Supporting Information

Self-Templated Formation of Fluffy Graphene-Wrapped Ni_5P_4 Hollow Spheres for Li-Ion Battery Anodes with High Cycling Stability

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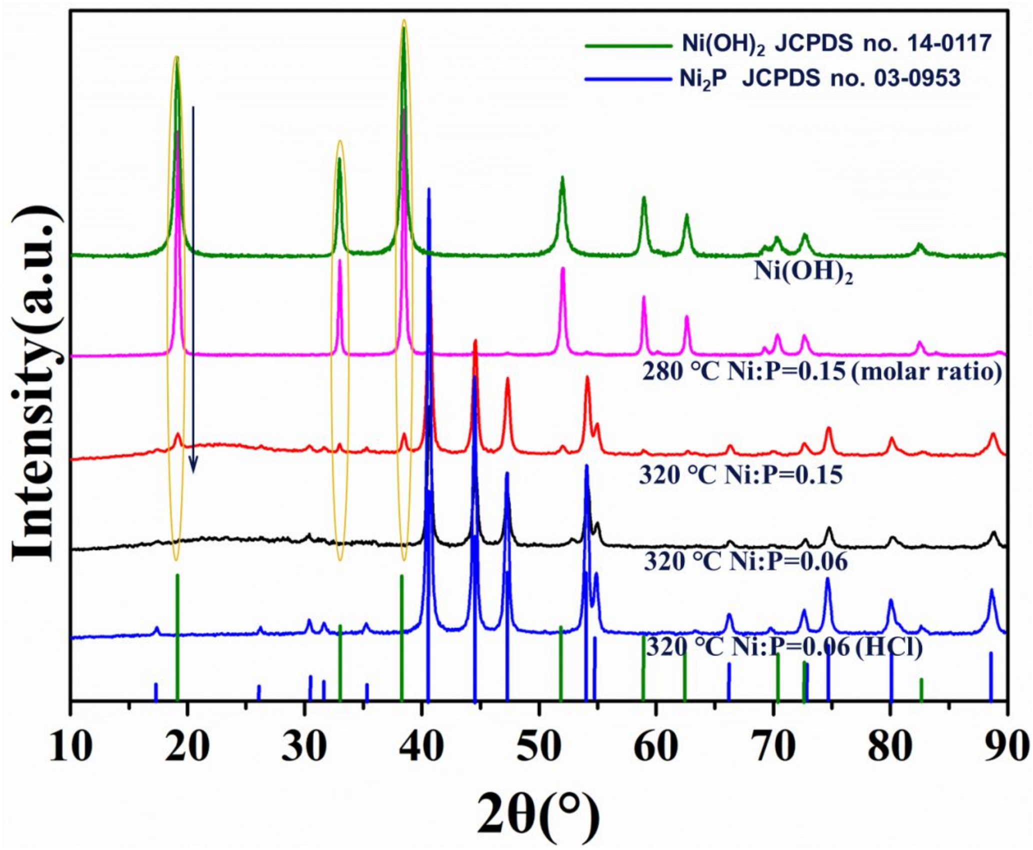


Figure S1. XRD patterns of $Ni(OH)_2$ and Ni_2P generated with different Ni/P molar ratios.

As shown in Figure S1, the phosphorization of $Ni(OH)_2$ will not occur at a temperature of 280 °C, and a great amount of $Ni(OH)_2$ can be phosphorized into Ni_2P at a temperature of 320 °C, which can be fully transformed into Ni_2P if the Ni/P molar ratio decreases to 0.06. By-products such as phosphates cover on the surface of Ni_2P can be removed by diluted HCl and high-quality Ni_2P is collected.

