

Electronic Supplementary Information:

Graphene–amorphous FePO₄ hollow nanosphere hybrid as a cathode material for lithium ion batteries

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1. Experimental details

1.1. Preparation of graphene oxide

The graphene oxide (GO) used in this work was prepared by a modified Hummers' method,¹⁻⁶ which involves graphite oxidation, exfoliation, and chemical reduction. Graphite powder (3 g, 325 mesh) was put into a mixture of concentrated H₂SO₄ (12 mL), K₂S₂O₈ (2.5 g), and P₂O₅ (2.5 g). The solution was heated to 80 °C in an oil bath and stirred for 4.5 h. Next, the mixture was cooled to room temperature and diluted with double-distilled water (0.5 L) and left overnight. Then, the product was obtained by filtering through a 0.2 micron Nylon film and washed with double-distilled water to remove the residual acid. The product was dried at ambient temperature.

The pretreated graphite powder was put into cold (0 °C), concentrated H₂SO₄ (120 mL). Then, KMnO₄ (15 g) was added gradually while stirring, and the temperature of the mixture was kept below 20 °C using an ice bath. Successively, the mixture was stirred at 35 °C for 2 h and then diluted with double-distilled water (0.5 L) to keep the temperature at 50 °C. After adding 250 mL of double-distilled water, the mixture was stirred for 2 h, and then additional water (1 L) was added. Shortly after the dilution, 30% H₂O₂ (20 mL) was added drop by drop, and the color of the mixture changed to a brilliant yellow while bubbling. The mixture was filtered and washed with a 1:10 HCl aqueous solution (1 L) to remove metal ions, which was followed by a double-distilled water wash (1 L) to remove the acid. The resulting solid was dried in air and diluted to make a graphite oxide dispersion (0.5% w/w). Finally, the mixture was purified by performing dialysis for one week to remove the remaining metal species.

Exfoliation was carried out by sonicating the graphite oxide dispersion (0.1 mg mL⁻¹) under ambient conditions for 20 min. The resulting homogeneous, yellow-brown dispersion was then subjected to 30 min of centrifugation at 3000 rpm to remove unexfoliated graphite oxide (usually present in a very small amount). Atomic force microscopy (AFM) images recorded with a Nanoscope IIIa scanning probe microscope (Digital Instruments) using the tapping mode indicated that the thickness of the prepared GO was approximately 1 nm (the AFM image is not shown here). The AFM result agrees

with the reported apparent thickness of GO sheets⁷⁻⁹ and suggests that the single-sheet nature of GO was obtained. The AFM images revealed that sheets thicker or thinner than 1 nm were not observed, demonstrating that complete exfoliation of GO down to an individual sheet level is achieved under our experimental conditions. The prepared GO (in a dispersion) was used for further experiments.

1.2. Preparation of graphene-amorphous FePO₄ hollow nanosphere hybrids

Graphene-amorphous FePO₄ hollow nanosphere hybrids were synthesized by a one-step hydrothermal approach using Fe²⁺ and PO₄³⁻ ions as precursors, sodium dodecylsulfate (SDS) as a capping ligand, and urea as a precipitant. In a typical synthesis, (NH₄)₂Fe(SO₄)₂·6H₂O (0.0392 g), H₃PO₄ (41 μL), urea (1.2 g), and SDS (0.1 g) were dissolved in the homogeneous GO suspension (20 mL, 0.25 mg mL⁻¹). The mixture was vigorously stirred for approximately 5 min, transferred to an autoclave, and heated to 80 °C for 12 h. After naturally cooling to ambient temperature, the resulting products were collected by centrifugation, washed sequentially with ethanol and double-distilled water at least three times, and then dried at 80 °C for 12 h. The graphene–amorphous FePO₄ hollow nanosphere hybrids are referred to as graphene–FePO₄ hybrids in this work.

The weight fraction of graphene in the prepared hybrids was estimated to be approximately 18 wt%, which was obtained by removing the FePO₄ component in a concentrated HCl solution, followed by centrifugation, washing with distilled water several times, and desiccations.

