Supplemental Material for

Spectroscopy understanding of ultrahigh-rate performance for $LiMn_{0.75}Fe_{0.25}PO_4$ nanorods-graphene hybrid in lithium ion battery

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1. Preparation of $LiMn_{0.75}Fe_{0.25}PO_4$ nanorods-graphene hybrid

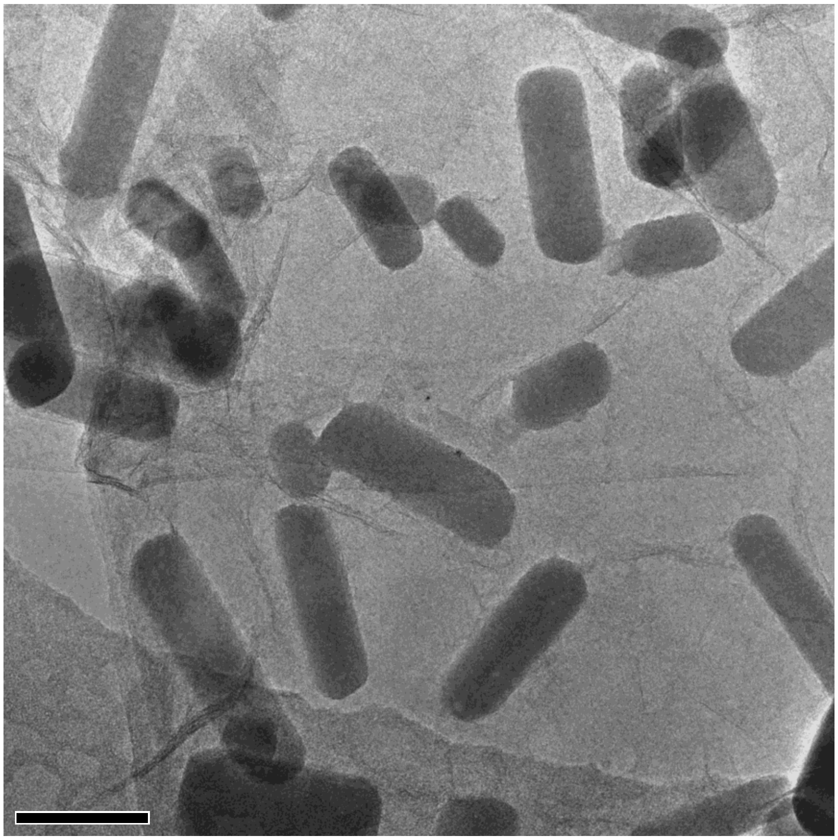
A: Making of Oxidized Graphene Oxide (GO)

GO was made by a modified Hummers method. Graphite flakes were first grounded with NaCl followed by washing away the NaCl in a vacuum filtration apparatus. The remaining graphite was dried in an oven at 70°C for 30 minutes. The dried solid was stirred with concentrated sulfuric acid at room temperature for 24 hours in a flask. Next, the flask was placed in an oil bath at 40°C and NaNO3 was added to the suspension and allowed to dissolve for 5 minutes. This step was followed by the slow addition of KMnO4 with much less amount compared to the original Hummers' method), keeping the reaction temperature below 45°C. The solution was allowed to stir for 30 minutes. Afterwards, water was added to the flask. After 15 minutes, the flask was removed from the oil bath and water and 30% H2O2 were added to end the reaction. This suspension was stirred at room temperature for 5 minutes. The suspension was then repeatedly centrifuged and washed twice with 5% HCl solution and then repeatedly with water. The collected precipitate was dispersed in 100 mL water and bath sonicated for 30 min. After 5000 rpm (3020 g) centrifuge for 5 minutes, a brown homogeneous supernatant was obtained.

B: Synthesis of LiMn0.75Fe0.25PO4/rmGO Hybrid

GO was transferred from the as-made suspension to pure anhydrous DMF after centrifuge. The concentration of the final mGO DMF suspension was ~0.2mg/ml. In the first step of synthesis, GO DMF suspension was first heated to 80°C in a 30ml vial with magnetic stirring. After the suspension reached 80°C, a mixture of 0.2M Mn(Ac)2 and 0.2M Fe(NO3)3 aqueous solution (volume ratio 4:1) was injected in. The reaction was kept at 80°C with stirring for 1 hour. After that, the as-made composite was collected by centrifuge. In the second step of synthesis, the as-made composite from the first step of synthesis was dispersed in DMF, to which 1M LiOH ,1M H3PO4, and 0.5M ascorbic acid DMF solution (volume ratio 1:1:5) were added. The mixture was then sealed in a 40ml Teflon lined stainless steel autoclave for solvothermal reaction at 180°C for 12 hours. A 50:1 DMF/H2O mixed solvent was used in order to suppress growth in free solution and restrict the transformation reaction to the surface of mGO sheets. The resulted product was washed with water and then centrifuged at 4000 g for 1 min, which was repeated for 6 times to remove side products such as Li3PO4.

