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$LiFePO_4$ Nanoparticles Encapsulated in Graphene Nanoshells for High-Performance Lithium-Ion Battery Cathode— Electronic Supplementary Information

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Experimental section

Preparation of Fe encapsulated in graphene nanoshell (Fe@GNS). Fe@GNS was prepared by a two-step CVD growth process, using Fe_3O_4 nanoparticles on graphene (Fe_3O_4-G) as starting material, similar to our previous report (Ref.13 in main manuscript).

The starting material Fe_3O_4-G used in this CVD process was prepared by thermally decomposing $Fe(acac)_3$ (300 mg) in a three-necked flask with the reducing reagent 2-pyrrolidone (40 mL) in the presence of graphene oxide (GO, 50 mg), which was synthesized from graphite flakes (~150 μm flakes) using the improved Hummers method.[1] The mixture was first bath-sonicated with N_2 bubbling for 10 min, then heated to 245 °C under N_2 and held at reflux for 30 min with stirring. The resulting black suspension was quenched with acetone, followed by filtration through a polytetrafluoroethylene (PTFE) membrane (0.45 μm) and washing the filter cake with 10 mL of acetone (3 ×). The final product was obtained after drying at 70 °C in vacuum (140 Torr) for 24 h.

Fe_3O_4-G was placed in a standard 1-in quartz tube furnace for 30 min at 450 °C while feeding H_2 (200 sccm) at ambient pressure. After that, the H_2 was turned off and CH_4 (200 sccm) was turned on. The temperature was increased to 800 °C and the reaction was allowed to proceed for another 30 min. The samples were fast-cooled to room temperature by quickly removing them from the hot zone of the CVD furnace under Ar flow.

Conversion of Fe@GNS to $LiFePO_4$@GNS. Fe@GNS was mixed with LiH_2PO_4(molar ratio of Fe:Li:P = 1:1:1) in ethanol as dispersing solvent and manually ground using a mortar and pestle for 1 h. The resulting mixture was then heated in air at 300 °C for 5 h to oxidize the metallic Fe in Fe@GNS into Fe^{3+}. Finally, the mixture was annealed at 500 °C in a slightly reducing atmosphere (Ar:H_2 = 95/5) for 8 h and the product $LiFePO_4$@GNS was obtained.

*Characterization***.**SEM was performed using FEI Quanta 400 high-resolution field emission scanning electron microscope in high vacuum mode. TEM was performed using JEOL 2100 field emission gun transmission electron microscope. XRD was carried out on a Rigaku D/Max Ultima II using Cu Kα radiation. TGA analyses were performed on a Q50 TA Instrument analyzer at temperatures ramping from 25 °C to 900 °C at a rate of 5 °C/min under air. XPS spectra were taken on a PHI Quantera SXM scanning X-ray microprobe. Al anode at 25 W was used as an X-ray source with a pass energy of 26.00 eV, 45° take off angle, and a 100 μm beam size. A pass energy of 140 eV was used for survey and 26 eV for atomic concentration.

*Electrochemical Measurement.*The electrochemical characteristics were determined by assembling the electrodes into 2032-type coin cells. The working electrode was composed of the active materials $LiFePO_4$@GNS (90 wt%) and poly(vinylidenedifluoride) (10 wt%) as binder. The working electrode slurry was pasted on Al foil and dried under vacuum at 120 °C for 12 h. The typical mass loading of the working electrode is 1.5 to 2 mg and the tap density is ~1.3

mg/cm^3. Lithium foils were used as counter and reference electrodes. A 1 M $LiPF_6$ in a 1:1 (vol/vol) mixture of ethylene carbonate and dimethyl carbonate was used as electrolyte and a polypropylene membrane was used as the separator. The batteries were assembled in an argon-filled glove-box and galvanostatic charge-discharge were performed at current density ranges from 17 mA/g to 3400 mA/g in the voltage range between 2 V and 4.3 V at room temperature.

