# Supporting Information

# Clean Block Copolymer Microparticles from Supercritical $CO_2$: Universal Templates for the Facile and Scalable Fabrication of Hierarchical Mesostructured Metal Oxides

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***Scaled Up Metal Oxide Microparticle Synthesis (20 fold).***

Metal oxide templating reactions were scaled up 20-fold for both the $TiO_2$ and $LiFePO_4$ materials, thus requiring 1 gram of BCP template. In each case these were performed in an almost identical fashion, with the exception that the glassware and reagent quantities were scaled proportionally while still targeting a final mass of 25 wt. % metal oxide relative to BCP. The sol-gel solution for $TiO_2$ templating was created in a 250 mL round bottom flask (RBF) by adding TTIP (1.24 mL) to a solution of concentrated hydrochloric acid (0.42 mL, 37 wt. % HCl in $H_2O$) in ethanol (158 mL) and stirring for 60 minutes. During this time, a slurry of PMMA-*b*-P4VP BCP microparticles (1 gram) in ethanol (40 mL) was created in a second flask by continuous stirring at 1000 rpm. The two solutions were then slowly combined (~200 mL total volume) and stirred magnetically at 500 rpm overnight, before being poured into in a large Pyrex dish (22 cm diameter, approx. 20 fold larger surface area) placed inside a larger plastic container acting as an evaporation chamber. The walls of this chamber were separated with thin spacers (~0.1 cm in height), which allowed for the controlled evaporation of this solution over a period of 24 – 36 hours at room temperature (~22 °C). Once the sample became dry in appearance the dish was removed from the chamber and allowed to dry further in an oven at 50 °C for 8 hours, being obtained as a fine white powder (1.493 g) that was loosely settled over the dish surface. The scaled up $LiFePO_4$ templating reactions were performed in the same way, with the exception that the sol-gel solution was created by combining solutions of FeCl(III) (2.20 mL of a 1 M ethanol solution), ascorbic acid (5.82 mL of a 1 M $H_2O$ solution), LiCl (2.26 mL of a 1 M 75/25 wt. % ethanol/$H_2O$ solution) and phosphoric acid (0.324 mL of a 50 wt. % $H_2O$ solution) in ethanol (150 mL). The product was obtained as a fine amber colored powder (2.087 g) that was loosely settled on the dish surface. The $TiO_2$ and $LiFePO_4$ products were calcined in a tube furnace at 500 °C for 2 hours (3 °C $min^{-1}$ ramp) in air or under a flow of $N_2$, respectively, and obtained in large quantities as either fine white (0.331 g) or black powders (0.691 g).

