Supporting Information

A densely packed air-stable free-standing film with FeP nanoparticles@C@P-Doped reduced graphene oxide for sodium-ion battery

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Materials and methods

Preparation of reduced graphene oxide (rGO)

Graphene oxide (GO) was synthesized by a modified Hummers method using graphite powder obtained from Sigma-Aldrich.¹ Reduced graphene oxide (rGO) was produced by a thermal expansion method. The appropriate mass of GO was put into the round flask, and it was heated at 190 °C under the vacuum state. Finally, it was kept at 300 °C for 3 h to obtain rGO.

Preparation of a monodisperse carbon-coated iron phosphide/p-doped reduced graphene oxide (FeP@C@ PG) composite

Iron(III) acetylacetonate (Fe(acac)₃), and phytic acid (PA, 50 % (w/w) in H₂O) were purchased from Sigma-Aldrich. In a typical process, 0.72 g of Fe(acac)₃ was mixed with 8 mL of phytic acid. After that, the dark red-colored ferric phytate precursors were mixed homogeneously with 0.1 g of rGO in a mortar. Then, the mixture was heated to 800 °C for 5 h with a heating rate of 5 °C min⁻¹ under a 5 vol % of H₂ in Ar atmosphere. The FeP@C composite was prepared by the same route without rGO.

Preparation of FeP@C@PG film

For the preparation of the densely packed free-standing FeP@C@PG film electrode, a facile filtration and separation process was introduced. In a typical process, 0.01 g of rGO was dispersed in 10 mL isopropyl alcohol (IPA) and 0.1 g of as-prepared FeP@C@PG composite was dispersed in 50 mL of IPA. The rGO solution – FeP@C@PG mixture – rGO solution was filtered in order. After drying in a vacuum oven at 60 °C for 8 h, a free-standing film was obtained. Finally, a free-standing film was pressed using roll-press machine for tuning the

thickness of the film. Corresponding to the thickness of 18 μ m, and the loading mass of the electrode is ~2.6 mg cm⁻².

Preparation of $Na_3V_2(PO_4)_3@C(NVP@C)$

Oxalic acid, vanadium(V) oxide, and sodium dihydrogen phosphate were purchased from Sigma-Aldrich. In a typical process, 1.44 g of oxalic acid, 0.72 g of vanadium oxide, and 1.66 g of sodium dihydrogen phosphate were dissolved in distilled water under stirring at 80 °C for 30 min. After the solution became transparent, the mixed solution was kept at 60 °C until all solvent evaporated and the gel was formed. The dried gel was ground in a mortar and heated at 350 °C for 5 h and at 800 °C for 10 h with a heating rate of 5 °C min⁻¹ under an Ar atmosphere.

Characterizations: The micro-structures and morphologies of the samples were observed by field emission scanning electron microscope (FE-SEM, Hitachi S-4800), and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-200), as well as energy dispersive spectrometer (EDS). The elemental analysis (EA) was performed on a Thermo Fisher Scientific (Flash2000). Raman analysis was conducted by raman spectrometer (DXR2xi). The crystal structures of the samples were analyzed by X-ray diffraction (XRD, Bruker D8 Advance, Cu-K α radiation). The nitrogen adsorption/desorption isotherms were obtained using BELSORP-mini II (MicrotracBEL Corp). X-ray photoelectron spectroscopy (XPS) analysis was conducted by Axis-HIS with Al irradiation. The contact angle was measured by CMT-100S.