2. TEM of $LiMn_{0.75}Fe_{0.25}PO_4$ nanorods-graphene hybrid



S1 TEM of $LiMn_{0.75}Fe_{0.25}PO_4$ nanorods-graphene hybrid

3. Raman and FTIR characterization

Raman spectroscopy measurements were carried out on a Renishaw InVia Reflex Raman microscope using an Ar^+ laser (Spectra-Physics Model 153-M42-010) operating at 514.5 nm, and a 1800 lines/mm grating. The microscope was focussed onto the sample a 20X N PLAN objective (NA = 0.40), and Raman spectra were obtained using linefocus mode with a 10 s detector exposure time, and 16-64 spectra accumulations. The laser power was 0.35 mW measured at the sample. The instrument calibration was verified using an internal Si sample, which was measured at 520 cm^{-1}.

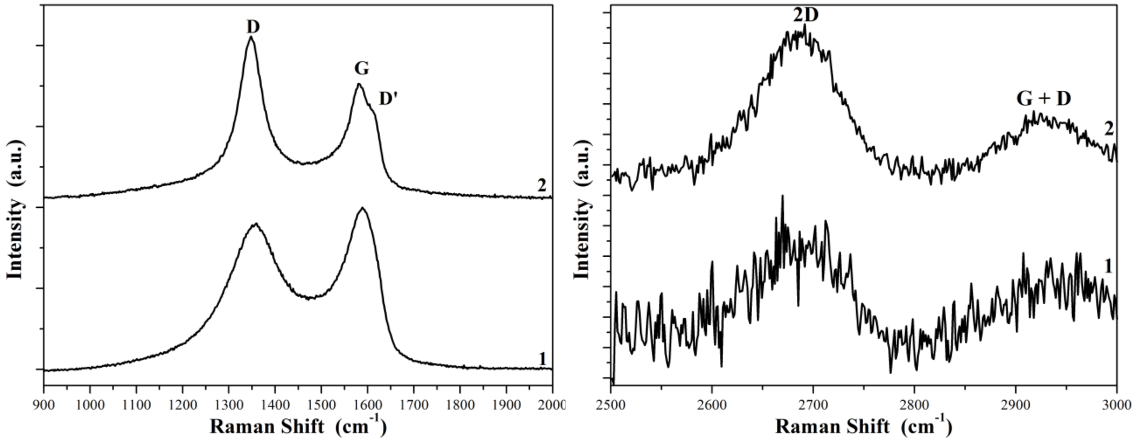


Figure S2. Raman spectra of (1) rGO and (2) LMFP-rGO taken with 514.5 nm laser excitation.

Three main peaks are found in the 1200-1700 cm^{-1} range shown in Figure S2(left). The G band (1580 cm^{-1}) is associated with the E_{2g} phonon mode. The D band (1350 cm^{-1}) is associated with disorder induced defects. If sufficient amount of defects are present in the sample, a second defect band called the D’ band (1620 cm^{-1}) may appear. Curve fitting this region is summarized in Table S1. For rGO, the peak located at 1589 cm^{-1} corresponds to the coalaescence of the G and D’ bands, observed when the L_D (average distance between defects) decreases below approximately 3 nm. [1] On the other hand, the LMFP-rGO sample shows a distinct separation between the G band (1584 cm^{-1}) and D’ band (1617 cm^{-1}) which means a larger L_D. The large L_D in LMFP/rGO corresponds to larger intact sp^2 carbon domain. This is also supported by the much narrow G and D band in LMFP relative to the broad band in rGO. 2D and G+D band also confirms this as shown in S2 (right) where an enhancement of 2D/G+D is visible in LMFP/rGO relative to that in rGO. [2]

[1] Jorio, A. *et al.* Phys. Status Solidi B, 247(11-12), 2980-2982 (2010)

[2] D. Zhan, Z. et al, *Carbon*, 2011, **49**, 1362-1366.

Table S1. Peak Fitting Analysis of rGO and LMFP-rGO samples.