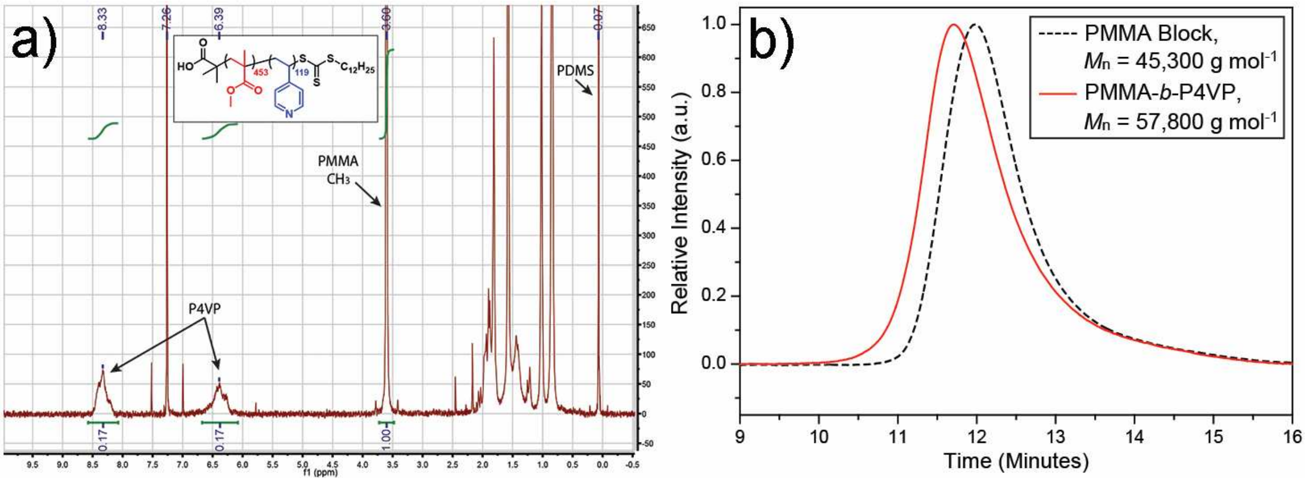

**Figure S1.** Characterization data for the BCP template. (a) $^1$H NMR spectrum enabling the relative P4VP content and block length to be calculated in combination with the GPC data for the PMMA block. (b) GPC data for the first PMMA block and the final block copolymer after chain extension with P4VP, confirming a unimodal, narrow peak in both cases.

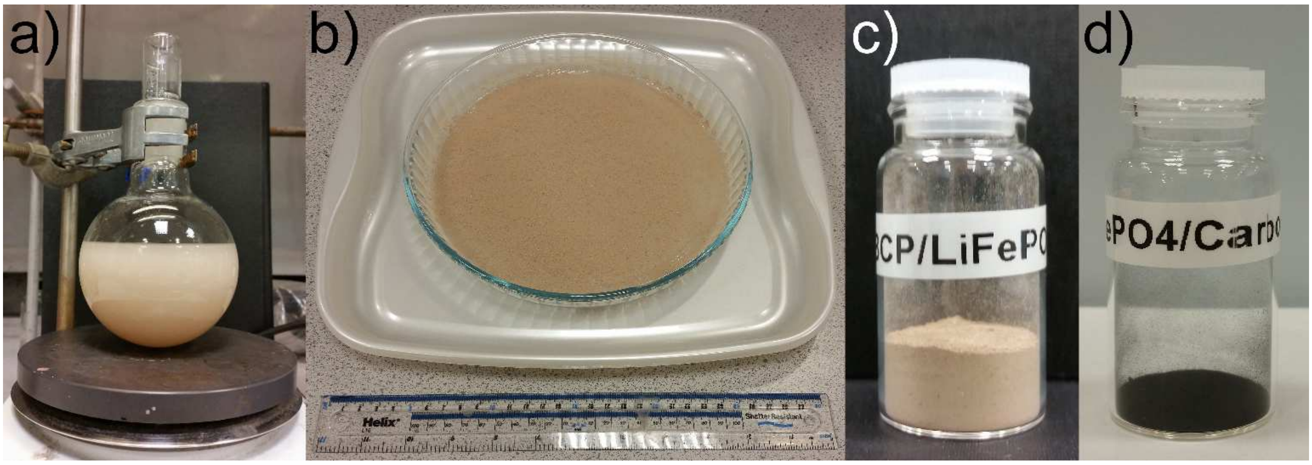

**Figure S2.** Photos taken during the scaled up (20 fold) synthesis of the BCP templating process with $LiFePO_4$. 1 gram of BCP was used in this reaction. a) BCP slurry in ethanol after mixing with the combined sol-gel precursor solution. b) The $LiFePO_4$ infused BCP microparticles obtained as a dry powder on the surface of the glass drying dish. The ruler in the image is 30 cm long. c) Vial containing the BCP/metal oxide hybrid microparticle powder collected from the dish after drying. d) Vial with the pure $LiFePO_4$/carbon microparticles collected after calcination in a tube furnace at 500 °C for 2 hours.

