Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

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Eco-efficient synthesis route of carbon-encapsulated transition metal phosphide with improved cyclic stability for lithium-ion batteries

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Experimental

1. Preparation

The precursor of SDP/Ni$(OH)_2$ was synthesized via a conventional precipitation method. Briefly, a 100 mL of aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.002 mol), SDP (0.01 mol), and hexamethylenetetramine (0.012 mol) was prepared in a Teflon vessel with deaerated water, and then heated at 120 °C for 24 h. After the reaction, the precipitates obtained were centrifuged, washed with distilled water and ethanol, and dried at room temperature. The precursor of SDS/NiAl-LDH was synthesized via a conventional co-precipitation method. Briefly, A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (0.015 mol), $Al(NO_3)_3 \cdot 9H_2O$ (0.005 mol) and SDS (0.1 mol) was dissolved in 100 mL of deaerated water under N_2 atmosphere, then titrated by adding a solution of NaOH (0.1 mol, 100 mL) with stirring under N_2 atmosphere at room temperature until pH = 10.5, and then heated at 120 °C for 24 h. After the reaction, the precipitates obtained were centrifuged, washed with distilled water and ethanol, and dried at room temperature.

The calcined products were obtained by calcination of the respective precursors in a fused quartz tube mounted in a programmable tube furnace at 700°C for 2h under N_2 atmosphere with a temperature ramping rate of 2 °C/min.

2. Characterization

Powder X-ray diffraction was carried out on Rigaku XRD-6000 powder diffractometer with CuKα radiation (40 kV, 30 mA, λ=1.542 Å), the data was collected at a scanning speed of 10^{o} min^{-1}. Room-temperature FTIR spectra were recorded in the range 400 – 4000 cm^{-1} with a resolution of 2 cm^{-1} on a Bruker Vector-22 Fourier transform spectrometer using the KBr pellet technique (1 mg of sample in 100 mg of KBr). Scanning electron microscope (SEM) images were obtained using a Zeiss Supra 55 scanning electron microscope on the platinum coated the samples. Samples were dispersed in ethanol and then deposited onto silicon wafer. Transmission electron microscopy (TEM) characterization was performed through a JEOL JEM-2100 electron microscope equipped with STEM and EDX at an accelerating voltage of 200 kV. Samples were dispersed in ethanol and then deposited onto a copper microgrid. Raman spectroscopy was recorded on a confocal Raman spectrometer (Renishaw RM2000) with a 514 nm excitation laser (laser spot size of 0.5 μm) operated at a low power level (~2 mW). Samples were drop-cast onto a silicon substrate for Raman measurements. The X-ray photoelectron spectroscopy (XPS) analyses were conducted through a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyzer.

Electrochemical measurements were performed with Swagelok-type cells assembled in an argon-filled glove box. For preparing working electrodes, a mixture of active material, super-P acetylene black, and poly(vinyl difluoride) (PVDF) at a weight ratio of 70:20:10 was pasted on a Cu foil. Lithium foil was used as the counter electrode. A glass fiber (GF/D) from Whatman was used as a separator. The electrolyte consisted of a solution of 1M $LiPF_6$ salt in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 in wt%) plus 2 wt% vinylene carbonate (VC) obtained from Tianjing Jinniu Power Sources Material Co. Ltd.. Galvanostatic cycling of the assembled cells was carried out using LAND CT2100A cell-testing system in the voltage range of 0.01–3.0 V (vs. Li^{+}/Li).

Figure S1

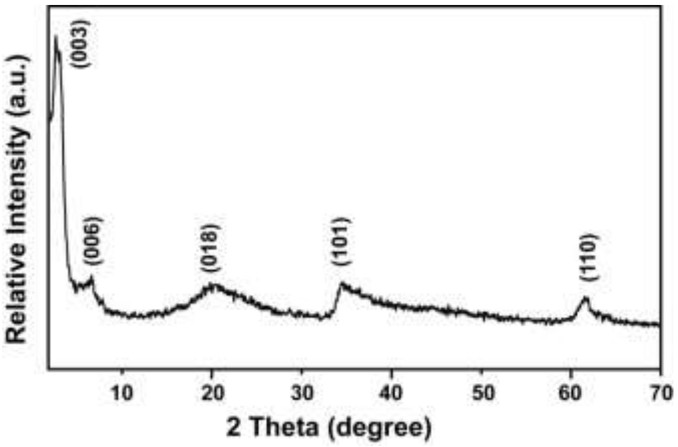

Fig. S1 XRD patterns of the precursor of intercalated dodecyl phosphate/Ni$(OH)_2$.