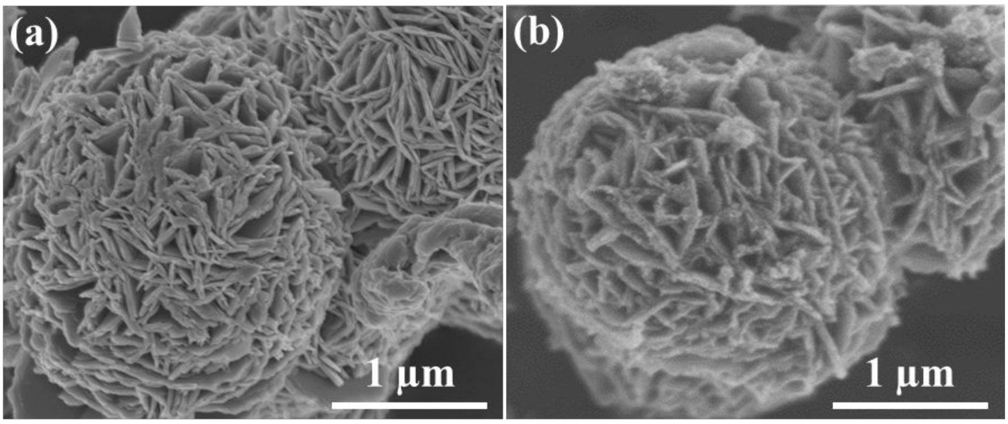


Figure S2. SEM images of $Ni(OH)_2$ and Ni_2P porous spheres.

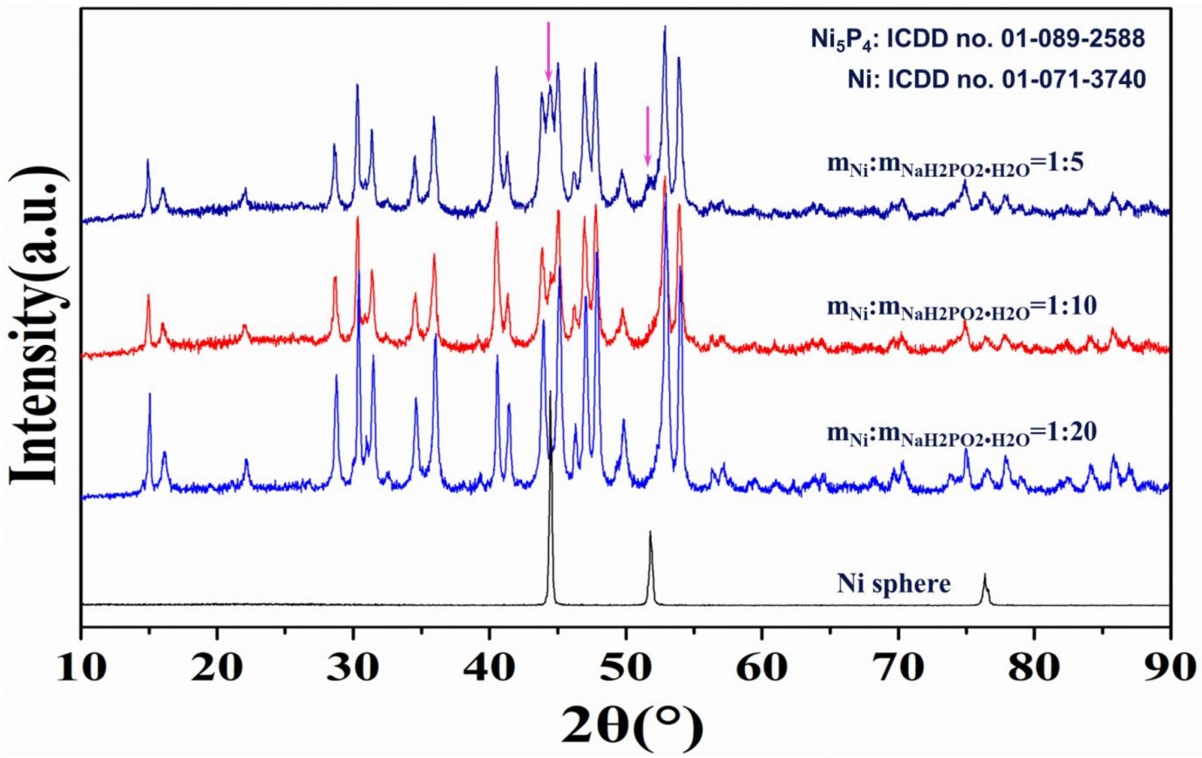


Figure S3. XRD patterns of Ni_5P_4 synthesized with different mass ratios of Ni spheres to $NaH_2PO_2{\bullet}H_2O$.