Sample	Band (cm^{-1})	Assignment
rGO (1)	1353 (111) 1589 (72) 2688 (113) 2951 (183)	D G + D’ 2D G + D
LiFeP-rGO (2)	1347 (59) 1584 (60) 1617 (21) 2686 (96) 2937 (128)	D G D’ 2D G + D

FTIR spectroscopy measurements were carried out on a IllumiatIR II IR microspecctrometer (Smiths Detection) mounted on a Renishaw Invia Reflex Raman microscope. The IR beam was focussed onto the sample using either a 15X ARO objective or a 36X diamond ATR objective (Smiths Detection). FTIR spectra were obtained on neat samples, and the spectral resolution was 4 cm^{-1}.

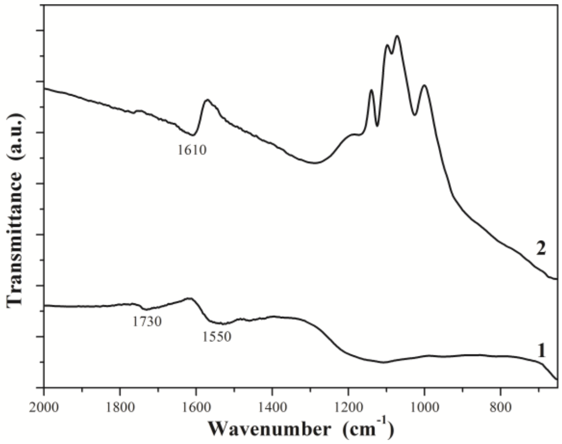


Figure S3. FTIR spectra of (1) rGO and (2) LMFP/rGO. Spectra were collected for 512 scans.

The FTIR spectrum for rGO (1) in Figure S3 showed a peak at 1730 cm^{-1} which can be assigned to the C=O stretching, and indicates that some oxygen containing functional groups are present on the rGO surface. A peak at about 1550 cm^{-1} is associated with aromatic C=C stretches. For the LMFP/rGO sample shown in Figure S3 (2), a peak at 1610 cm^{-1} is associated with aromatic C=C stretching, and the peaks in the 900-1200 cm^{-1} range are associated with the LMFP coating. No vibration bands associated with oxygen containing functional groups are observed for the LMFP/rGO sample

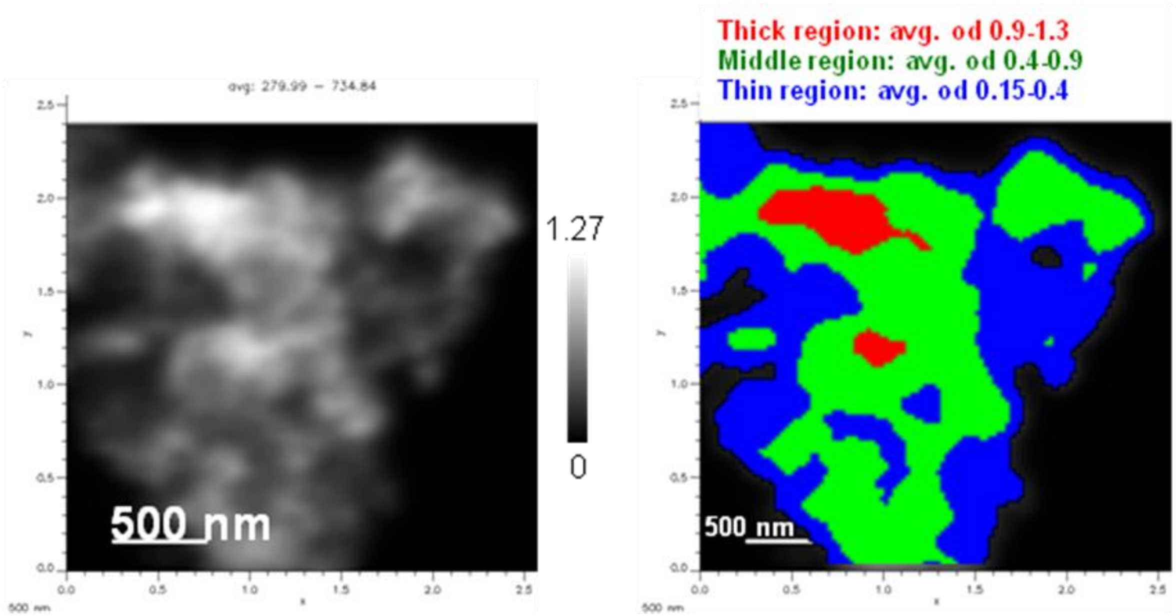
4. STXM sample preparation

In order to measure spectro-microscopy for individual LiMn0.75Fe0.25PO4/rGO Hybrid. It needs to be first dispersed in methanol with sonication before casting the dispersion onto Si_3N_4 window. After solvent was evaporated, the sample was transferred into the STXM chamber for pumping to coarse vacuum (~0.25 torr) , then the chamber was filled with ~1/6 atm helium for STXM measurement.

