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Ultracentrifugation: An effective novel route to ultrafast nanomaterials for hybrid supercapacitors

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Energy storage devices are some of the most important environmental technologies that are highly influential in advancing our life in the future society. Specifically, electrochemical capacitor is an energy facilitator that exhibits an efficient/economical charging and discharging characteristics with long lifespan. Thus, the capacitor technology is regarded as promising due to an increasing effectiveness when combined with renewable (solar/wind/micro hydraulic) energy sources. In this connection, Li-ion-based hybrid supercapacitors and their functional materials are being vigorously researched in hopes to improve their capacity/voltage and therefore their energy density. Transition metal oxides are among the most popular materials utilized in this purpose. Thanks to high voltage and associated high energy density, they are tuned as both high energy and high power materials. In recent years, the structural/textural properties of oxides, including particle size, crystallinity, defects, and porosity, were successfully fine-tuned to achieve high rate performance over 300C. The present review will describe pseudo-capacitive nanosized oxides prepared with *in situ* synthesis technique called “ultracentrifugation”, showing ultrafast electrochemical response even more than EDLC.

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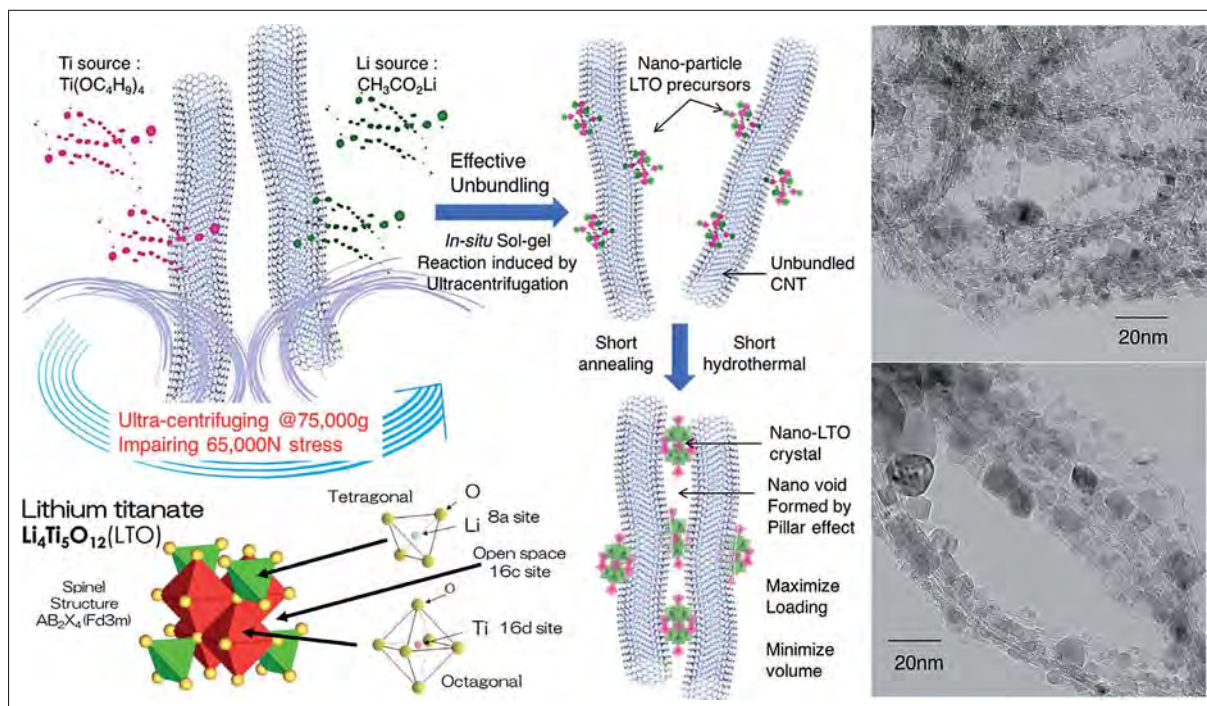
Introduction