1.3. Preparation of FePO₄ solid nanospheres

The FePO₄ solid nanospheres were prepared by a microwave heating method.¹⁰ The nucleation and growth processes were controlled by adjusting the applied microwave power and the reaction time. In a typical preparation, urea (1.2 g) and cetyltrimethylammonium bromide (CTAB, 0.1 g) were dissolved in (NH₄)₂Fe(SO₄)₂·6H₂O solution (40 mL, 0.0196 g), which was followed by the addition of H₃PO₄ (6.8 μL). The mixture was vigorously stirred until a homogeneous solution was formed. The mixture was then transferred to a round-bottom flask and placed in a homemade microwave refluxing synthesis

system at 200 W for 6 min. The resulting products were collected by centrifugation, washed sequentially with double-distilled water at least three times, and dried in air at ambient temperature.

1.4. Characterizations

The crystalline structures of the prepared FePO₄ nanostructures were examined using X-ray diffraction (XRD, Rigaku/Max-3A X-ray diffractometer) with Cu K α radiation ($\lambda = 0.15418$ nm). The size distribution and the mean sizes of the FePO₄ hollow nanospheres were determined using a BI-200SM dynamic light scattering (DLS) instrument (Brookhaven Instruments). The scanning electron microscopic (SEM) images were recorded with a FEI Quanta 200 field emission scanning electron microscope (FEI Company). The transmission electron microscopic (TEM) images were recorded on a JEOL-2010 transmission electron microscope operating at an accelerating voltage of 120 kV. The samples were prepared for TEM measurements by dispersing the graphene-FePO₄ hybrids in ethanol and evaporating one drop of the suspension onto a carbon-coated film supported on a copper grid. The composition of the prepared graphene-FePO₄ hybrids was analyzed by energy-dispersive spectroscopy (EDS), which was recorded with an Oxford Link ISIS energy-dispersive spectrometer attached to the microscope. The surface characteristics of the hybrids were examined by X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250 XPS spectrometer (VG Scientifics) and the monochromatic Al K α line at 1486.6 eV. The binding energies were calibrated with respect to the C (1s) peak at 284.6 eV. The peak fitting analysis was performed using the XPS PEAK program (version 4.0). The FT-IR spectra were measured using a Nexus 670 FT-IR spectrophotometer (Nicolet Instruments) and a KBr disk.

1.5. Electrochemical measurements

The electrochemical performance of the graphene-FePO₄ hybrids as a cathode for lithium ion batteries (LIBs) was evaluated in coin-type half cells (2032-type) at ambient temperature. The as-synthesized hybrids were mixed with carbon black (Super-P) and polytetrafluoroethylene (PTFE) in a

weight ratio of 75:15:10 in N-methyl-2-pyrrolidone to prepare a working electrode. The measurements were carried out galvanostatically in the potential range of 2.0–4.2 V using a battery cycle tester (Land, Wuhan, China), with lithium foil as the counter electrode and LiPF_6 (1 M) in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte. A polymer membrane separator (Celgard 2400) was placed between the electrodes.

The electrochemical performance of the solid FePO_4 nanospheres was measured in a similar manner and compared with that of the graphene– FePO_4 hybrids.

The active cathode material for graphene– FePO_4 hollow nanosphere and FePO_4 solid nanosphere was controlled to be about 1.8 mg cm^{-2} . The size of the electrode is about 14 mm in diameter.

2. DLS size-distribution, the EDS spectrum, and XRD pattern of the graphene-FePO₄ hybrids

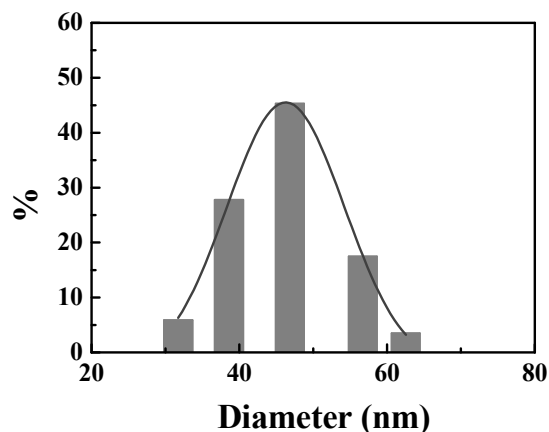


Fig. S1. DLS size-distribution diagram of the as-prepared amorphous FePO₄ hollow nanospheres.

