Electronic Supporting Information

 $Ni_{12}P_5$ Nanoparticles Decorated on Carbon Nanotubes with

Enhanced Electrocatalytic and Lithium Storage Properties

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Figure S1. EDX spectrum of the as-synthesized monodisperse $Ni_{12}P_5$ nanoparticles. The signal of Cu and C arises from the TEM grid made of Cu.



Figure S2. Statistic histogram of size distribution for the $Ni_{12}P_5$ nanoparticles. The data are obtained based on manual counts of 100 nanoparticles from TEM images.



Figure S3. (a) XRD patterns, and (b) corresponding HRTEM images of the monodisperse $Ni_{12}P_5$ nanoparticles, and (c-e) corresponding EDX maps of the elements of Ni and P.



Energy (keV)

Figure S4. EDX spectrum of the Ni₁₂P₅/CNT nanohybrids.



Figure S5. An electron diffraction pattern of the Ni₁₂P₅/CNT nanohybrids.



Figure S6. XPS spectra of (a) C 1s, (b) Ni 2p, (c) P 2p and (d) survey spectrum regions for the $Ni_{12}P_5/CNT$ nanohybrids.

Table S1. Comparison of HER performance in acidic media for $Ni_{12}P_5/CNT$ with other non-noble metal HER electrocatalysts.

Catalyst	Current density (j, mA/cm²)	Overpotential at the corresponding j (mV)	Reference
CoP/CNT	10	122	Angew. Chem. Int. Ed. 2014, 53, 6710
Amorphous WP	10	120	Chem. Commun.
nanoparticles	20	140	2014, 50, 11026
FeP	10	~240	Chem. Commun. 2013, 49, 6656
CoP/Ti	10	90	Chem. Mater.
	100	146	2014, 26, 4326
MoS ₂ /Graphene/CP	10	150	J. Am. Chem. Soc. 2011, 133, 7296
Ni ₂ P /CNT	10	124	J. Mater. Chem. A 2015, 3 , 13087
MoS ₂ /graphene/Ni	10	141	Adv. Mater.
foam	100	263	2013, 25, 756
MoS ₂ /MoO ₃ /FTO	10	300	Nano Lett. 2011, 11, 4168
	2	84	Adv. Mater.
MoP nanoparticles	10	125	2014, 26, 5702
	100	200	
Ni ₂ P hollow	10	116	J. Am. Chem. Soc.
nanoparticles/Ti	100	180	2013, 135, 9267
Amorphous MoP	10	90	Chem. Mater.
Nanoparticles		=0	2014, 26, 4826
	1	79	Angew. Chem. Int. Ed.
GU3F 1999/GF	10	143	2014, 33, 7377
	100	276	m) ·]
Ni ₁₂ P ₅ /CNT	2	65	This work
	10	129	



Figure S7. Calculation of the exchange current density of $Ni_{12}P_5$, $Ni_{12}P_5$ /CNT and Pt/C by extrapolation method.



Figure S8. Time dependence of the current density under a constant overpotential of 160 mV of $Ni_{12}P_5/CNT$.



Figure S9. TEM image, XRD pattern and XPS spectra of $Ni_{12}P_5/CNT$ catalysts after 1000 cycling.



Figure S10. Polarization curves for $Ni_{12}P_5$ in H_2SO_4 solution (0.5 M) with a scan rate of 5 mV s⁻¹ before and after 1000 cycles.



Figure S11. Cycling performance and the corresponding Coulombic efficiency of the annealed $Ni_{12}P_5/CNT$ nanohybrids at a current density of 2.0 A g⁻¹.



Figure S12. SEM (a) and TEM (b) images of the $Ni_{12}P_5/CNT$ nanohybrids electrodes after 100 cycles at 100 mA g⁻¹.



Figure S13. Rate performance and the corresponding Coulombic efficiency of the annealed bare $Ni_{12}P_5$ nanoparticles.



Figure S14. Nyquist plots of the annealed $Ni_{12}P_5/CNT$ nanohybrids and the annealed bare $Ni_{12}P_5$ nanoparticles.



Figure S15. Typical I–V curves measured of the different samples at room temperature.