Highly efficient and stable energy storage devices are needed to develop efficient smart mobility system for urban transportation or stationary applications large-scale storage of energy produced from renewable sources. Among such devices, supercapacitors, also called electric double layer capacitors (EDLCs), show superior performances such as high power electrochemical devices with fast charging–discharging capability, remarkable stability and cycle life compared to Li-ion batteries [1^{••},2]. The energy density of supercapacitors is low and needs to be enhanced to further expand their range of applications. Designing hybrid supercapacitor is a promising route to further improve the performance of supercapacitors, by combining both an activated carbon electrode and a large capacity faradic (pseudocapacitive or battery-like) electrode [3]. Transition metal oxides are among the most popular materials utilized in this purpose [4–11[•]]. Thanks to high voltage and associated high energy density, they are tuned as both high energy and high power materials. In recent work, the synthesis of active materials by means of the “ultracentrifugation” process, called UC treatment, has been explored to further extend the performance of lithium metal oxides such as Li₄Ti₅O₁₂ (LTO) [12], bronze-type TiO₂ (TiO₂(B)) [13], Li₃VO₄ (LVO) [14^{••}], and phosphate compounds such as LiFePO₄ (LFP) [15^{••}] and Li₃V₂(PO₄)₃ [16]. The UC treatment enables the preparation of nanosized and dimension-controlled (1D or 2D) materials directly bonded on high-surface area conducting nanocarbons such as carbon nanotubes (CNT) (see the example of nano-LTO/CNT shown in Figure 1) [3,12]. Using UC treatment and depending on the nature of nanocarbons, structural/textural properties of such active materials—including particle size, crystallinity, defects, and porosity—can be fine-tuned to achieve ultrafast electrochemical performance with high stability. This review presents three examples of metal oxides (TiO₂(B), LVO, LFP)/nanocarbon composites prepared via UC treatment, showing promising electrochemical performances which are needed to develop the next generation of hybrid supercapacitors.

TiO₂(B): dimension control and hyper-dispersion of nano metal oxides within a nanocarbon matrix

Bronze-type TiO₂ (TiO₂(B)) has a good potential to enhance the electric conductivity ($\approx 10^{-2} \Omega^{-1} \text{ cm}^{-1}$) compared to other Ti-based oxides, like LTO ($\approx 10^{-13} \Omega^{-1} \text{ cm}^{-1}$) [12] and TiO₂ polymorphs such

Figure 1



Schematic illustration of synthesis of nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [3,12,17] which were prepared with the nanocarbons (MWCNT) co-existence through ultracentrifugation ($\sim 75,000\text{ g}$) along with high-resolution transmission electron (HRTEM) images of nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /MWCNT composites.

as anatase and rutile (10^{-14} – $10^{-13}\ \Omega^{-1}\ \text{cm}^{-1}$) [18]. $\text{TiO}_2(\text{B})$ has a theoretical capacity of $335\ \text{mAh}\ \text{g}^{-1}$ which is twice of LTO. Its Li^+ diffusion proceeds normally along the b -axis tunnel resulting in relatively poor Li^+ diffusion coefficient of 10^{-14} – $10^{-16}\ \text{cm}^2\ \text{s}^{-1}$ [19–21], while the LTO shows 3–6 orders of magnitude (10^{-8} – $10^{-13}\ \text{cm}^2\ \text{s}^{-1}$) [12,22]. Conventional $\text{TiO}_2(\text{B})$ synthesis via hydrothermal treatment from alkaline titanates leads to cylindrical morphology with long b -axis, resulting in poor C -rate capability [23]. Downsizing the particle size is an effective way to shorten the b -axis diffusion length in $\text{TiO}_2(\text{B})$ crystal [24,25]. Operation over $100C$, however, has been hampered because of the inevitable agglomeration of $\text{TiO}_2(\text{B})$ nanoparticles below $10\ \text{nm}$ [26–28], that limits the accessibility of Li^+ from the bulk electrolyte.