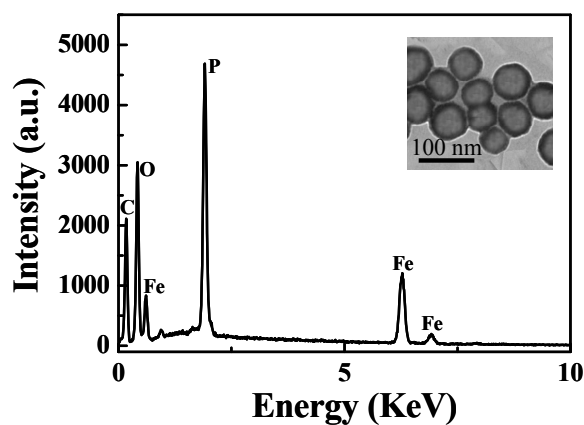


Fig. S2. EDS spectrum of the as-prepared graphene-FePO₄ hybrids. The inset indicated the EDS mapping area (about 250 × 250 nm).

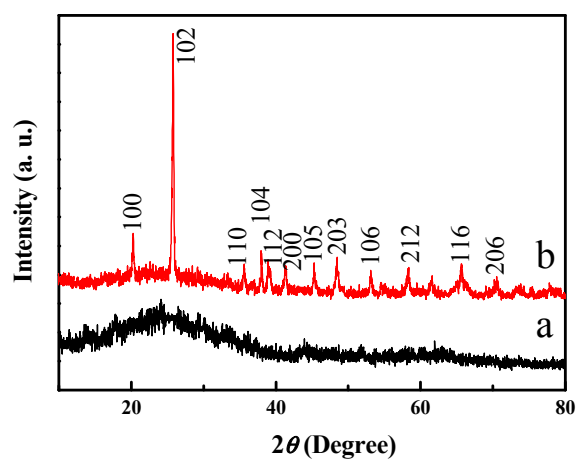


Fig. S3. XRD pattern of the hybrids before (a) and after annealing at 800 °C in air for 5 h (b).

3. FTIR Spectrum of the graphene–FePO₄ hybrids

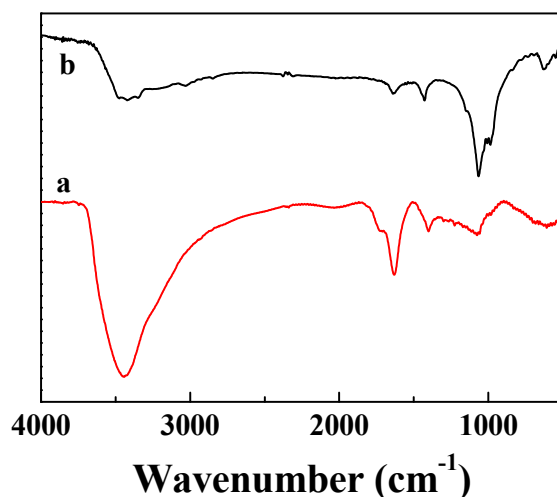


Fig. S4. FT-IR spectra of GO (a) and the as-prepared graphene–FePO₄ hybrids (b).

The IR spectrum of GO (curve (a), Fig. S4) displays the characteristic stretching vibration modes of the O–H ($\sim 3440\text{ cm}^{-1}$), C=O (1735 cm^{-1}), C–OH (1220 cm^{-1}), and C–O–C (1070 cm^{-1}) bonds, as well as the deformation mode of O–H (1401 cm^{-1}).¹¹ These results indicate that some oxygen-containing functional groups are present on the GO surface, such as hydroxyl groups, carboxyl groups, and epoxy groups. The peak at 1633 cm^{-1} is assigned to the vibrations of adsorbed water molecules.¹²

The IR spectrum of the graphene–FePO₄ hybrids (curve (b), Fig. S4) shows a strong peak at 1063 cm^{-1} , which is assigned to the stretching vibration of the Fe–O–P bond.¹³ The bands at 548 and 633 cm^{-1} can be attributed to the bending mode of the O–P–O bond¹⁴ and the symmetric stretching vibration of the P–O bond,¹⁵ respectively. These results indicate the formation of FePO₄.

By comparing the IR spectra presented in curves (a) and (b), it is apparent that the intensities of the peaks corresponding to the C=O (1735 cm^{-1}), C–O–C (1070 cm^{-1}), O–H (1401 cm^{-1}), and C–OH (1220 cm^{-1}) bonds decrease significantly after the introduction of Fe²⁺ ions. This decrease is indicative of the considerable deoxygenation of GO due to reduction by Fe²⁺ ions, which were oxidized to Fe³⁺ ions in the reduction process. These results demonstrate the formation of the graphene–FePO₄ hybrids.