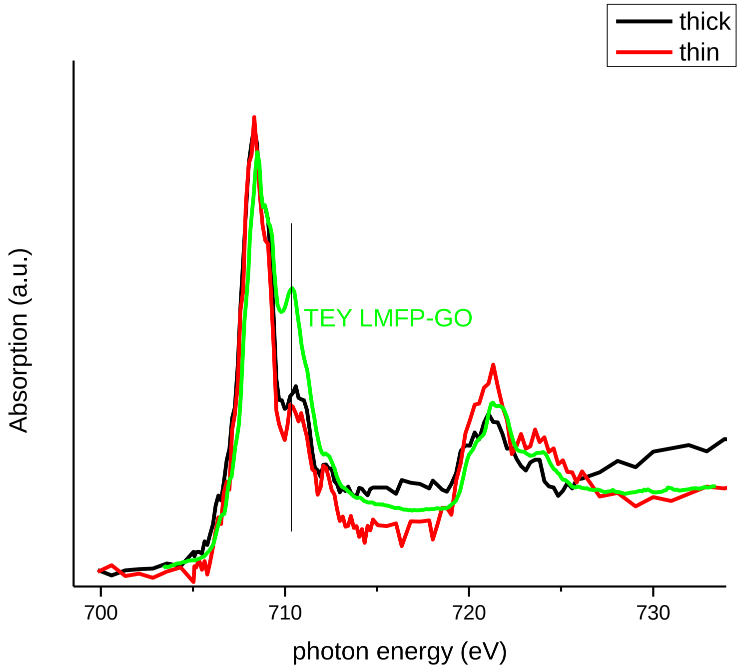
5. STXM measurement

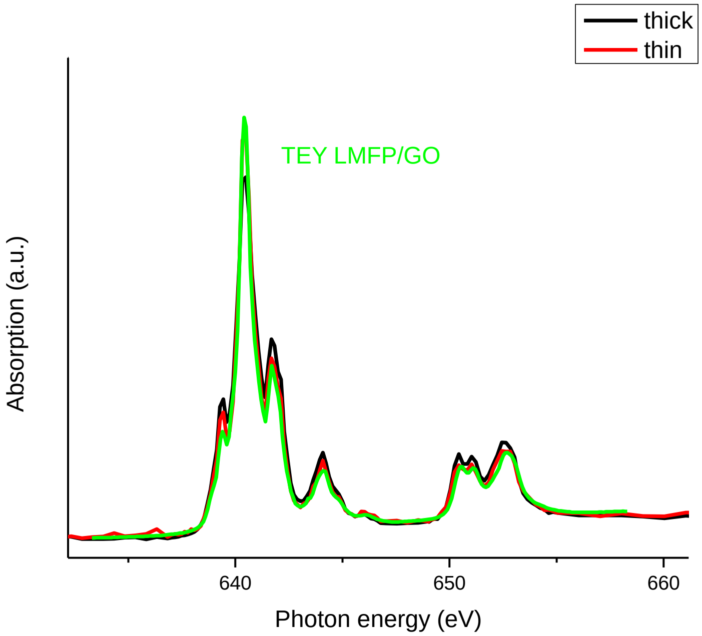
STXM measurement was conducted using the STXM at the SM beamline of the Canadian Light Source (CLS). In order to achieve the best spatial resolution, a 25 nm outer-zone zone plate (CXRO, Berkeley Lab) was used. The diffraction-limited spatial resolution for this zone plate is 30 nm. Circularly polarized soft X-ray beam generated from SM elliptically polarized undulator (EPU) was used to remove the linear dichroism effect originated from different orientations of the graphene in the plane of the Si_3N_4 window membrane. A 250 l/mm plane grating monochromator (PGM) was used for both C and O K-edges and Mn, Fe L-edges measurements. The incident photon flux (Io) was tuned to be ~20 MHz as read by the STXM detector in a hole of the STXM sample plate at 320 eV with exit slits at 35/35 μm (dispersive/non-dispersive) for the C K-edge, and at 560 eV with slits at 25/25 μm for the O K-edge.