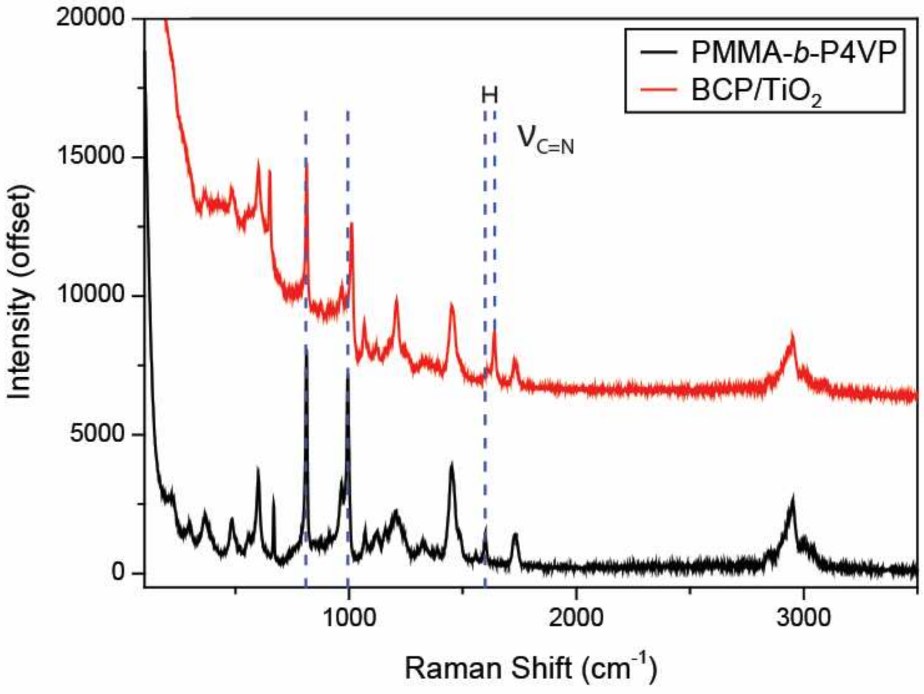

**Figure S3.** Micro Raman spectra ($\lambda_{ex}$ = 785 nm, resolution > 0.8 cm$^{-1}$) for the BCP template and the BCP/TiO$_2$ composite. The spectrum of the BCP template represents a clear superposition of the spectra expected for PMMA[1] and P4VP,[2] confirming the co-existence of both polymer blocks. Shifts in the frequency of characteristic vibrational modes of the pyridyl group (e.g. $\nu_{C=N}$ at 1639 cm$^{-1}$) after templating with TiO$_2$ indicate that it preferentially associates with the P4VP block. The BCP/TiO$_2$ spectrum has been offset on the y-axis for clarity.

