Supporting Information for

Supported Nickel–Iron Nanocomposites as a Bifunctional Catalyst towards Hydrogen Generation from $N_2H_4 \cdot H_2O$

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1. Experimental section

Preparation of pristine $Ni_{1.5}Fe_{1.0}$-alloy, Ni/MgO and Fe/MgO catalysts

NiFe-LDHs precursor with a Ni^{2+}/Fe^{3+} molar ratio of 1.5 was prepared by using SNAS method and was used as a reference sample.[1] The synthetic process is the same as 2.1.1 step. The product was calcined in air at 500 °C for 5 h with a heating rate of 2 °C min^{-1} (denoted as $Ni_{1.5}Fe_{1.0}$-MMO). After reduction by hydrogen at 500 °C for 3 h with a heating rate of 5 °C min^{-1}, the final product was labeled as $Ni_{1.5}Fe_{1.0}$-alloy catalyst. The reference samples Ni/MgO and Fe/MgO were synthesized by the impregnation method, in which the metal contents of Ni and Fe were controlled to be 35wt.% and 22wt.%, respectively. The commercial MgO (2g) was pretreated in a muffle furnace at 700 °C for 4 h and then impregnated in a $Ni(NO_3)_2 \cdot 6H_2O$ solution or a $Fe(NO_3)_3 \cdot 9H_2O$ solution by mechanical

agitation at 60 °C for 12 h, followed by evaporation at 60 °C until the water was removed. The resultant solid was dried at 120 °C for 12 h, calcined at 500 °C for 5 h in air (denoted as NiO/MgO and Fe_2O_3/MgO), and then reduced at 500 °C or 800 °C for 3 h in hydrogen to obtain 35wt.%Ni/MgO and 22wt.%Fe/MgO, respectively.

2. Characterization

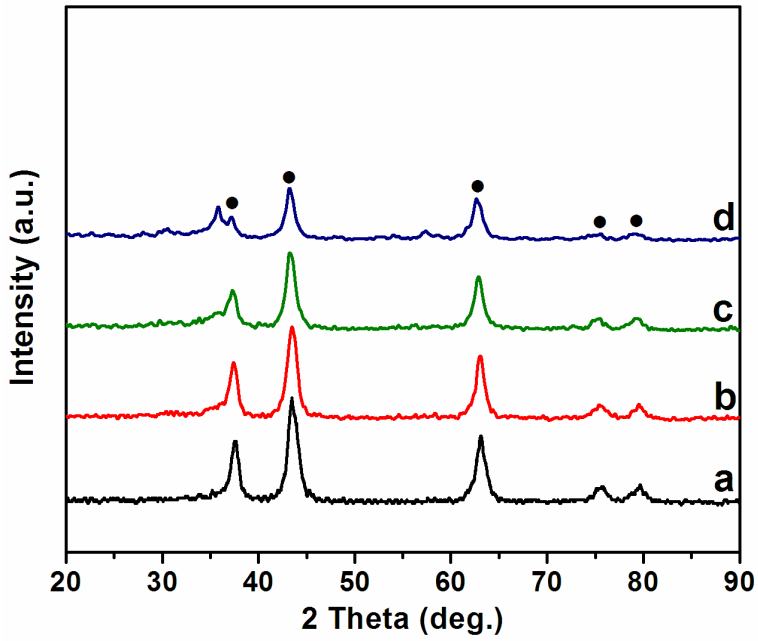

Fig. S1 XRD patterns of $Ni_xFe_{1.0}Mg_{2.5}$-MMO samples: (a) x = 3.7, (b) x = 2.5, (c) x = 1.5, (d) x = 0.4.