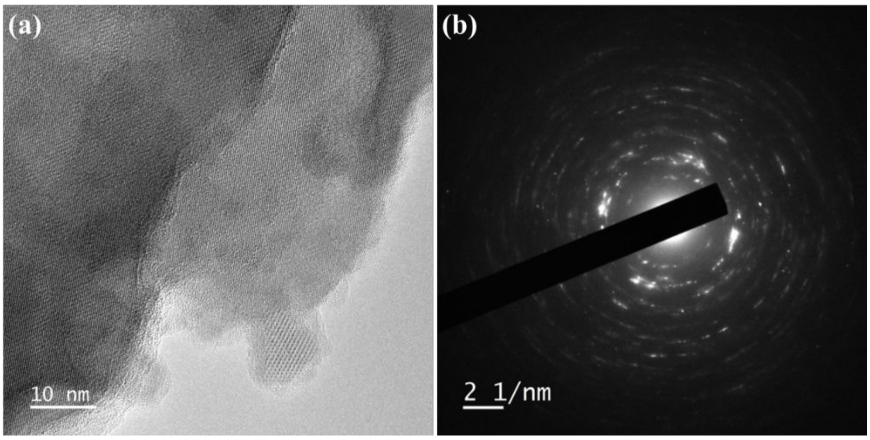


Figure S4. HR-TEM image (a) and SAED pattern (b) of Ni_5P_4.

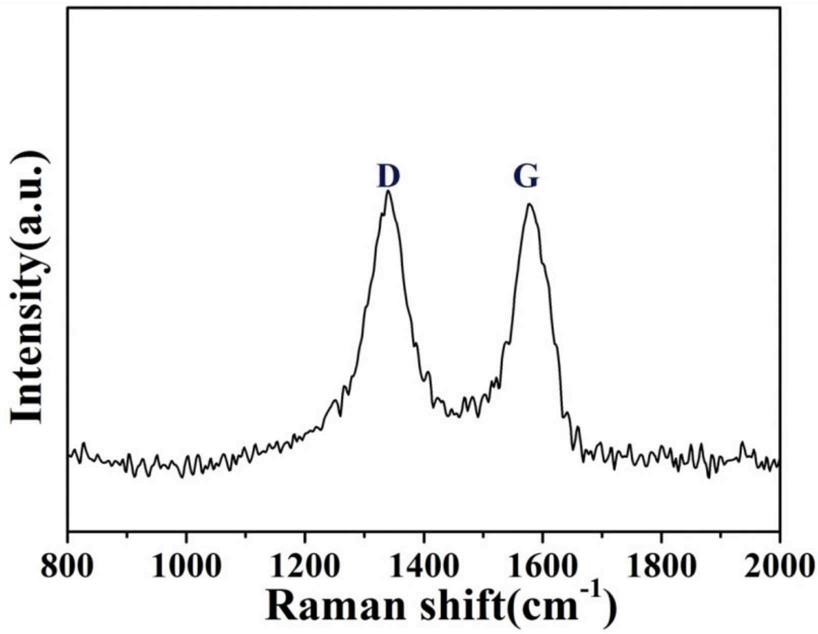
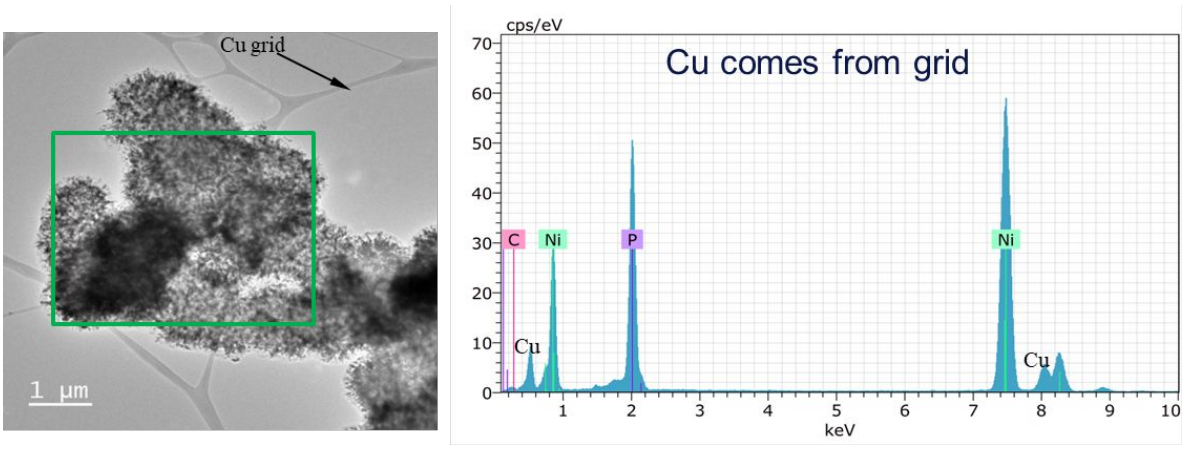
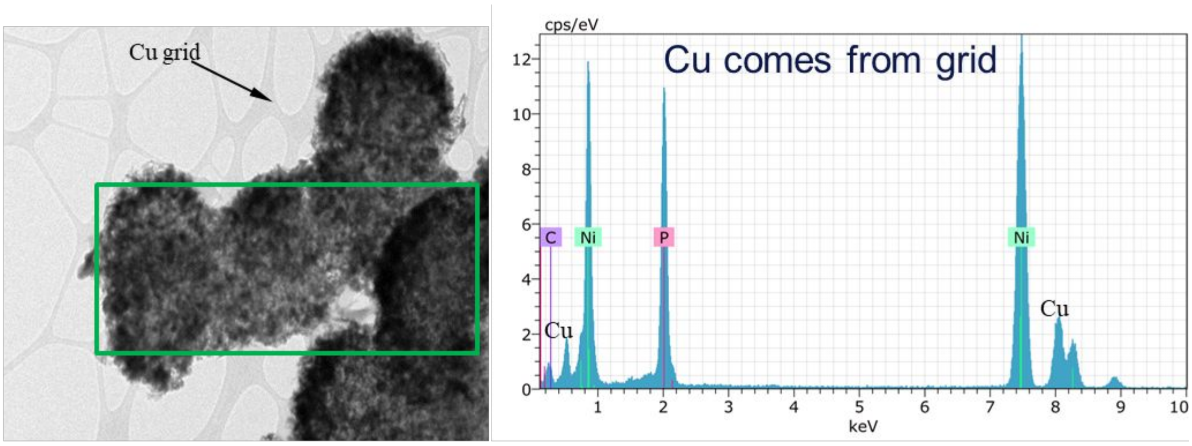