Figure S2

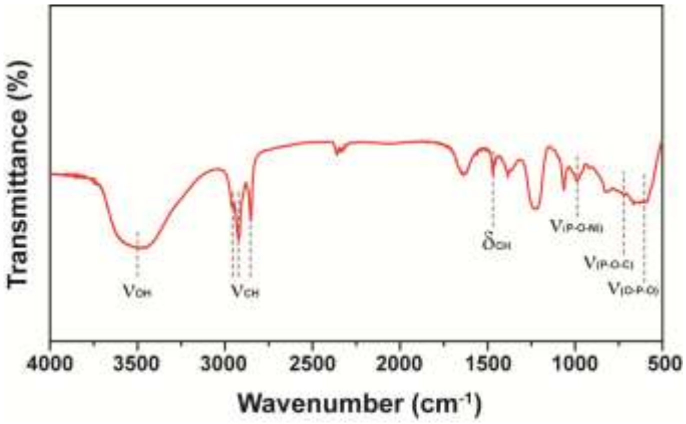

Fig. S2 FT-IR spectrum of the precursor of interclated dodecyl phosphate/Ni$(OH)_2$.

Figure S3

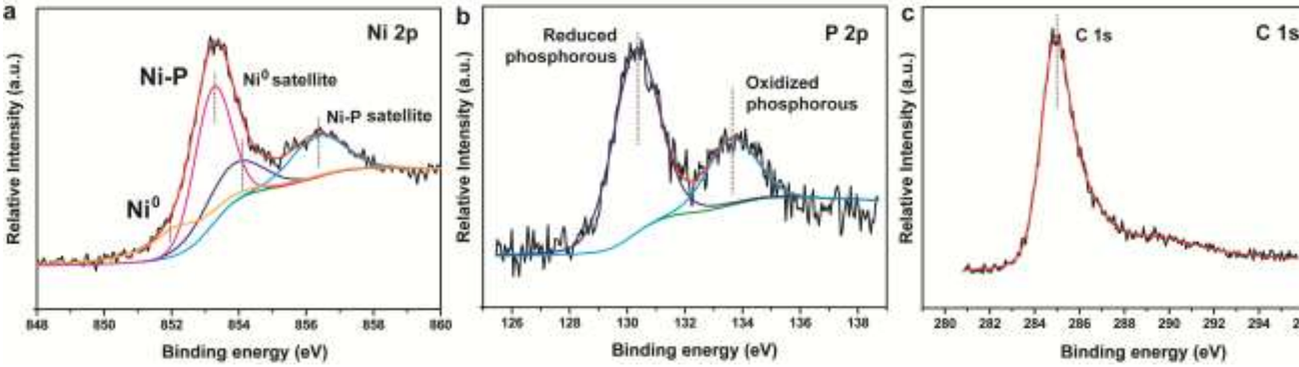

Fig. S3 XPS spectra of (a) Ni 2p3/2, (b) P 2p, and (c) C1s for the C@Ni_3P/Ni/C nanocomposite.

Figure S4

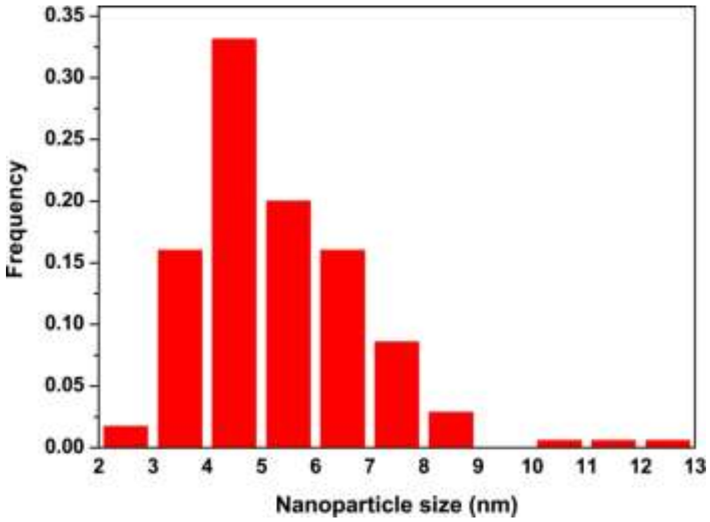

Fig. S4 Histogram of nanoparticle sizes obtained by manually measuring the sizes of >100 nanoparticles from TEM images.