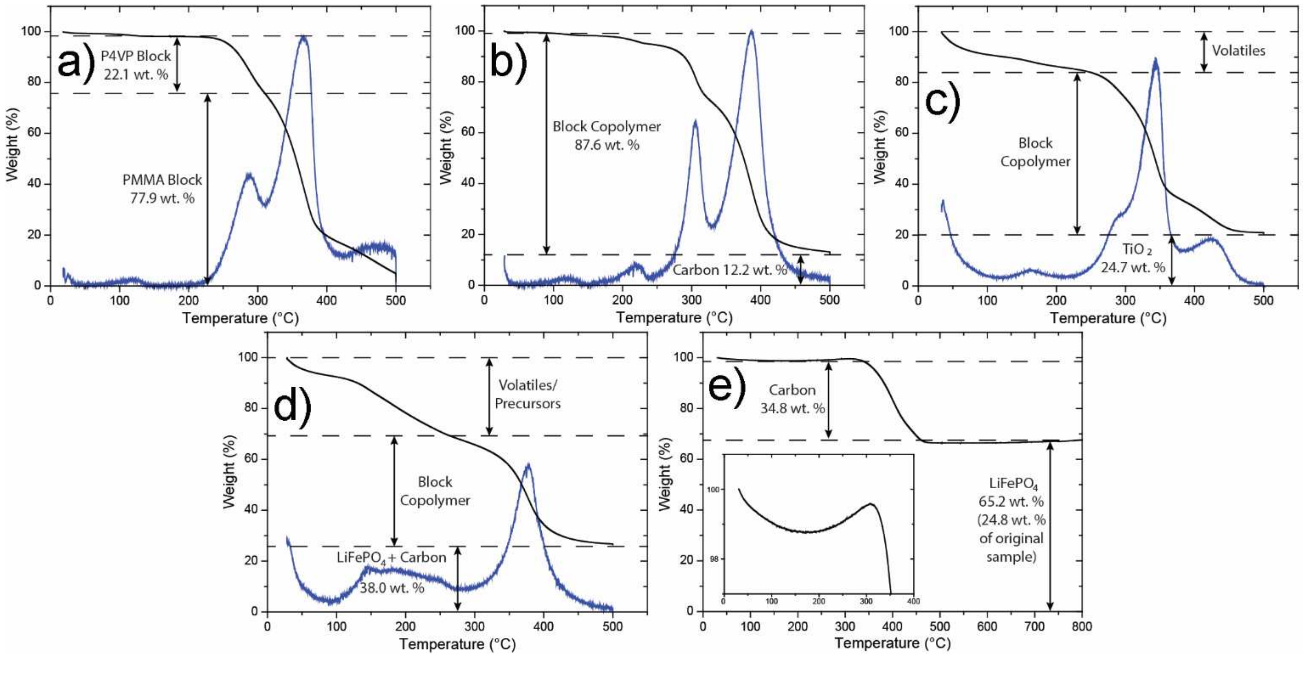

**Figure S4.** TGA data from the materials at each step in the synthesis process. The blue traces are *d*(Weight)/*d*(Time)(%)/(min) derivative plots of the data, scaled proportionally. (a) The BCP heated in air, showing a PMMA and P4VP composition in agreement with the $^1$H NMR data. (b) The BCP heated in N$_2$. (c) The BCP/TiO$_2$ composite heated in air, revealing a comparable final TiO$_2$ content to the targeted value of 25 wt. % based on the reagent quantities used. (d) The BCP/LiFePO$_4$ composite heated in N$_2$. (e) LiFePO$_4$/carbon microparticles heated in air, showing the weight loss from burning off the carbon coating. The insert highlights the initial weight gain due to oxidation of the LiFePO$_4$.

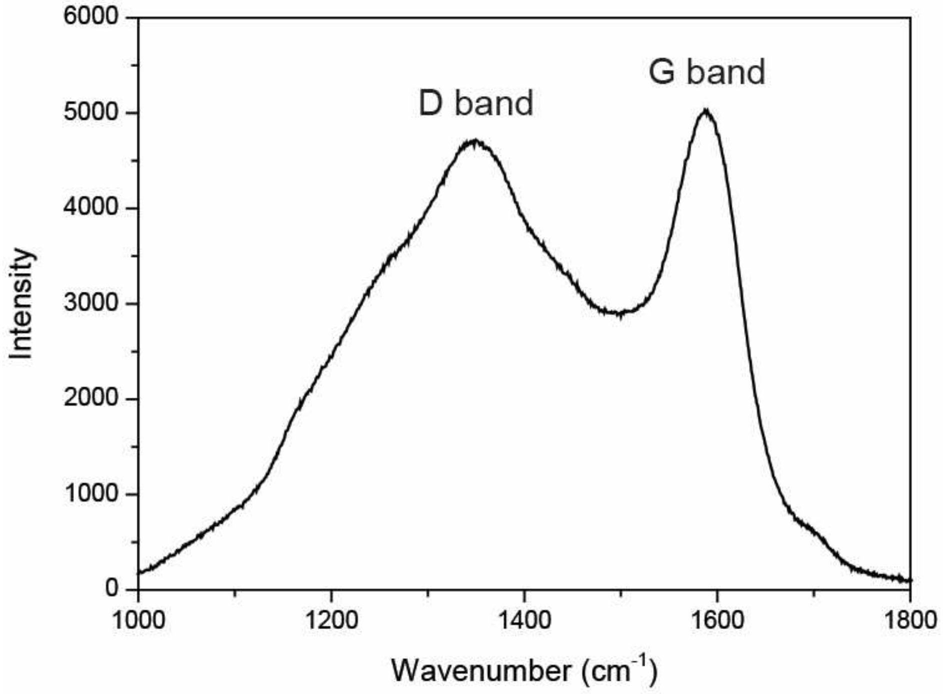

**Figure S5.** Micro Raman spectrum ($\lambda_{ex}$ = 660 nm, resolution > 1.0 cm$^{-1}$) of the carbon coating afforded after pyrolysis of the BCP/$LiFePO_4$ composite, highlighting the formation of a partially graphitized carbon coating. The spectrum represents the mean of three spectra collected at three random sample locations.