6. STXM results



S4: STXM imaging (left) and thickness mapping (right) of LMFP/rGO

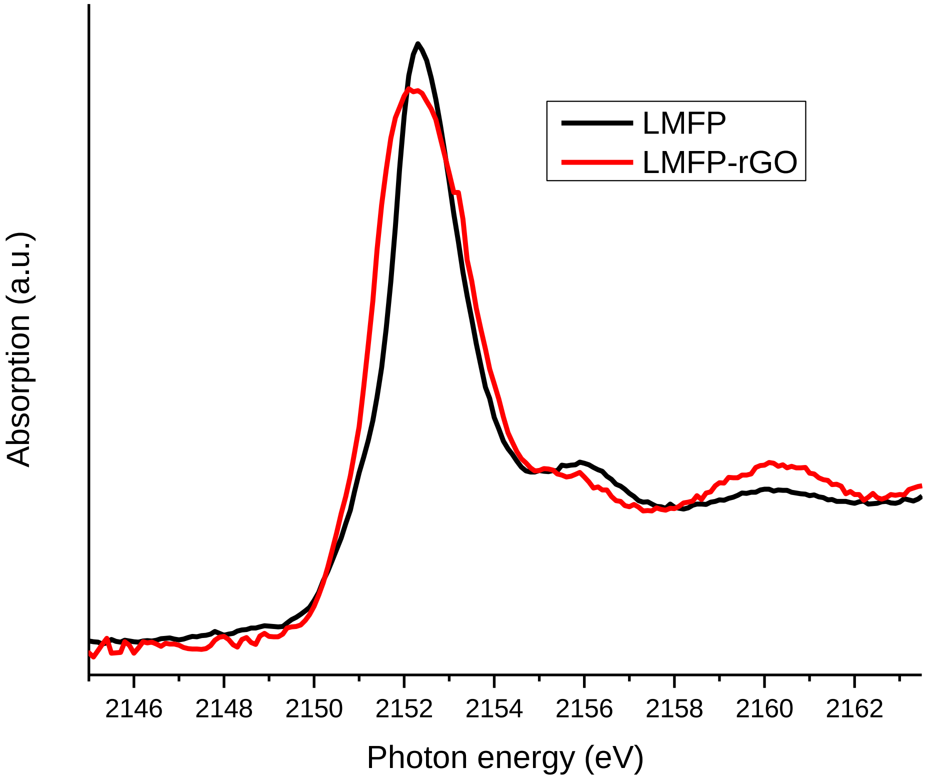




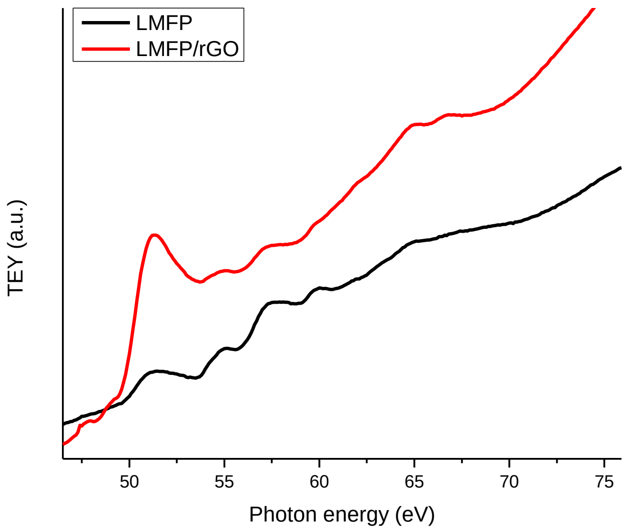
S5 XANES of LMFP/rGO at Fe (top) and Mn (bottom) L-edges extracted from thick (black) and thin (red) region and compared to TEY results (green).

6. P K-edge result

P K-edge XANES of LMFP and LMFP/rGO were performed on the Soft X-ray Microcharacterization Beamline (SXRMB, Δ*E*/*E*: ~10^{-4}) at the Canadian Light Source (CLS). The apparent broadening in LMFP/rGO relative to LMFP clearly shows the bonding of P-O to graphene in LMFP/rGO.



S6: P K-edge XANES of LMFP and LMFP-rGO



S7: Li K-edge XANES of LMFP and LMFP/rGO recorded at TEY.