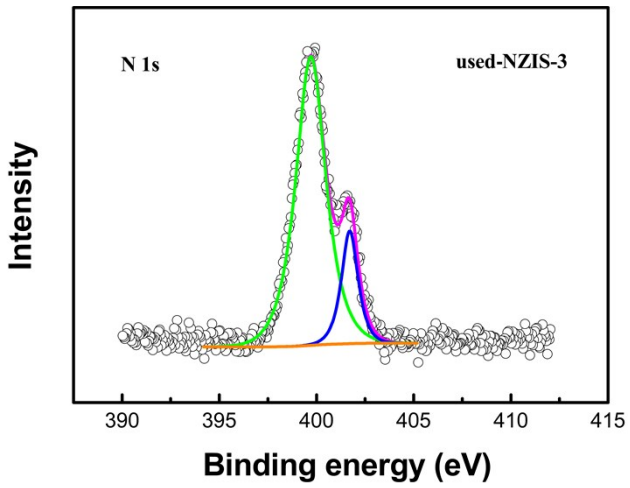

Figure 6 N 1s XPS spectra of NZIS-3 using for a long time.

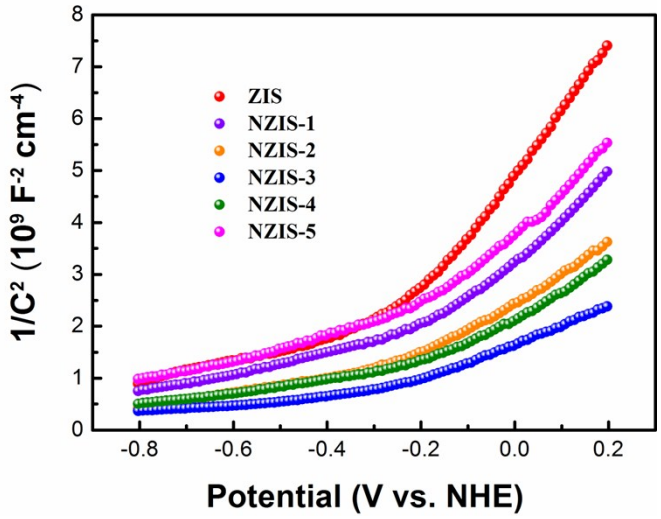

Figure 7 Mott-Schottky curve of all the as-prepared photocatalysts.

Table 1 N amount (wt%) and N contents (at%) of the N-doped $ZnIn_2S_4$ samples determined by EA and XPS

	NZIS-1	NZIS-2	NZIS-3	NZIS-4	NZIS-5
N (wt%)	0.53	0.81	0.87	0.82	0.81
N (at %)	2.08	2.33	3.32	2.52	2.14

Table 2. Lifetime Parameters of all the as-prepared photocatalysts from the TRPL result.

	τ_1 (ns)	A_1(%)	τ_2 (ns)	A_2 (%)	τ_A (ns)
ZIS	0.5993	56.46	2.4681	43.54	1.87
NZIS-1	0.7327	46.83	3.0359	53.17	2.50
NZIS-2	0.7476	48.97	3.116	51.03	2.53
NZIS-3	0.7425	40.09	3.064	59.91	2.64
NZIS-4	0.8248	44.56	3.3629	55.44	2.80
NZIS-5	0.769	41.1	3.3836	58.9	2.92

Table 3. Comparison of the photocatalytic H_2 generation over the doped $ZnIn_2S_4$.

Photocatalysts	Light source	Sacrificial agent	H_2 volution rate (umol/h/g)	Enhancement factor	Ref.
O-doped $ZnIn_2S_4$	300W Xe lamp (λ >420nm)	Na_2S/Na_2SO_3	2120	4.5	1
P-doped $ZnIn_2S_4$	350W Xe lamp (λ >420nm)	Triethanolamine	390.10	1.68	2
N-doped $ZnIn_2S_4$	300W Xe lamp (λ >400nm)	Triethanolamine	11086	13.8	This work
Cu-doped $ZnIn_2S_4$	300W Xe lamp (λ >430nm)	Na_2S/Na_2SO_3	757.5	5.85	3
Ni-doped $ZnIn_2S_4$	350W Xe lamp (λ >430nm)	Na_2S/Na_2SO_3	N	2	4
Mn-doped $ZnIn_2S_4$	500W Xe lamp (λ >420nm)	Na_2S/Na_2SO_3	1040	1.2	5
Ca-doped $ZnIn_2S_4$	300W Xe lamp (λ >430nm)	Na_2S/Na_2SO_3	692	2	6
Co-doped $ZnIn_2S_4$	500W Xe lamp (λ >400nm)	Na_2S/Na_2SO_3	1002.5	N	7
La-doped $ZnIn_2S_4$	350W Xe lamp (λ >420nm)	Na_2S/Na_2SO_3	583	2.4	8

Table 4. BET and Areal H_2 evolution rates of all the photocatalysts.

	ZIS	NZIS-1	NZIS-2	NZIS-3	NZIS-4	NZIS-5
BET (m^2/g)	57.60	62.8	75.3	62.4	78.2	70.6
Areal H_2 evolution rates ($umol/h/m^2$)	13.9	105.2	119.3	177.7	105.4	96.5

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