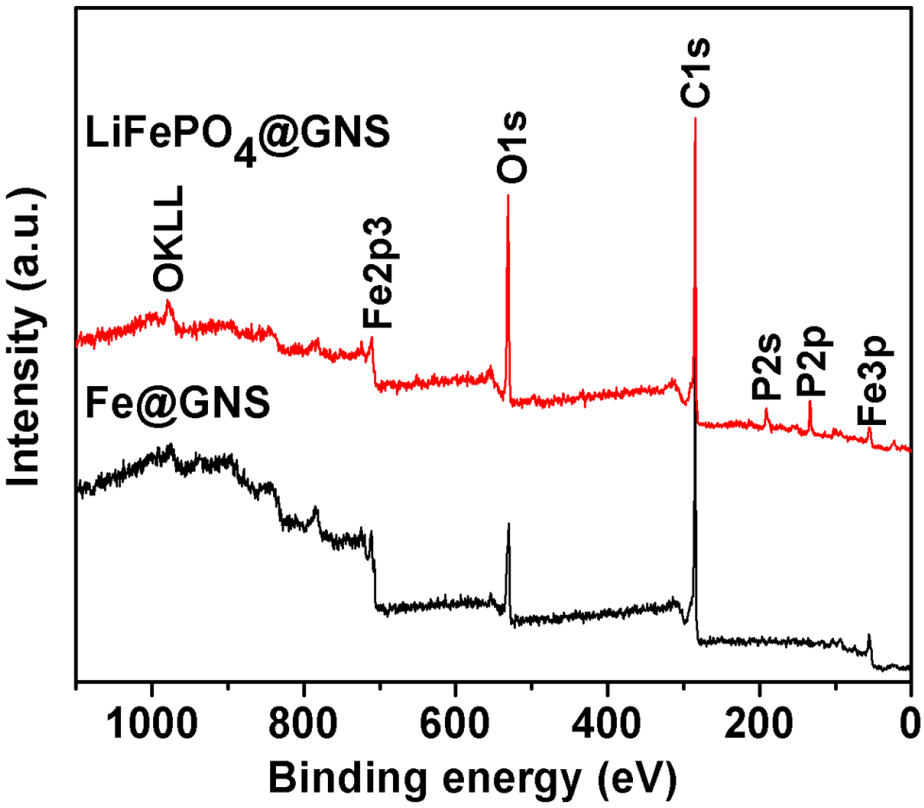

Figure S1. XPS survey spectra of Fe@GNS and $LiFePO_4$@GNS.

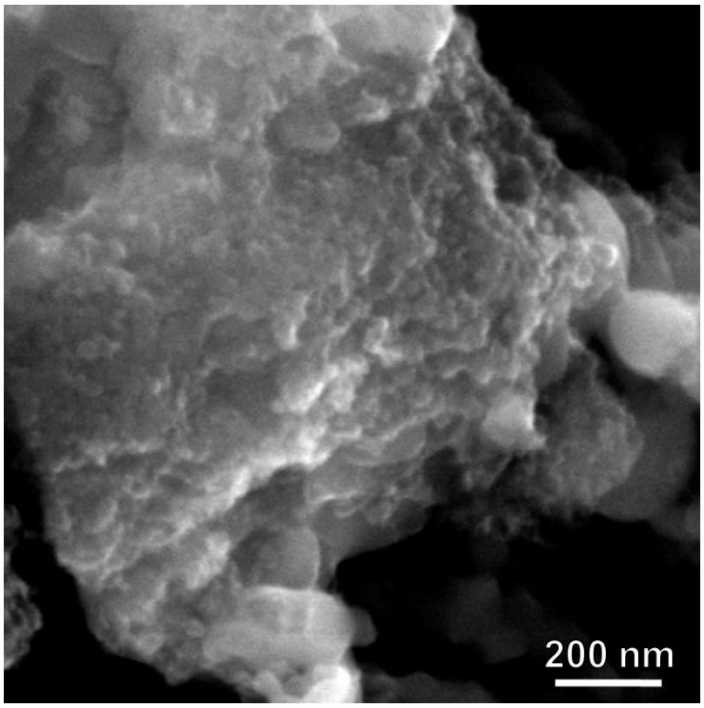

Figure S2. SEM image of $LiFePO_4$@GNS.