Figure S5

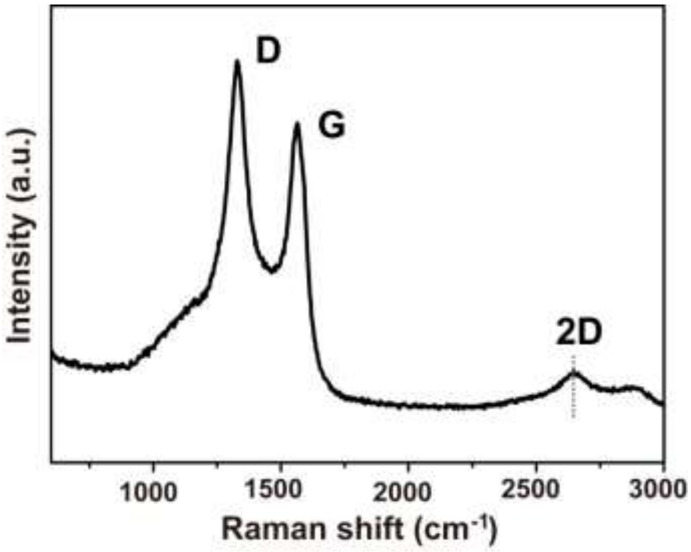

Fig. S5 Raman spectrum of the C@Ni_3P/Ni/C nanocomposite derived from the SDP surfactant/$Ni(OH)_2$ precursor.

Figure S6

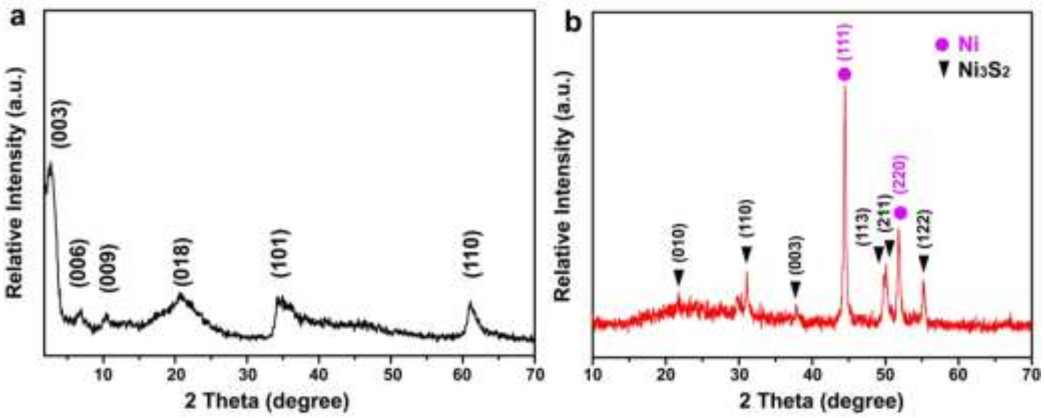

Fig. S6 XRD patterns of (a) the precursor of intercalated SDS/NiAl-LDH, showing a typical shift of the basal (00*l*) reflections towards low angles, and (b) the calcined production derived at 700 °C under N_2 atmosphere.

Figure S7

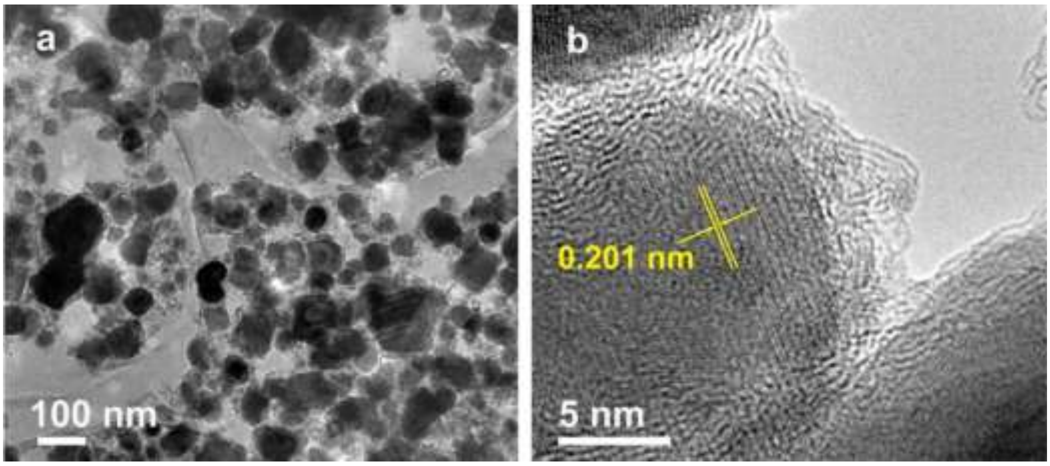

Fig. S7 (a) TEM image of the calcined production derived from the precursor of intercalated SDS/NiAl-LDH at 700 °C under N_2 atmosphere, and (b) HRTEM image shows the nanostructures of carbon shell@Ni_3S_2/Ni nanoparticle core.