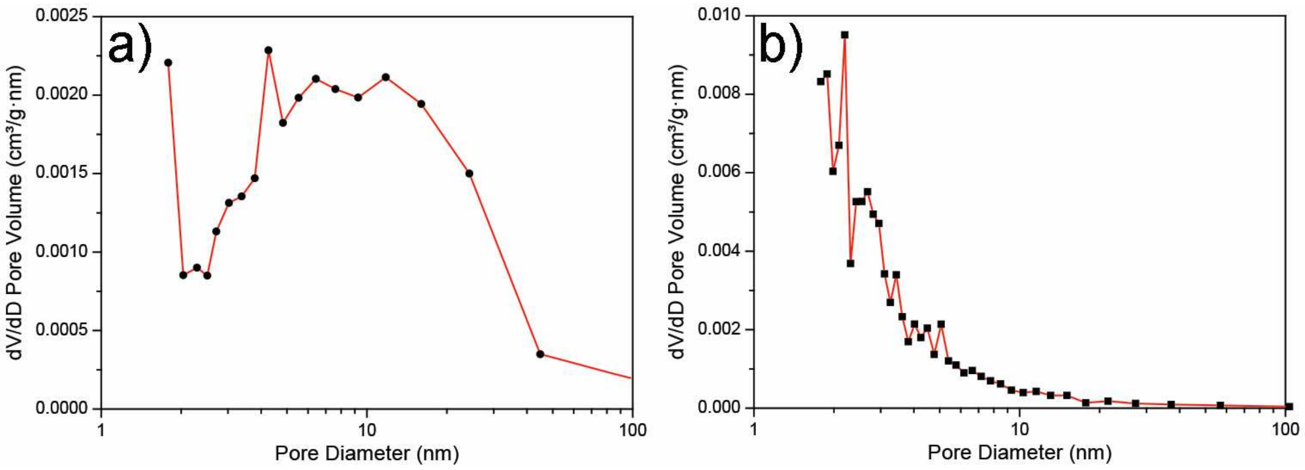

**Figure S6.** Corresponding pore-size distributions determined by applying the BJH method to the desorption branch of the physisorption isotherms for (a) the titania microparticles and (b) the $LiFePO_4$/carbon microparticles.