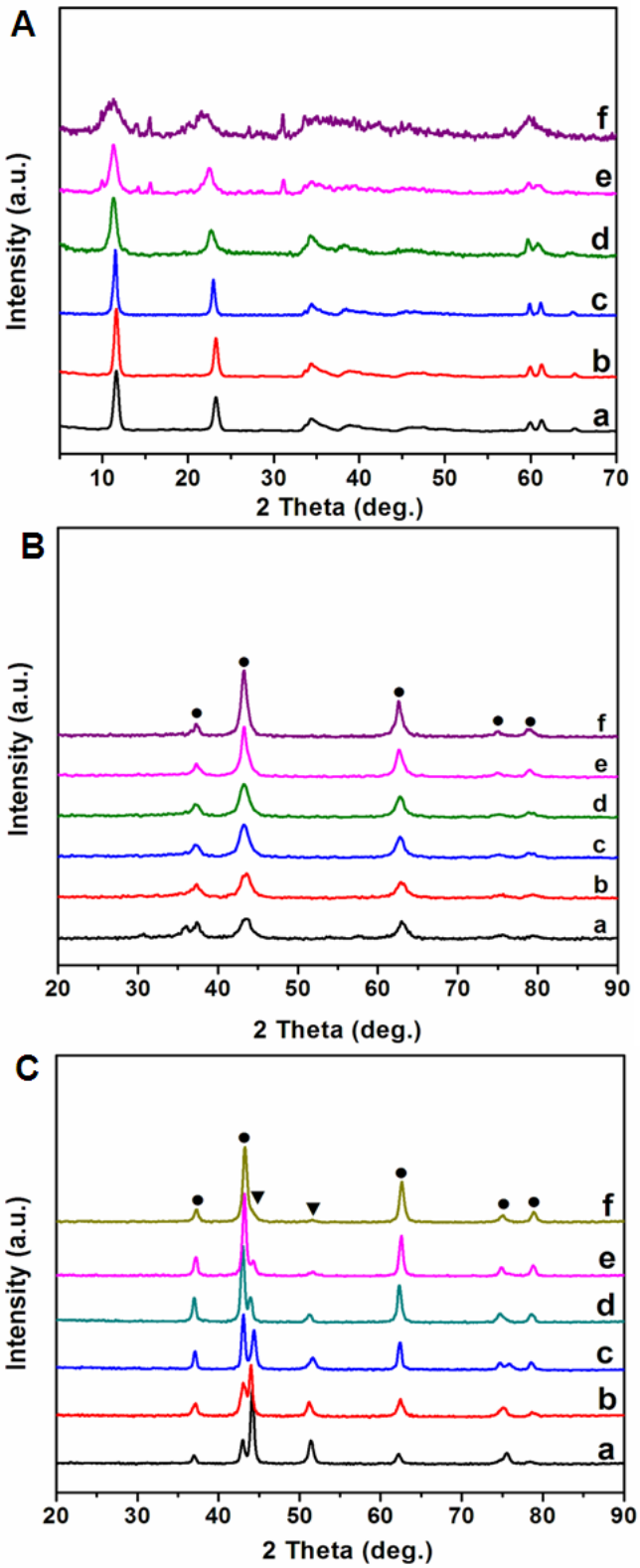

Fig. S2 XRD patterns of (A) $Ni_{1.5}Fe_{1.0}Mg_z$-LDHs precursors, (B) $Ni_{1.5}Fe_{1.0}Mg_z$-MMO samples, (C) $Ni_{1.5}Fe_{1.0}$-alloy/$(MgO)_z$ samples: (a) z = 0.6, (b) z = 1.4, (c) z = 2.5, (d) z = 3.5, (e) z = 5.0, (f) z = 10.0. Crystalline phase: (●) MgO, Mg(Ni, Fe)O, (▼) NiFe alloy.

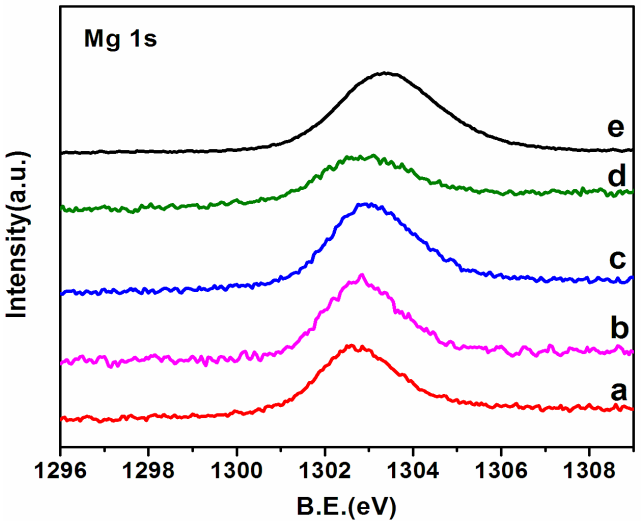

Fig. S3 Mg 1s XPS spectra of $Ni_xFe_{1.0}$-alloy/$(MgO)_{2.5}$ samples: (a) x = 0.4, (b) x = 1.5, (c) x = 2.5, (d) x = 3.7, (e) MgO.