4. XPS analysis on the oxidation state of Fe and the composition of carbon atoms in the hybrids

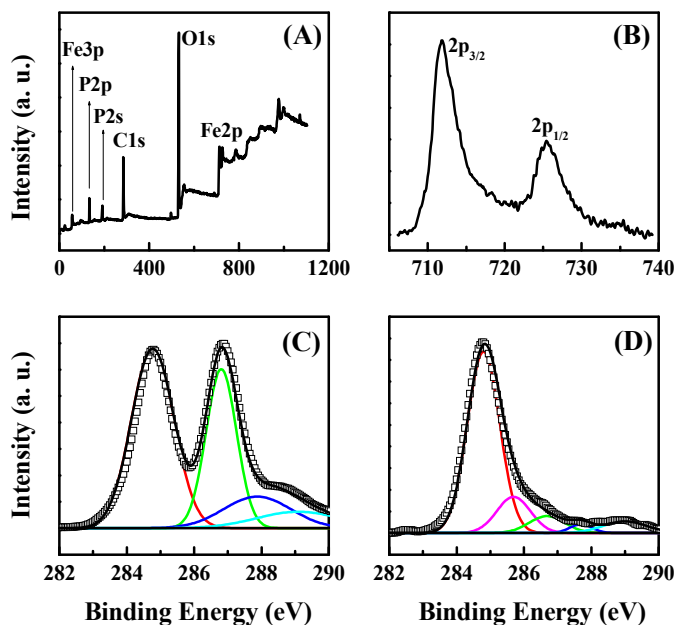


Fig. S5. (A) Survey XPS spectrum of the graphene-FePO₄ hybrid; (B) spectrum in the region of the Fe2p peak of a graphene-FePO₄ hybrid; (C) XPS spectrum of the C1s region for graphene oxide; and (D) XPS spectrum of the C1s region for the graphene-FePO₄ hybrid. Parts (C) and (D) also include the curves resulting from the deconvolution procedure.

The oxidation state of Fe in the prepared hybrids was verified by X-ray photoelectron spectroscopy (XPS) measurements. The typical survey spectrum shows peaks for Fe2p, Fe3p, P2p, P2s, O1s, and C1s core levels at binding energies of approximately 711.6, 56.0, 133.2, 188.8, 531.2, and 284.6 eV (Fig. S5A), respectively. The binding energy of Fe2p_{3/2} appears at a value (approximately 711.6 eV, Fig. S5B) very close to that reported for FePO₄ (711.4 eV).^{16,17} There is no evidence of Fe(II) in the samples because the XPS peak of Fe(II) should be at approximately 708.2 eV.¹⁸ These results further verify that the prepared hollow nanospheres are FePO₄.

The composition of carbon atoms in the graphene-FePO₄ hybrids was also analyzed by deconvoluting the C1s peak into its relative components and comparing it with those peaks in GO. The two main peaks for GO at 284.6 and 286.7 eV are assigned to the C-C and C-O (includes epoxide and hydroxyl) bonds (Fig. S5C), respectively. The peaks at 287.6 and 288.9 eV are attributed to C=O and

O–C=O, respectively. The C1s peaks in the graphene–FePO₄ hybrids exhibit the same oxygen functionalities as those that have been assigned to GO (Fig. S5D), but some peak intensities (for example C–O and O–C=O) are much lower than those in GO. This lower intensity indicates considerable deoxygenation due to reduction by Fe²⁺ ions, which were oxidized to Fe³⁺ ions at the same time, as verified by XPS measurements.

4. The TEM image of the prepared FePO₄ solid nanospheres

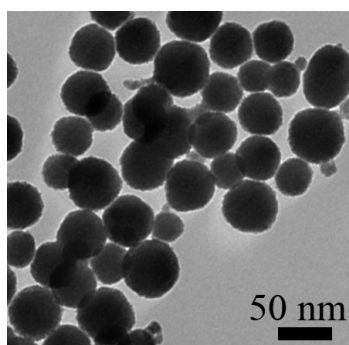


Figure S6. TEM image of the prepared amorphous FePO₄ solid nanospheres.

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