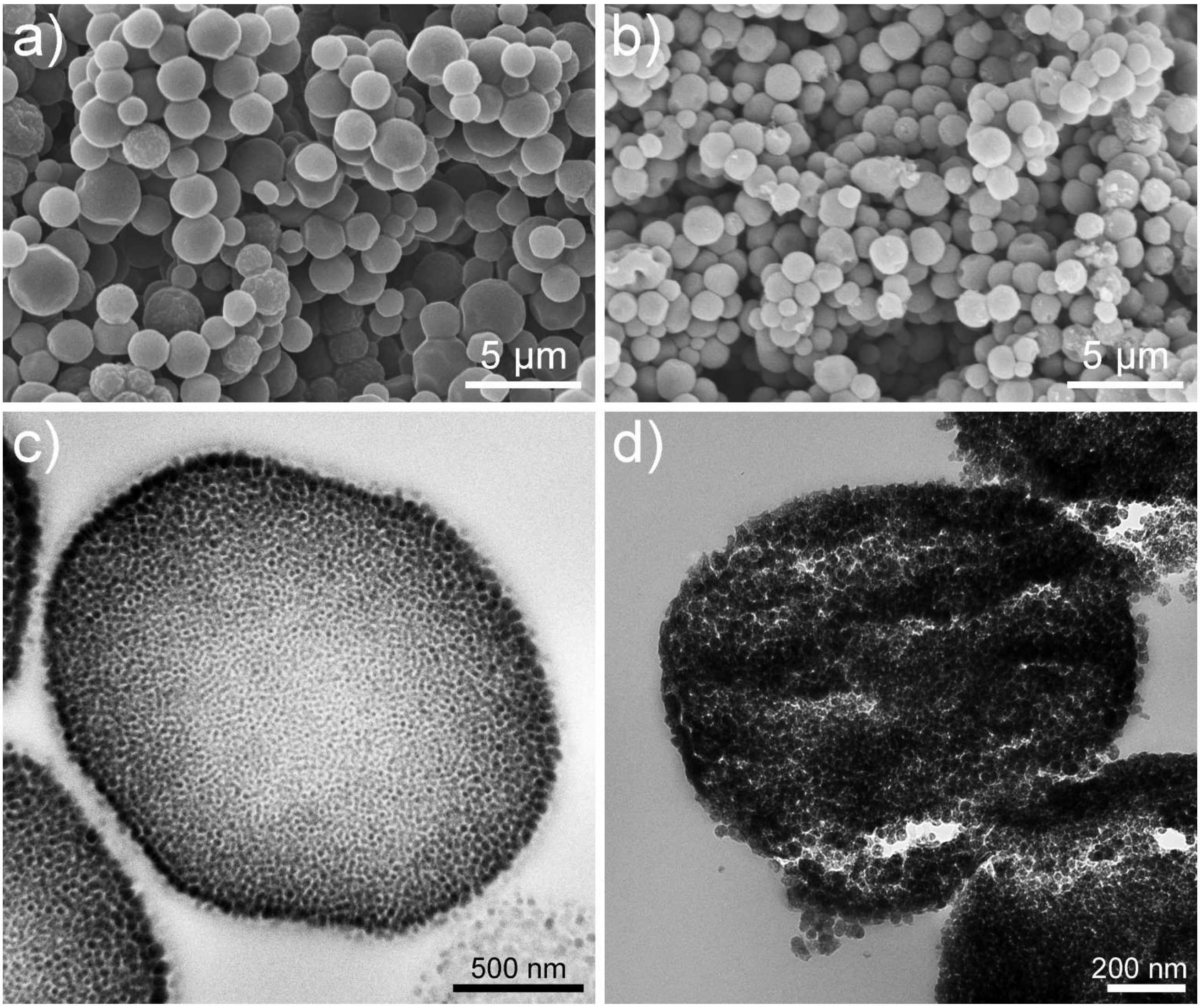

**Figure S7.** (a) SEM image of the PMMA-*b*-P4VP BCP template synthesized with 5 wt. % PDMS-MA stabilizer. (b) SEM image of the corresponding calcined $TiO_2$ microparticles fabricated by sol-gel templating this BCP. (c) TEM image of cross-sectioned PMMA-*b*-P4VP BCP microparticles synthesized with 5 wt. % PDMS-MA stabilizer. (d) TEM image of a cross-section of the corresponding calcined $TiO_2$ microparticle sample prepared from this template.