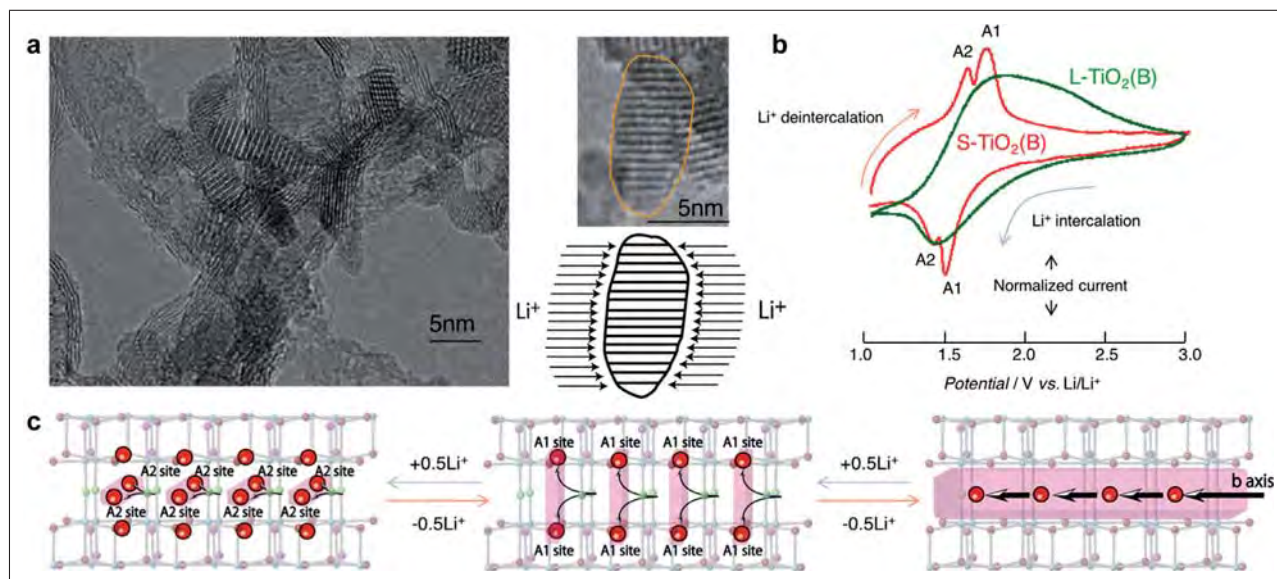
Hyper-dispersed single-nano $\text{TiO}_2(\text{B})$ crystals were uniformly formed in a MWCNT matrix using UC treatment combined with a follow-up hydrothermal treatment. These $\text{TiO}_2(\text{B})$ /MWCNT composites have size-controlled crystalline $\text{TiO}_2(\text{B})$ particles ($5\ \text{nm}$ in average) and anisotropic crystal growth (ultrashort along b -axis) limiting the agglomeration of the $\text{TiO}_2(\text{B})$ nanoparticles (see Figure 2a), described as short- $\text{TiO}_2(\text{B})$ (S- $\text{TiO}_2(\text{B})$) [13]. For comparison purpose, we prepared rod-type $\text{TiO}_2(\text{B})$ crystals with long b -axis (eight times longer than S- $\text{TiO}_2(\text{B})$ in average [13]) which contains same amount

of MWCNT (30 wt%) as the S- $\text{TiO}_2(\text{B})$. Cyclic voltammograms for S- and L- $\text{TiO}_2(\text{B})$ at $10\ \text{mV}\ \text{s}^{-1}$ (Figure 2b) shows that the shape and the number of the peaks are different between the two samples; the S- $\text{TiO}_2(\text{B})$ shows two sharp peaks at 1.55 and $1.65\ \text{V}$ vs. Li/Li^+ , while the L- $\text{TiO}_2(\text{B})$ possesses single broad peak which is similar to the reported CV shape of $\text{TiO}_2(\text{B})$ nanowire [29,30]. The sharpening of the peaks for S- $\text{TiO}_2(\text{B})$ comes from the shortening of b -axis length and the increased number of diffusion paths, which enable a fast Li^+ access and intercalation into $\text{TiO}_2(\text{B})$ A1 and A2 sites along the b -axis diffusion channel in the $\text{TiO}_2(\text{B})$ crystals (Figure 2c). Such ultrashort b -axis length and hyper dispersion of $\text{TiO}_2(\text{B})$ within the MWCNT matrix improves the power capability of $\text{TiO}_2(\text{B})$ by enabling ultrafast Li^+ deintercalation ($235\ \text{mAh}\ \text{g}^{-1}$ at $300C$, $1C = 335\ \text{mA}\ \text{g}^{-1}$), which is far superior to the L- $\text{TiO}_2(\text{B})$ [13]. These UC-treated $\text{TiO}_2(\text{B})$ /MWCNT nanocomposites with controlled (ultrashort) b -axis length can be used to prepare hybrid supercapacitor with higher energy density.

Li_3VO_4 : electrochemical activation; control of crystal structure of nano metal oxides for Li^+ diffusion enhancement via electrochemical method

To further increase the energy density, one way is to replace more positive $\text{TiO}_2(\text{B})$ electrode (1.2 – $1.6\ \text{V}$ vs.