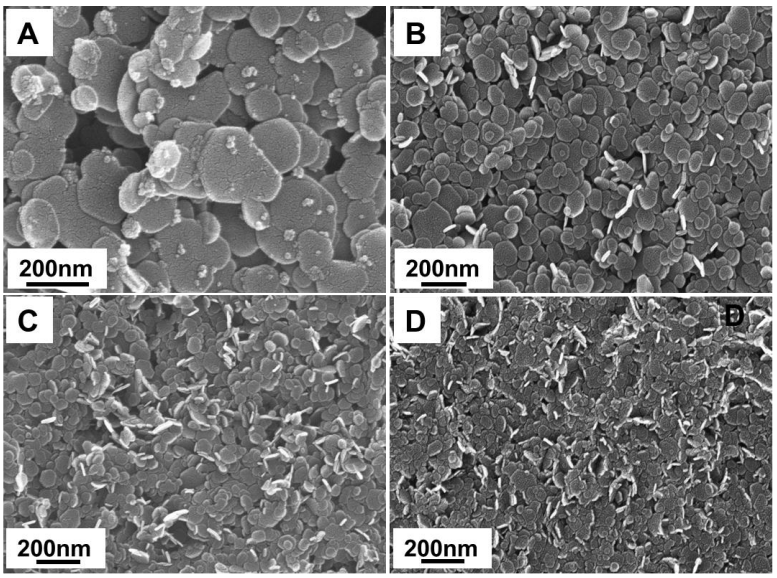

Fig. S4 SEM images of the $Ni_xFe_{1.0}Mg_{2.5}$-LDHs precursors: (a) x = 0.4, (b) x = 1.5, (c) x = 2.5, (d) x = 3.7.

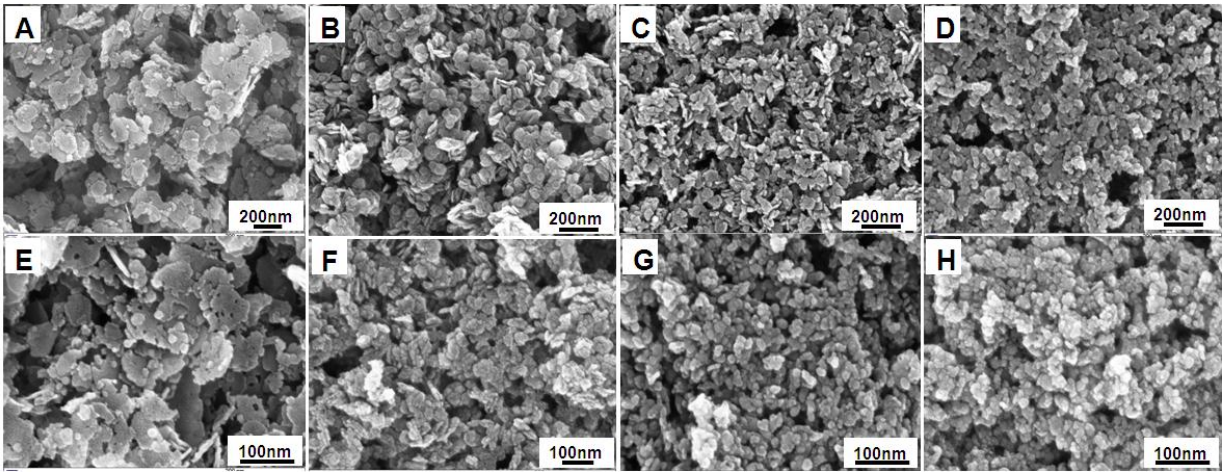

Fig. S5 (A-D) SEM images of the $Ni_xFe_{1.0}Mg_{2.5}$-MMO samples; (E-H) SEM images of the $Ni_xFe_{1.0}$-alloy/$(MgO)_{2.5}$: (a) x = 0.4, (b) x = 1.5, (c) x = 2.5, (d) x = 3.7.

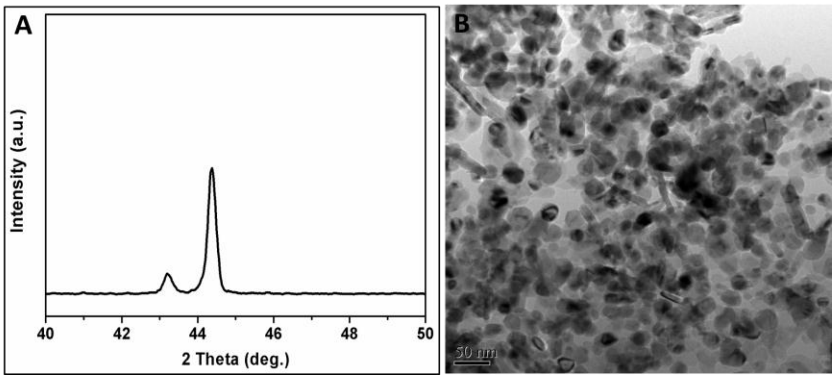

Fig. S6 (A) XRD pattern and (B) HRTEM image of the used $Ni_{1.5}Fe_{1.0}$-alloy/$(MgO)_{3.5}$ catalyst.

