Phosphorus Doped Single Wall Carbon Nanotube Loaded with Nanoparticles

of Iron phosphide and Iron Carbide for Efficient Hydrogen Evolution

Cuncai Lv,^{ab} Qianpeng Yang,^{ab} Qingli Huang,^c Zhipeng Huang,^{*ab}, Han Xia^{ab} and Chi Zhang^{*ab}

^a Department of Chemistry, Advanced Research Institute, and China-Australia Joint Research Center for Functional Materials, Tongji University, Shanghai, 200092, China.

*Email: zphuang@tongji.edu.cn; chizhang@tongji.edu.cn.

^b Functional Molecular Materials Research Centre, Scientific Research Academy, and China-

Australia Joint Research Center for Functional Materials, Jiangsu University, Zhenjiang, 212013, China.

^c Testing Center, Yang zhou University, Yangzhou, 225009, China

Electronic Supplementary Information

Synthesis S1: Synthesis of SWNT(P)-TPP

In this experiment, commercial SWNT and TPP were dispersed ultrasonically in ethanol for approximately 30 min. Then the mixture was dried under stirring at 60 °C overnight. The resulted powder was ground in a mortar, and then loaded in a quartz tube mounted in a tube furnace. The respective mixture was then annealed at 950 °C for 3 h under static 5% H₂/95% N₂ and were allowed to cool to room temperature (heating rate: 5 °C min⁻¹). After the reaction, the furnace was cooled naturally to room temperature.

Synthesis S2: Synthesis of SWNT(P)-HNO₃

In this experiment, IP-IC@SWNT(P) was dispersed ultrasonically in nitric acid for approximately 30 min. Then the mixture was refluxed at 100 °C for 4 h. After filtration and washing with deionized water for three times, the obtained sample was dried in vacuum at 60 °C. Then the mixture was annealed in 5% H₂/95% N₂ up to 800 °C for 2 h with a heating rate of 5 °C min⁻¹ and were allowed to cool to room temperature (flow rate: 200 sccm).



Figure S1. Optical photograph of IP-IC@SWNT(P) collected by a stainless steel wire mesh.



Figure S2. (a) A typical low magnification TEM image of the IP-IC@SWNT(P). Diameter distribution of (b) nanoparticles (including iron carbide and iron phosphide) and (c) SWNT bundles in the IP-IC@SWNT(P).



Figure S3. Raman spectra of the IP-IC@SWNT(P) in (a) RBM region and (b) high-frequency region.



Figure S4. XPS survey spectrum of the IP-IC@SWNT(P).



Figure S5. (a) XRD pattern and (b) TEM image of the IC@SWNT. Diameter distribution of (c) iron carbide nanoparticles and (d) SWNT bundles in the IC@SWNT. Raman spectra of the IC@SWNT in (e) RBM region and (f) high-frequency region.



Figure S6. (a) STEM image of the IC@SWNT. Chemical maps for the spatial distribution of (b) C and (c) Fe obtained from the EDS elemental mapping of region in (a).

Catalyst	Substrate	Mass density (mg cm ⁻²)	η_{10} (mV)	$\begin{array}{c} \eta_{20} \\ (mV) \end{array}$	Tafel slope (mV dec ⁻¹)	Electrolyte
Cobalt-embedded nitrogen-rich carbon nanotube ¹	GCE	0.28	260 370		80	0.5M H ₂ SO ₄ 1 M KOH
FeCo@NCNT ²	GC	0.32	320		72	0.1M H ₂ SO ₄
Co-N-C complex ³	carbon fiber foam		138	160	55	1M KOH
CoNi nanoalloy encapsulated in graphene ⁴	GC	1.6	142		107	$0.1M \ H_2 SO_4$
Co encapsulated in nitrogen-rich carbonitride nanotubes ⁵	GCE	0.285	200	230	82	$0.5M\ H_2SO_4$
Fe ₂ P nanoparticles loaded on nitrogen-doped graphene ⁶	GCE	1.71	138	164	65	$0.5M\ H_2SO_4$
FeP ₂ /C nanohybrids ⁷	GCE	0.425	500 (ŋ ₅)		66	$0.5M H_2SO_4$
M ₃ C(M=Fe,Co,Ni) nanocrystals encased in graphene nanoribbons ⁸	GCE		45 90 45	70 120 74	46 57 54	$0.5M\mathrm{H_2SO_4}$
Single-shell carbon-encapsulated iron nanoparticles ⁹	GCE	0.18	77	97	40	0.5M H ₂ SO ₄
Ni ₂ P/CNT Ni ₁₂ P ₅ /CNT Ni/CNT ¹⁰	GCE	0.199	124 240 345	150 275 395	41 81 124	0.5M H ₂ SO ₄
Ni ₁₂ P ₅ Ni ₂ P Ni ₅ P ₄ ¹¹	GCE	0.199	208 137 118	260 180 155	75 49 42	$0.5M H_2 SO_4$
CoP/NCNTs ¹²	GCE	0.199	79	100	49	$0.5M H_2SO_4$
Ni ₂ P/carbon nanospheres-40 ¹³	GCE	0.199	92	105	46	0.5M H ₂ SO ₄
Ni ₂ P/NRGO ¹⁴	GCE	0.199	102	120	59	0.5M H ₂ SO ₄
CoP/MoS ₂ -CNTs Hybrid ¹⁵	GCE	0.199	12	25	42	$0.5M \ H_2 SO_4$
FeP NA/Ti ¹⁶	Ti	3.2	55	72	38	$0.5M H_2SO_4$
FeP NAs/CC ¹⁷	Carbon cloth	1.5	58	75	45	$0.5M H_2SO_4$
FeP/CC ¹⁸	Carbon cloth	4.2	39	54	32	0.5M H ₂ SO ₄
FeP/NCNT ¹⁹	GCE	0.36	113	134	59	0.5M H ₂ SO ₄
IP-IC@SWNT(P) (This work)	GCE	0.855	140 301	157 393	60.8 87.6	0.5M H ₂ SO ₄ 1 M KOH

Table S1. Summary of HER performance of representative carbon-based hybrid nanocomposites



Figure S7. (a) P 2p and (b) C 1s windows of XPS spectra of the SWNT(P)-TPP.