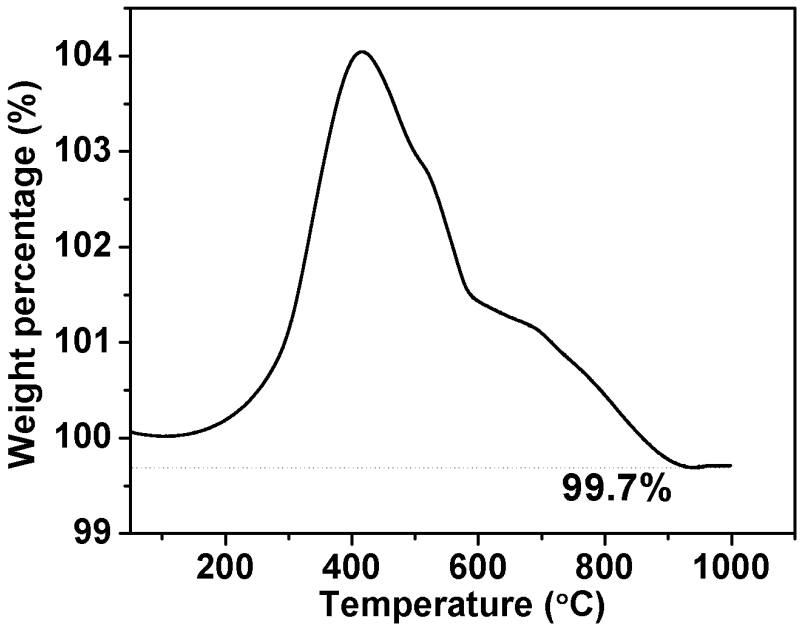

Figure S3. TGA curve of $LiFePO_4$@GNS performed in air.

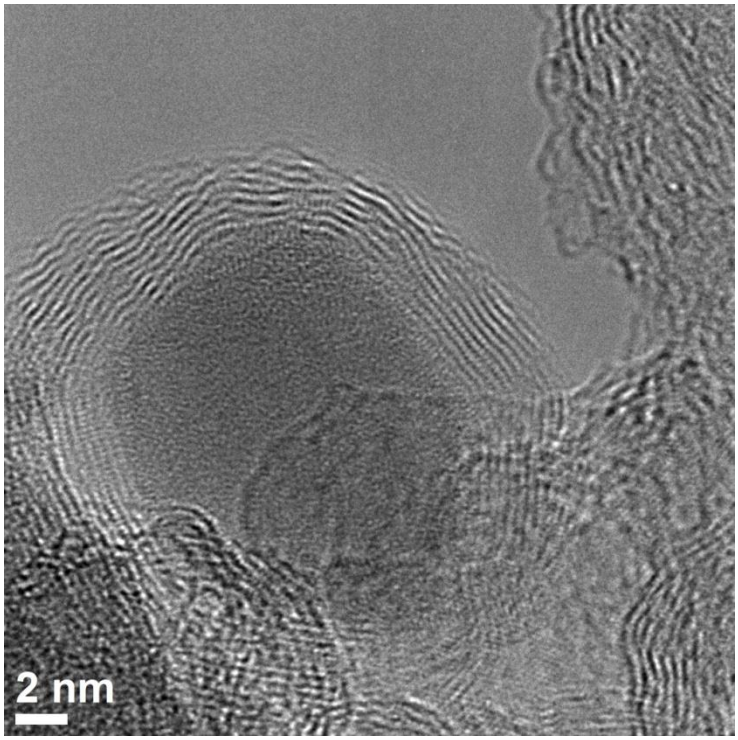

Figure S4. HRTEM image shows an amorphous nanoparticle encapsulated in graphene nanoshells. These may reduce the charge capacity value.

Reference

1. Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. Improved Synthesis of Graphene Oxide. *ACS Nano***2010**, *4*, 4806.