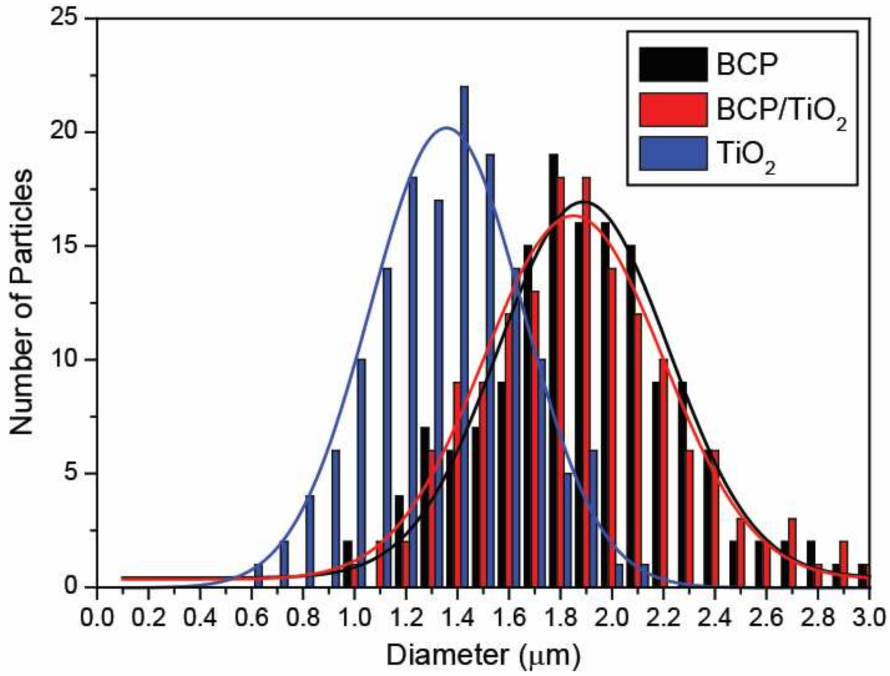

**Figure S8.** Microparticle size histograms obtained by measuring 150 microparticles in SEM images of the second BCP template synthesized with 5 wt. % PDMS-MA stabilizer and the derived organic/inorganic hybrid and pure titania materials. The lines represent Gaussian distribution fits to the data.