Table S1 Metal contents in the $Ni_{1.5}Fe_{1.0}$-alloy/$(MgO)_z$ samples determined by ICP-AES

Catalysts	Metal content (wt.%)	
	Ni	Fe
$Ni_{1.5}Fe_{1.0}/(MgO)_{0.6}$	58.9	37.3
$Ni_{1.5}Fe_{1.0}/(MgO)_{1.4}$	43.8	28.0
$Ni_{1.5}Fe_{1.0}/(MgO)_{2.5}$	35.4	22.4
$Ni_{1.5}Fe_{1.0}/(MgO)_{3.5}$	29.5	18.6
$Ni_{1.5}Fe_{1.0}/(MgO)_{5.0}$	23.6	14.9
$Ni_{1.5}Fe_{1.0}/(MgO)_{10.0}$	14.2	8.9

Table S2 Metal contents in various catalysts determined by XPS

Catalysts	Surface metal Content (at.%)	
	Ni	Fe
Ni/MgO	7.65	—
Fe/MgO	—	5.26
$Ni_{0.4}Fe_{1.0}/(MgO)_{2.5}$	4.2	6.89
$Ni_{1.5}Fe_{1.0}/(MgO)_{2.5}$	7.85	5.07
$Ni_{2.5}Fe_{1.0}/(MgO)_{2.5}$	7.75	4.77
$Ni_{3.7}Fe_{1.0}/(MgO)_{2.5}$	8.64	3.31
$Ni_{1.5}Fe_{1.0}/(MgO)_{0.6}$	8.07	7.18
$Ni_{1.5}Fe_{1.0}/(MgO)_{1.4}$	7.98	6.62
$Ni_{1.5}Fe_{1.0}/(MgO)_{2.5}$	7.85	5.07
$Ni_{1.5}Fe_{1.0}/(MgO)_{3.5}$	7.06	4.68
$Ni_{1.5}Fe_{1.0}/(MgO)_{5.0}$	5.37	4.89
$Ni_{1.5}Fe_{1.0}/(MgO)_{10.0}$	3.06	2.32

Table S3 Reduction Degree and specific surface area of the NiFe alloy particles in the $Ni_xFe_{1.0}/(MgO)_{2.5}$ and $Ni_{1.5}Fe_{1.0}/(MgO)_z$ catalysts

Catalysts	Ni/Fe/MgO ratio[a]	Reduction degree (%)[b]		Specific surface area (m^2g^{-1})[c]
		Ni	Fe	
$Ni_{0.4}Fe_{1.0}/(MgO)_{2.5}$	0.39:0.98:2.47	62	55	78
$Ni_{1.5}Fe_{1.0}/(MgO)_{2.5}$	1.52:0.96:2.49	65	61	70
$Ni_{2.5}Fe_{1.0}/(MgO)_{2.5}$	2.53:0.95:2.51	69	58	68
$Ni_{3.7}Fe_{1.0}/(MgO)_{2.5}$	3.68:1.03:2.50	73	66	62
$Ni_{1.5}Fe_{1.0}/(MgO)_{0.6}$	1.48:0.98:0.59	58	56	82
$Ni_{1.5}Fe_{1.0}/(MgO)_{1.4}$	1.52:0.96:1.49	62	60	78
$Ni_{1.5}Fe_{1.0}/(MgO)_{2.5}$	1.52:0.96:2.49	65	61	70
$Ni_{1.5}Fe_{1.0}/(MgO)_{3.5}$	1.46:1.03:3.50	60	58	69
$Ni_{1.5}Fe_{1.0}/(MgO)_{5.0}$	1.47:1.01:5.03	68	58	60
$Ni_{1.5}Fe_{1.0}/(MgO)_{10.0}$	1.51:1.02:9.96	59	55	56

[a]Determined by ICP-AES. [b]Calculated by O_2 consumption from TPO. [c]Calculated from the volume of chemisorbed H_2.

References

[1] Y. Zhao, F. Li, R. Zhang, D. G. Evans and X. Duan, *Chem. Mater.*, 2002, **14**, 4286.