Figure S8. (a) Fe 2p, (b) P 2p and (c) C 1s windows of XPS spectra of the SWNT(P)-HNO₃.



Figure S9. The polarization curves of the SWNT(P)-TPP and SWNT(P)-HNO₃.



Figure S10. (a) Fe 2p, (b) P 2p and (c) C 1s windows of XPS spectra of the IP-IC@SWNT(0.1P).



Figure S11. (a) Fe 2p, (b) P 2p and (c) C 1s windows of XPS spectra of the IP-IC@SWNT(0.5P).



Figure S12. The polarization curves of IP-IC@SWNT(0.1P), IP-IC@SWNT(0.3P) and IP-IC@SWNT(0.5P)



Figure S13. (a) Fe 2p, (b) P 2p and (c) C 1s windows of XPS spectra of the IP-IC@SWNT(P) scrapped from GCE after galvanostatic electrolysis experiment.



Figure S14. TEM image of the IP-IC@SWNT(P) scrapped from GCE after galvanostatic electrolysis experiment.



Figure S15. (a) TEM and (b) STEM images of the acid treating IP-IC@SWNT(P). The corresponding elemental mapping images of (c) C, (d) Fe and (e) P.



Figure S16. (a) Polarization curves of the IP-IC@SWNT(P) on the GCE (loading amount: 0.855 mg cm⁻²) in basic solution (scan rate: 5 mV s⁻¹). The polarization curves of Pt@C (loading amount: 0.285 mg cm⁻²), IC@SWNT (loading amount: 0.855 mg cm⁻²) and bare GCE are shown for comparison. All the potentials were corrected with iR drop. (b) Corresponding Tafel plots of IP-IC@SWNT(P), IC@SWNT and Pt@C. (c) The theoretical and measured volume of hydrogen during potentiostatic electrolysis measurement in basic solution. (d) The relationship of potential and time in a galvanostatic electrolysis in basic solution (applied current density: 20 mA cm⁻²). The inset shows the CV curves of the initial and 5000th scans in CV sweeps measured in basic solutions. The potentials were not corrected with the iR drop.



Figure S17. Equivalent circuit used to fit the EIS data. Rs is the overall series resistance, CPE_1 and R_1 are the constant phase element and resistance describing electron transport at substrate/catalyst interface, respectively, CPE_{dl} is the constant phase element of the catalyst/electrolyte interface, and R_{ct} is the charge transfer resistance at catalyst/electrolyte interface.

Sample	R _s	Q _{ct}	n _{ct}	R _{ct}	Q1	n ₁	R_1
	(Ω)	$(F \text{ cm}^{-2} S^{n-1})$		(Ω)	(F cm ⁻² S ⁿ⁻¹)		(Ω)
IP-IC@SWNT(P)	3.448	3.169e-4	0.8529	76.51	8.449e-5	0.7873	9.148
IC@SWNT	2.968	1.587e-6	0.8134	164.6	4.017e-4	0.8493	10.47

Table S2. The fitting results of EIS spectra in acid solution



Figure S18. Nitrogen adsorption-desorption isotherm of the IP-IC@SWNT(P) and IC@SWNT.

Electrochemical active surface area.

To measure electrochemical capacitance, the potential was swept between 0.10 to 0.20 V vs. RHE at eleven different scan rates , including 20, 40, 60, 80, 100, 120, 140, 160, 180, 200 and 220 mV s⁻¹. The cyclic voltammograms of the IP-IC@SWNT are plotted in Figures S10a and that of the IC@@SWNT in Figure S10b. The capacitance current density ($\Delta J=J_a-J_c$ at 0.15 V vs. RHE) was plotted against the scan rate (Figure S10c) and specific capacitance is obtained by a data fitting of the plot, being 16 mF cm⁻² for the IP-IC@SWNT(P) and 9 mF cm⁻² for the IC@SWNT. An electrochemical active surface area (ECSA) can be estimated from the specific capacitance using the specific capacitance value for a flat standard with 1 cm² of real surface area. In general, the specific capacitance for a flat surface ranges in 20 to 60 μ F cm⁻². In our calculations a specific capacitance for a flat surface area of 40 μ F cm⁻² was adopted and those of 20 and 60 μ F cm⁻² were used to compute the lower and upper limit (see Figure 7).

Calculated electrochemical active surface area.

AIP-IC@SWNT(P) ECSA= $(16 \text{ mF cm}^{-2})/(40 \mu \text{F cm}^{-2} \text{ per cm} 2 \text{ ECSA})=400 \text{ cm} 2 \text{ ECSA}$

AIC@SWNT ECSA= $(9 \text{ mF cm}^2)/(40 \mu \text{F cm}^2 \text{ per cm} 2 \text{ ECSA})=225 \text{ cm} 2 \text{ ECSA}$



Figure S19. Cyclic voltammograms in the region of 0.1-0.2 V vs. RHE for the (a) IP-IC@SWNT(P) and IC@SWNT at pH 7. (c) The measured capacitive currents plotted as a function of scan rate.

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