Electrochemical measurement : To evaluate the electrochemical performance of FeP@C@PG film composite and FeP@C composite, a half-cell was assembled by a CR2016 coin-type cell in an Ar-filled glove box ($O_2 < 0.1$ ppm). 1 M NaClO₄ in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC), a glass filter (Whatman), and a sodium metal foil were employed as a electrolyte, separator, counter electrode, respectively. The FeP@C electrode was prepared by adding active material (80 wt%), carboxymethyl cellulose (10 wt%), and carbon black (10 wt%). The slurry was coated on a Cu foil with a doctor blade and vacuum dried at 60 °C for 5 h. The loading mass of the active material was ranged between 1.00 mg cm^{-2} and 1.03 mg cm⁻². The pouch-type full-cell was assembled with Na₃V₂(PO₄)₃@C as the cathode and FeP@C@PG film as the anode. The electrode was cut into rectangular pieces with a size of 3 cm \times 6 cm (cathode) and 3.2 cm \times 6.2 cm (anode). Then, the cathode, separator, and anode were put together and connected with aluminum (cathode) and nickel (anode) tab. Finally, the electrolyte was injected, and vacuum sealing was conducted in the glove box. Electrochemical tests were performed by a WBCS3000s cycler (WonATech) in a voltage range of 0.01-3.00 V (vs. Na⁺/Na) at 25 °C. Electrochemical impedance spectroscopy (EIS) was performed by a ZIVE SP1 (ZIVE LAB).



Fig. S1 Surface zeta potential of rGO, rGO + PA, and rGO + $PA + Fe^{3+}$.



Fig. S2 SEM image of FeP@C@PG with high ratio of Fe precursor.







Fig. S4 SEM image of FeP@C@PG film thickness before roll-press method.



Fig. S5 EDS spectrum of FeP@C@PG.

Sample	Line Type	Wt %	Atomic %
С	K series	24.1	46.7
0	K series	12.2	17.7
Р	K series	27.4	20.5
Fe	K series	36.3	15.1
Total		100.0	100.0

Table S1 A summary of EDS analysis of FeP@C@PG.



Fig. S6 BJH pore size distribution curve of the FeP@C@PG film, and FeP@C.

Sample	Carbon content _ (wt %)	Oxygen content (wt %)	
		Fresh	80 °C in air for 40h
FeP@C@PG	25.1	10.1	12.8
FeP@C	10.4	7.4	25.6

Table S2 Elemental analysis of FeP@C@PG film and FeP@C.



Fig. S7 a) XPS survey spectrum of FeP@C and the corresponding high-resolution spectra of b) Fe 2p, and c) C 1s.



Fig. S8 Ex-situ XRD patterns of FeP@C@PG film.



Fig. S9 Electrochemical performance of FeP@C; a) CV curves at 0.1 mV s⁻¹ of scan rate and 0.01-3.00 V of voltage range, b) Galvanostatic discharge/charge curves at 0.1 A g⁻¹.



Fig. S10 Cycling performance of FeP@C@PG at a lower current density (0.1 A g⁻¹).



Fig. S11 Comparison with reported metal-phosphide@carbon nanocomposite anode materials for SIBs.²⁻⁸



Fig. S12 Schematic illustration of the morphology evolutions and cycled SEM images of a) FeP@C electrode and b) FeP@C@PG film.



Fig. S13 Galvanostatic discharge/charge curves at 0.1 A g⁻¹ of a) FeP@C@PG film with $Na_3V_2(PO_4)_3@C$ and b) only $Na_3V_2(PO_4)_3@C$.



Fig. S14 Contact angle images between water and electrodes of a) FeP@C (fresh), and b) FeP@C (hot-drying).



Fig. S15 HR-TEM image of FeP@C@PG film (hot-drying), and FeP@C (hot-drying).



Fig. S16 XRD patterns of FeP@C@PG film (hot-drying), and FeP@C (hot-drying).



Fig. S17 Equivalent circuits for FeP@C@PG film (fresh), FeP@C@PG film (hot-drying), FeP@C (fresh), and FeP@C (hot-drying).

Samples	$R_s / \Omega \cdot cm^{-2}$	R_{SEI}/Ω ·cm ⁻²	$R_{ct}/\Omega \cdot cm^{-2}$
FeP@C@PG film (fresh)	11.7 ± 0.2	22.2 ± 2.3	90.7 ± 1.3
FeP@C@PG film (hot-drying)	11.9 ± 0.1	29.7 ± 5.2	95.9 ± 2.4
FeP@C (fresh)	8.3 ± 1.1	17.0 ± 3.8	210.6 ± 10.1
FeP@C (hot-drying)	7.8 ± 0.7	13.0 ± 5.3	440.8 ± 6.1

Table S3 The fitting values of the resistance components in the simplified equivalent circuit.

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