Figure 2



(a) HRTEM image for the short b -axis $\text{TiO}_2(\text{B})$ (S- $\text{TiO}_2(\text{B})$, b -axis length = 3–5 nm) nanoparticles dispersed within MWCNT matrix along with a representative HRTEM image and its schematic illustration. (b) Cyclic voltammograms for S- $\text{TiO}_2(\text{B})$ and long b -axis $\text{TiO}_2(\text{B})$ (L- $\text{TiO}_2(\text{B})$, b -axis length = 40–60 nm) [13] at a scan rate of 10 mV s^{-1} . (c) Schematic illustration of Li insertion into S- $\text{TiO}_2(\text{B})$.

Li/Li^+) with other negative electrodes operating at lower redox potential [31]. Li_3VO_4 (LVO) has been recently reported to reversibly intercalate up to 2 Li per LVO at low potential (0.1–1.0 V vs. Li), leading to a capacity of 394 mAh g^{-1} [32–37]. However, LVO exhibits a very low electronic conductivity ($<10^{-10} \Omega^{-1} \text{ cm}^{-1}$), which is detrimental to achieving high-power performance [38–40]. It shows as well a large voltage hysteresis between charge and discharge ($<500 \text{ mV}$) that limits its use as a negative electrode in electrochemical energy storage devices [41,42].

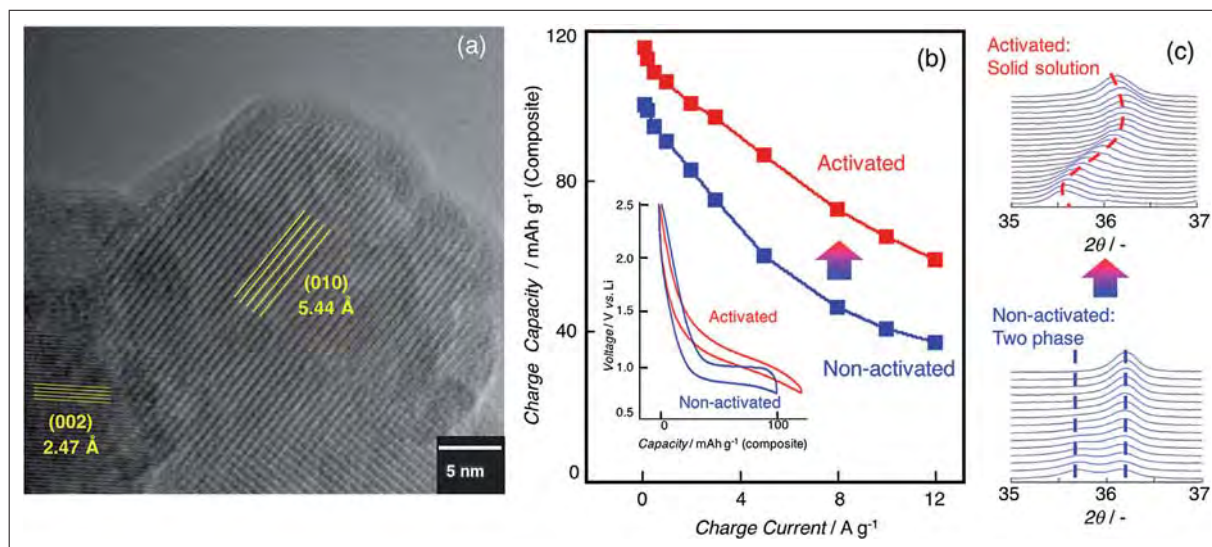
Using the UC treatment process, nanoparticles of LVO were successfully entangled on the surface of MWCNT (40 wt%) and uniformly dispersed within the MWCNT matrix [14**]. Magnified TEM images show that the composite is made of nanoparticles (size below 50 nm) clearly identified as LVO by the lattice fringes of (0 1 0) and (0 0 2) phases (Figure 3a). The capacity of the composite reached 330 mAh g^{-1} when cycled in a potential range of 2.5 V down to 0.1 V vs. Li. It shows high rate capability, with 50% of capacity retention at 20 A g^{-1} , corresponding to about 50C rate for LVO and 500C for AC. Moreover, after removal of the contribution of the MWCNT matrix, LVO shows a faradic efficiency of 95% at 1st cycle, constant over 1000 cycles. Such high reversibility of LVO enabled the investigation of the Li insertion mechanism into LVO crystal. A careful investigation by means of *in operando* XRD and X-ray absorption fine structure (XAFS) measurements revealed the existence of an irre-

versible structure transformation during the first lithiation reaction, assimilated as an activation process. This activation switches the reaction mechanism from a slow “two-phase” to a fast “solid-solution” process in a limited potential window (2.5 V down to 0.76 V vs. Li), as shown in Figure 3b and c. In this potential range, the Li^+ intercalation is accelerated thanks to a fast solid-solution insertion mechanism with a small hysteresis, leading to higher energy efficiency that is required for hybrid supercapacitors.