Figure S5. G- and D-bands of graphene in the Raman spectrum of Ni_5P_4@FG.



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Ni	28	K-series	72.82	72.82	57.97	2.22
P	15	K-series	26.75	26.75	40.36	0.83
C	6	K-series	0.43	0.43	1.67	0.05
		Total:	100.00	100.00	100.00	

Figure S6. EDX analysis of Ni_5P_4



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Ni	28	K-series	70.77	70.77	52.21	2.19
P	15	K-series	26.10	26.10	36.49	0.84
C	6	K-series	3.13	3.13	11.30	0.19
		Total:	100.00	100.00	100.00	

Figure S7. EDX analysis of pristine Ni_5P_4@FG

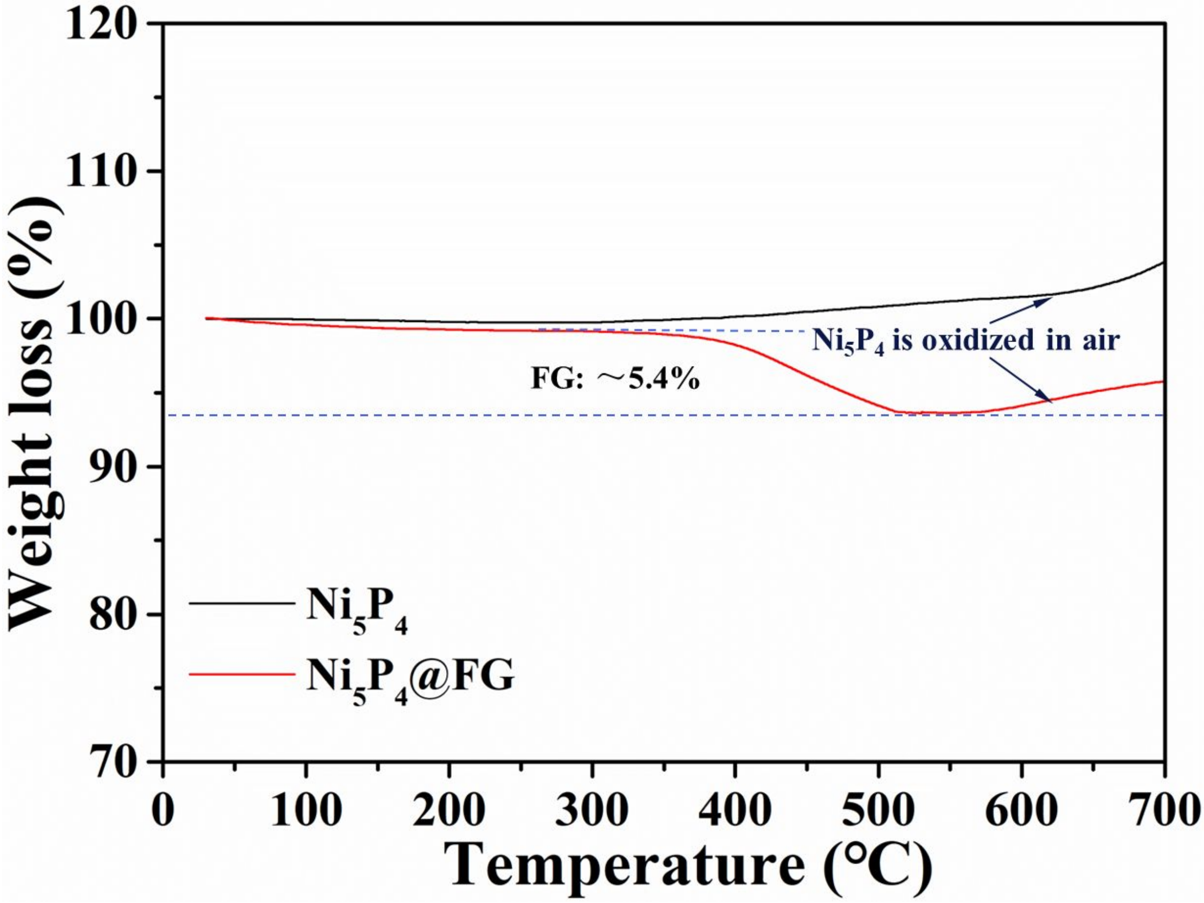


Figure S8. TG analysis of the pristine Ni_5P_4 and Ni_5P_4@FG samples

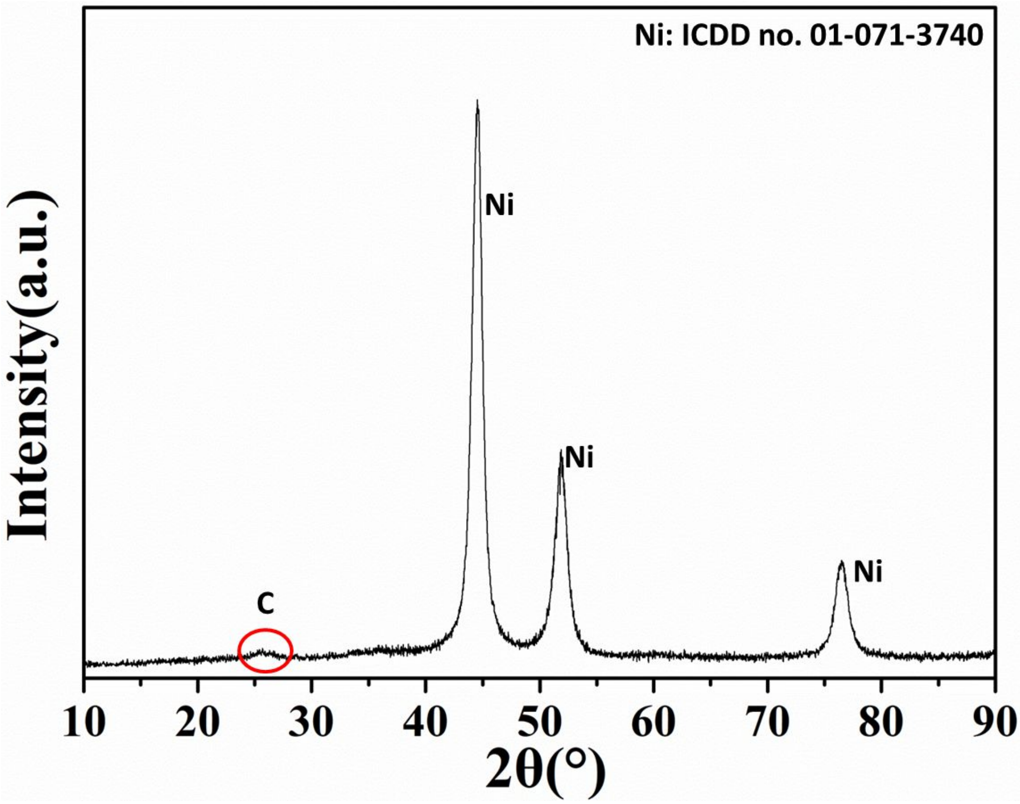