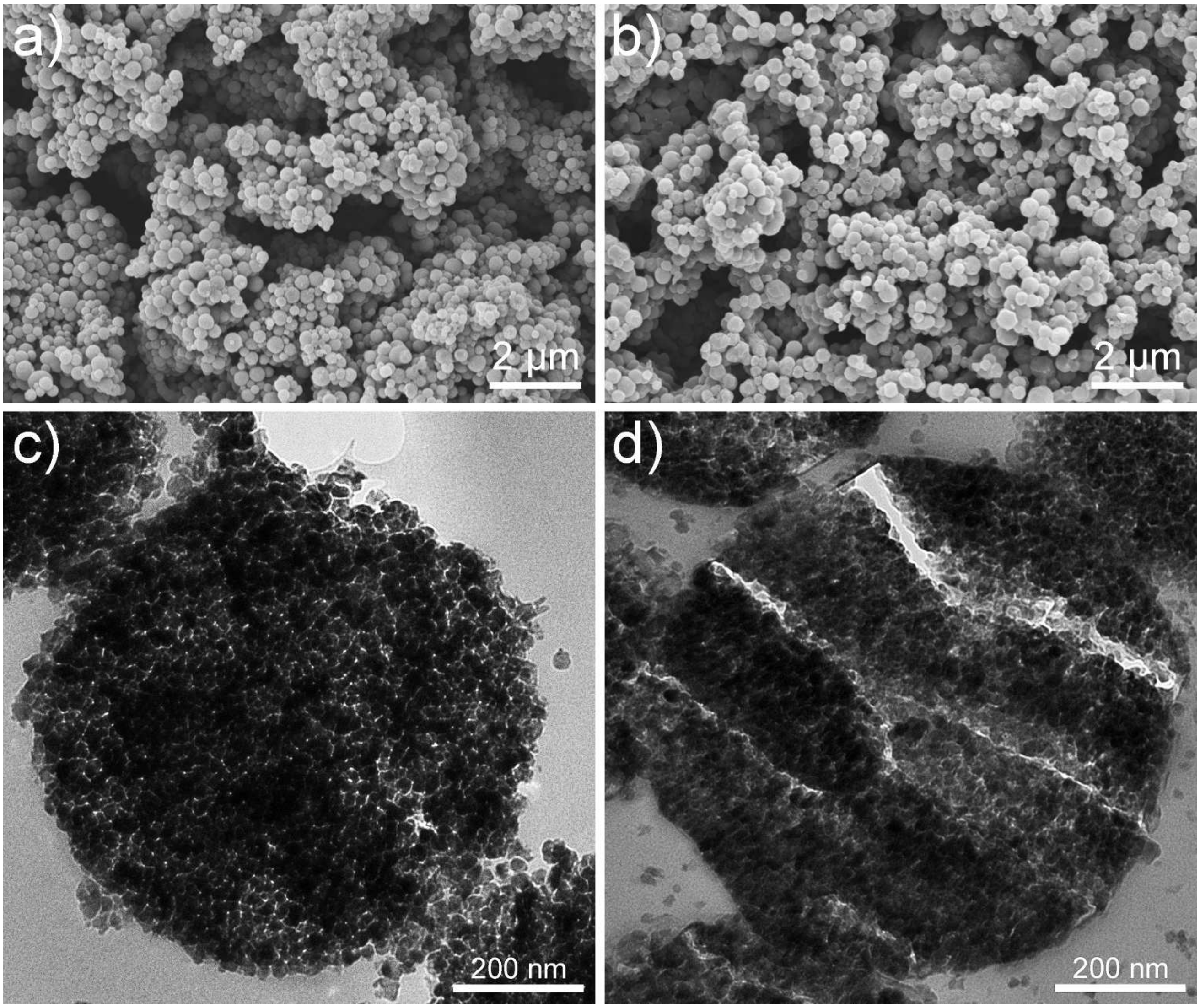

**Figure S9.** (a) SEM image of the pure titania microparticles after calcination at 700 °C for 2 hours in air. (b) SEM image of the carbon containing $LiFePO_4$ microparticles after calcination at 700 °C for 2 hours in $N_2$. (c) and (d) TEM images of microtomed cross-sections prepared from the samples shown in (a) and (b), respectively. The fracture lines across the microparticle shown in (d) are artifacts of the microtoming process.

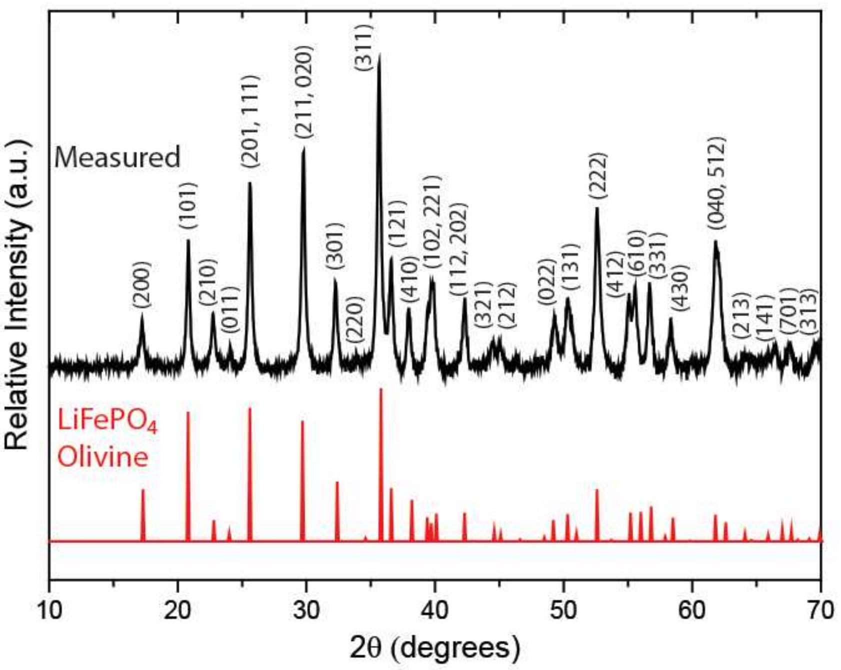

**Figure S10.** XRD patterns of $LiFePO_4$ microparticles crystallized at a higher temperature of 700 °C for 2 hours. Expected diffraction patterns of olivine $LiFePO_4$ are shown for reference.

## References

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2. Garrell, R. L.; Beer, K. D., *Langmuir* **1989,** 5, 452-458.