LiFePO₄ (LFP): defective (crystalline/amorphous) control of nano metal oxides within the peculiar core-shell LFP/graphitic carbon structure

LiFePO₄ (lithium iron phosphate, LFP) has long been investigated as a cathode material in Li-ion batteries because of its relatively high theoretical capacity of 170 mAh g^{-1} , low cost and high electrochemical and thermal stabilities [43]. The Li intercalation electrochemical reaction of LFP proceeds through a two-phase reaction between Li-rich $\text{Li}_{1-a}\text{FePO}_4$ (LFP) and Li-poor Li_bFePO_4 (FP) [44] with Li insertion/deinsertion occurring along the b axis [45]. However, the limited diffusion kinetics of Li ions at the LFP/FP interface together with the poor electronic conductivity of the pristine olivine-LFP (10^{-10} – $10^{-7} \Omega^{-1} \text{ cm}^{-1}$) [46] limit the power capability of the material. Downsizing the particle size (5–100 nm) failed to enhance the power performance due to the re-aggregation of particles and the difficulty in creating efficient electron pathways [47]. The synthesis

Figure 3



(a) HRTEM image of UC-derived Li_3VO_4 (LVO) nanocrystals (b) Capacity plots with different discharge (lithiation) current densities for activated and non-activated UC-LVO. Inset: Charge discharge curves for activated and non-activated UC-LVO between 0.76–2.5 V vs. Li. (c) Comparison of XRD patterns of $2\theta = 35\text{--}37^\circ$ showing different reaction mechanism for activated and non-activated UC-LVO.

of carbon coatings onto LFP particles has also been proposed, by adding carbon precursors during the synthesis of LFP [48,49]. However, non-conformal amorphous carbon coatings did not show enough improvement in electrical conductivity when nanosized LFP particles were prepared [15**].

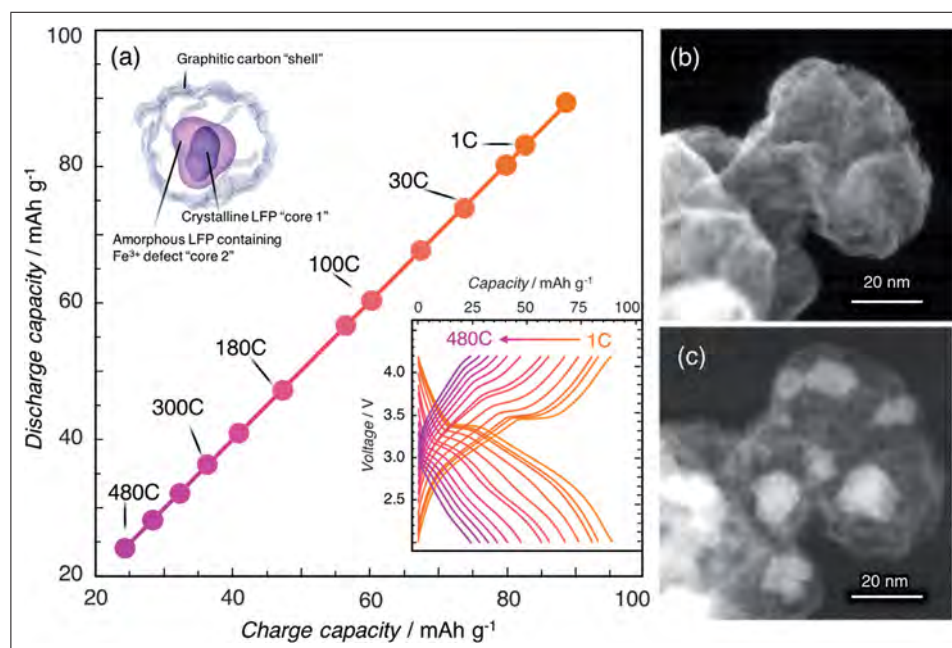
Single nanosized LFP crystals encapsulated within hollow-structured graphitic carbons were synthesized via UC treatment. Evidenced by the combination of spectroscopic and X-ray diffraction characterization [15**], the LFP/graphitic carbon composite material has a core LFP (crystalline (core 1)/amorphous (core 2))/graphitic carbon shell structure as illustrated in Figure 4a inset top. Comparison of the scanning electron microscope (SEM, Figure 4b) and dark-field images show the encapsulation of LFP particles core (white spots in Figure 4c) with the size of 10–20 nm within a carbon shell. Unlike conventional LFP where Li^+ intercalation is achieved at constant potential through a two-phase reaction mechanism [44], the galvanostatic charge/discharge profile of the composite showed different electrochemical signatures both with plateau and sloping region (Figure 4a inset below). The sloping profiles below 3.4 V corresponds to amorphous LFP containing Fe^{3+} defects [50*,51], and the Li^+ diffusion coefficient of the amorphous LFP ($10^{-11} \text{ cm}^2 \text{ s}^{-1}$) was found to be two orders of magnitude higher than that of crystalline LFP core phase ($10^{-13} \text{ cm}^2 \text{ s}^{-1}$) in the plateau region. The LFP/graphitic carbon composites have an extremely high rate capability both in charge and discharge; 89, 60, 36, and 24 mAh g^{-1} at 1, 100, 300, and 480C, respectively (Figure 4a). Such a linear relationship