Figure S9. XRD spectrum of Ni@G

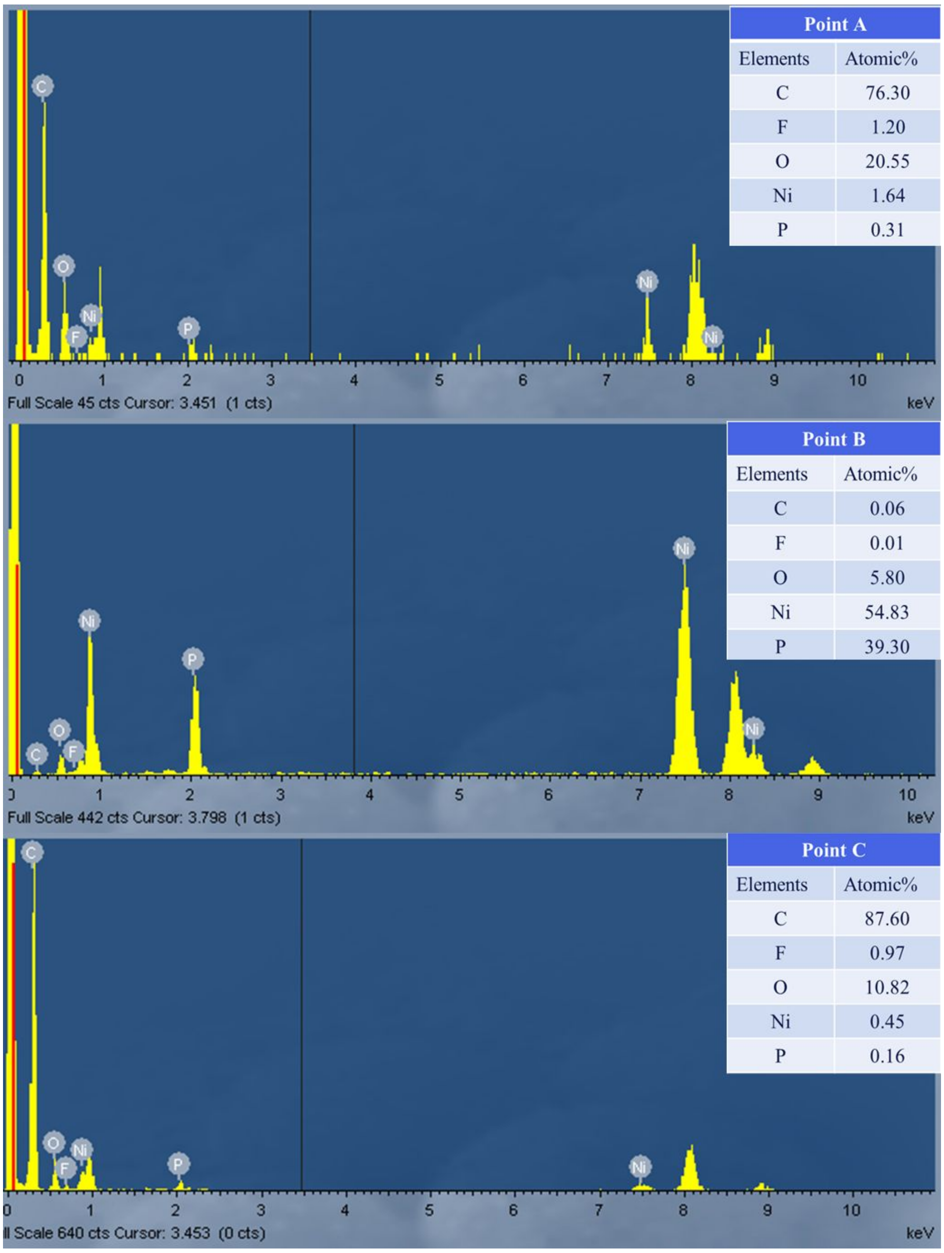


Figure S10. EDX analysis of C, F, O, Ni and P elements on the different points shown in Figure 6b and d. The trace amount of Ni is also detected in the SEI layers (points A and B), which may result from surface contamination when the samples were detached from the copper foils.