Figure S8

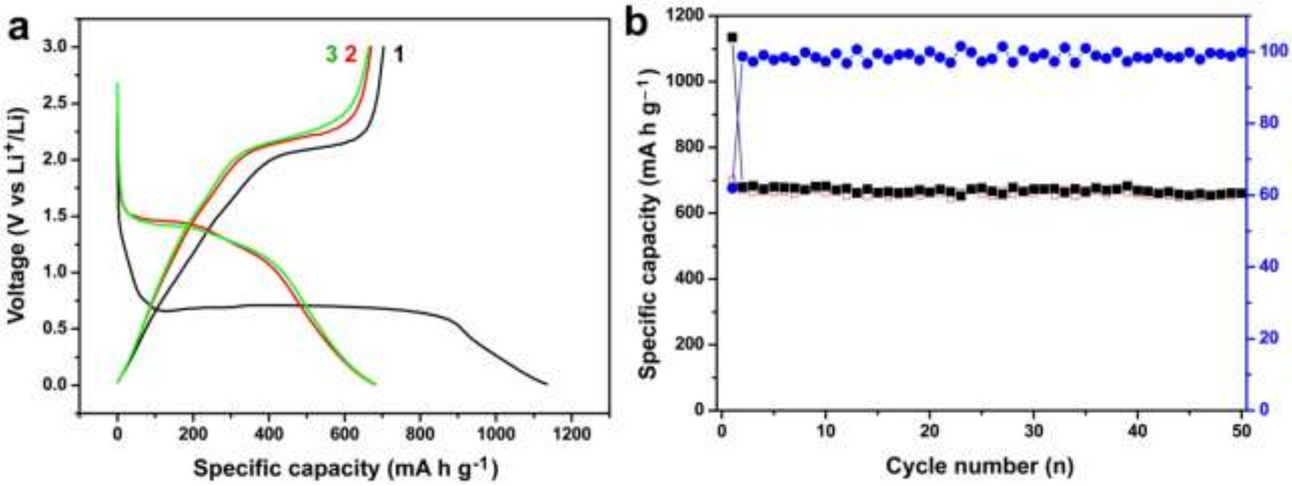

Fig. S8 (a) The first three charge-discharge profiles of the C@Ni_3S_2/Ni/Al_2O_3 nanocomposite and (b) cycling behaviors of C@Ni_3S_2/Ni/Al_2O_3 nanocomposite electrode at a rate of 100 mA g^{-1}.

Figure S9

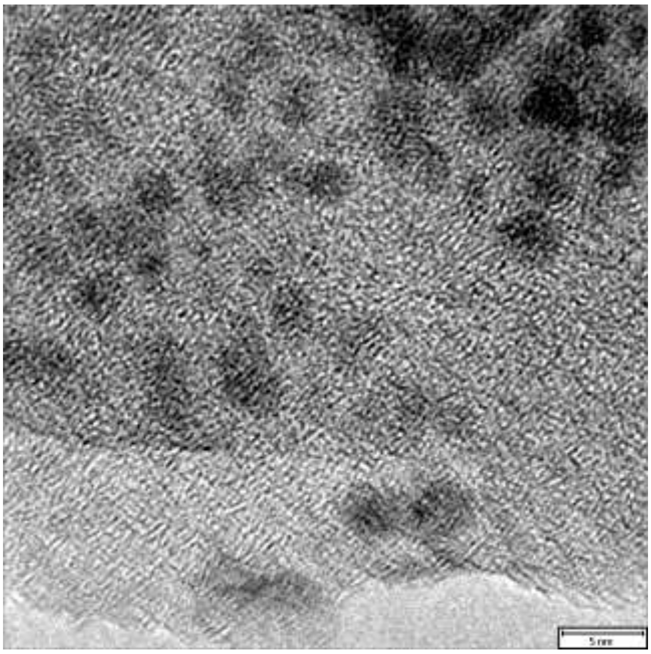

Fig. S9 TEM image of the C@Ni_3P/Ni/C nanocomposite after 200 cycles.