This ESI for *J. Mater. Chem. A*, 2015, 3, 11066-11073, originally published on 17th April 2015, was updated on 9th November 2018. The elemental mapping images and SAED patterns in Fig. S4a-c were updated; the caption was not changed.

Supporting Information

Co₃ZnC core-shell nanoparticle assembled microspheres/reduced graphene oxide as an advanced electrocatalyst for hydrogen evolution reaction in an acidic solution

Lianbo Ma, Xiaoping Shen,* Jun Zhu, Guoxing Zhu and Zhenyuan Ji

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, P. R. China, Fax: (+86)511-88791800; Tel: (+86)511-88791800; E-mail: <u>xiaopingshen@163.com</u>



Fig. S1. XRD pattern of the precursor of $Zn_3[Co(CN)_6]_2$.



Fig. S2. EDS spectrum of the Co₃ZnC/RGO-6 composite.



Fig. S3. FESEM images of the pure $Zn_3[Co(CN)_6]_2$ product synthesized without GO.



Fig. S4. (a) The element mapping of the Co₃ZnC microsphere. (b) and (c) show the SAED patterns of Co₃ZnC/RGO-6 composite and bare Co₃ZnC, respectively.



Fig. S5. The size distribution diagram of the nanoparticles composing Co_3ZnC microspheres in $Co_3ZnC/RGO-6$ composite.



Fig. S6. FESEM images of (a) $Co_3ZnC/RGO-2$, (b) $Co_3ZnC/RGO-4$, and (c) $Co_3ZnC/RGO-8$ composites.



Fig. S7. (a) FESEM and (b) TEM images of pure Co₃ZnC microspheres.



Fig. S8. Optical photograph showing the generation of hydrogen bubbles on $Co_3ZnC/RGO-6$ composite modified GCE.



Fig. S9. LSV polarization curves of the $Co_3ZnC/RGO-6$ catalyst in neutral (phosphate buffered saline (PBS, PH = 7)) and basic (1 M KOH) solutions.



Fig. S10. (a) The iR-corrected LSV polarization curves of Co_3ZnC/RGO composites, Co_3ZnC and RGO as the electrocatalysts in 0.5 M H₂SO₄, and (b) the corresponding Tafel plots of Co_3ZnC/RGO composites and Co_3ZnC electrocatalysts. The numbers in (b) represent the Tafel slopes of the plots.



Fig. S11. LSV polarization curves of Co₃ZnC electrode at the different scan numbers.



Fig. S12. (a) SEM and (b) TEM image of the Co₃ZnC catalyst after the stability test.

Complex	*Co contents	*Zn contents	#C content	#N content	
Samples	(wt%)	(wt%)	(wt%)	(wt%)	
Co ₃ ZnC	39.4	14.2	28.2	7.3	
Co ₃ ZnC/RGO-2	32.8	11.6	37.5	4.7	
Co ₃ ZnC/RGO-4	27.6	9.4	43.1	3.6	
Co ₃ ZnC/RGO-6	23.4	8.2	47.8	3.1	
Co ₃ ZnC/RGO-8	21.8	7.4	50.2	2.4	

Table S1. The Co, Zn, C and N contents in the samples determined by ICP-OES and
 elemental analyzer.

*The contents of Co and Zn elements were determined by ICP-OES.

#The contents of C and N elements were determined by elemental analyzer.

Table	S2.	The	HER	parameters	calculated	from	the	Tafel	plots	of	Co ₃ ZnC/RG	O
composites and Co ₃ ZnC catalysts.												

Comple	Tafel slope	Exchange current	Overpotential	Potential
Sample	(mV per decade)	density (mA/cm ²)	(mV)	range (V)
Co ₃ ZnC/RGO-2	112.6	1.7×10 ⁻²	170	0.170-0.220
Co ₃ ZnC/RGO-4	90.4	9.3×10 ⁻³	121	0.121-0.171
Co ₃ ZnC/RGO-6	83.4	2.1×10 ⁻²	108	0.108-0.158
Co ₃ ZnC/RGO-8	104.1	1.4×10 ⁻²	142	0.142-0.192
Co ₃ ZnC	118.8	8.7×10 ⁻³	193	0.193-0.243

Catalyst	Tafel slope		El satura la sta	Ref.	
	(mV per decade)	η_{onset} (mV)	Electrolyte		
Pt/C	28-35	< 40	0.5 M H ₂ SO ₄	15,39	
PtNiCu	28	8	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$	67	
PtCu	29	18	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	67	
PtNi	41	30	$0.5 \text{ M H}_2 \text{SO}_4$	67	
Graphene/Pt		About 250	0 0 M H SO	69	
hollow			0.9 101 112504	08	
Graphene/Pt		About 340	12 M H SO	68	
nanoparticles	-		1.2 101 112504	08	
$Pd_{60}Pt_{40}$	20.3	About 30	0.5 M H ₂ SO ₄	69	
CuPt	28.7		$0.1 \text{ M} \text{H}_2\text{SO}_4$	70	
Graphene/PtPd	10		0.5 M H.SO.	71	
nanocubes	10		$0.5 \text{ M} \text{ H}_2 \text{ S} \text{ O}_4$	/1	
Pd	85		0.5 M H ₂ SO ₄	71	
PdAu/C	136-156	300-400	0.1 M HCl	72	
Pd/C	154	350	0.1 M HCl	72	
Au/C	165	500	0.1 M HCl	72	

Table S3. The parameters of the Pt metal group-related electrocatalyst for HER.