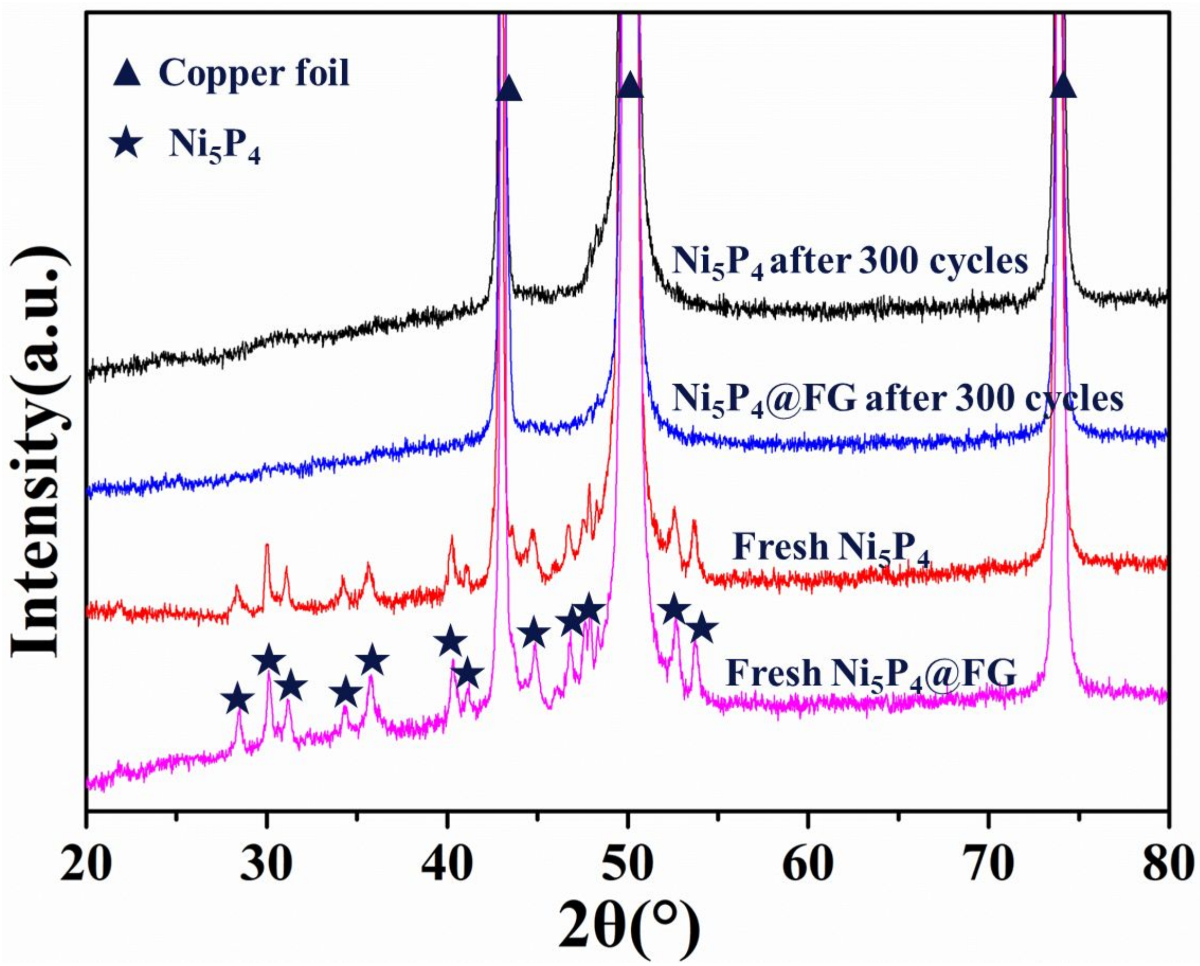


Figure S11. Ex-situ XRD of Ni_5P_4 and Ni_5P_4@FG in copper foils detached from the cells before and after 300 cycles