means that the composites can offer a high-power capability of the material in discharge as well as in charge, such as expected for the practical use of hybrid supercapacitors. Such results pave the way for designing high energy and high power materials to be used in hybrid supercapacitors.

Conclusions and remarks

The ultracentrifugation (UC)-treated transition metal oxides/nanocarbon composites described in this review are newly synthesized materials, which may be excellent candidates as electrode active materials for the next generation hybrid supercapacitors. Nanosized and dimension-controlled materials directly bonded on high-surface area conducting carbons through the UC treatment showed ultrafast electrochemical performance. Hyper-dispersed single nano $\text{TiO}_2(\text{B})$ crystals with anisotropic crystal growth (ultrashort along b -axis) were uniformly formed in a MWCNT matrix using UC treatment combined with a follow-up hydrothermal treatment. The ultrashort b -axis length and hyper dispersion of UC- $\text{TiO}_2(\text{B})$ overcome its poor Li^+ diffusion coefficients and improve the power capability of $\text{TiO}_2(\text{B})$ by enabling ultrafast Li^+ deintercalation (235 mAh g^{-1} at 300C). To further increase the energy density of the more positive $\text{TiO}_2(\text{B})$, LVO whose operation potential is below 1.0 V (down to 0.1 V vs. Li/Li^+) was chosen. The combination of the activation process of UC-LVO/MWCNT composites and limited-voltage-range operation (2.5 V down to 0.76 V vs. Li) improved the Li^+ intercalation and deintercalation with a small voltage hysteresis (below 0.1 V), thanks to the fast solid-solution process of the LVO after activation. Highly dispersed

Figure 4



(a) Plots of discharge capacity vs. charge capacity of a half-cell consisting of Li/1 M LiPF₆ in EC+DEC/(LFP/graphitic carbon composites) as a function of C-rate: Inset top: Schematic illustration of the core-shell nanostructure of the LFP/graphitic carbon composite, representing a minute structure consisting of an amorphous outer sphere of a LFP containing Fe³⁺ defects and an inner sphere of crystalline LFP. Inset bottom: Charge-discharge profiles of composites at different charge C-rates from 1 to 480C. (b) Scanning electron microscope (SEM), (c) dark-field images of the UC-derived LFP/graphitic carbon composites, whereby each sphere LFP core is accommodated/encapsulated within the hollow structured graphitic carbon shells.

defective (crystalline/amorphous) LFP nanoparticles encapsulated within hollow-structured graphitic carbon enabled ultrafast discharge rates (60 mAh g⁻¹ at 100C, 36 mAh g⁻¹ at 300C) and ultrafast charge rates (60 mAh g⁻¹ at 100C, 36 mAh g⁻¹ at 300C), showing promising characteristics as a positive electrode for the next generation hybrid supercapacitors. The specific structures of the composites prepared by the UC-treatment contribute to achieve ultrafast electrochemical performance which are needed to develop the next generation of supercapacitors.

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