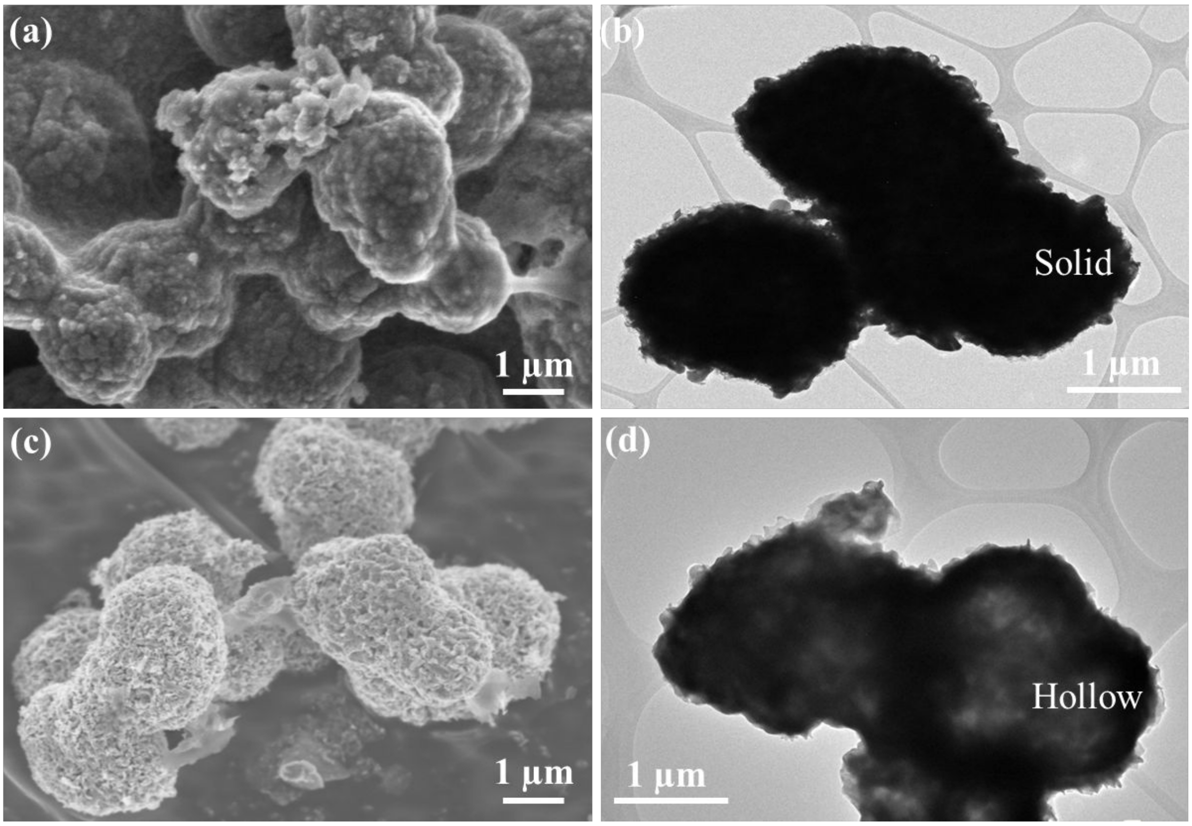


Figure S12. SEM and TEM images of Ni_5P_4 (a,b) and Ni_5P_4@FG (c,d) after 300 cycles

Table S1. Ni_5P_4-based Li-ion battery anodes and their performance.

Structures	**Methods**	**Current density (mA g^{-1})**	**Specific capacity (mAh g^{-1}) #**	**Cycle number**
Ni_5P_4@C[1] sphere	Wet-chemistry and a solid-state reaction	0.1 C	644	50
Ni_5P_4/C[2] Nanoparticle	Triphenylphosphine-based solvothermal reaction	0.2 C	600	100
Ni_5P_4[3] Nanosheet	P-assisted reaction with Ni foam	0.5 C	400	100
Ni_5P_4[4] Nanofoam	PH_3-assisted reaction with Ni-P nanofoams	50 (~0.07 C)*	~500	100
Ni_5P_4 **(This work)** Hollow sphere	PH_3-assisted reaction with hollow Ni sphere	500 (~0.7 C)*	583	300
Ni_5P_4@FG **(This work)** Hollow sphere	PH_3-assisted reaction with hollow Ni@G sphere	500 (~0.7 C)*	739	300

* The rate is calculated on the basis of the theoretical specific capacity of Ni_5P_4 (767 mAh g^{-1})

Determined after each specified cycle numbers.

Table S2. Representative resistances in the equivalent circuits of different Ni_5P_4 and Ni_5P_4@FG cells.

Cells	**R_s (Ω)**	**R_{sf} (Ω)**	**R_{ct} (Ω)**	**C_{int} (F)**
Fresh Ni_5P_4	7.30	467.9	75.5	/
Ni_5P_4 after 1 cycle	7.33	216.0	39.9	/
Fresh Ni_5P_4@FG	10.11	524.0	25.5	/
Ni_5P_4@FG after 1 cycle	11.00	297.7	6.2	/
Ni_5P_4@FG after 300 cycles	21.65	122.1	36.9	0.095
Ni_5P_4 after 300 cycles	17.27	190.0	58.9	0.89

References

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