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Self-Assembled $LiFePO_4$ Nanowires with High Rate Capability for Li-ion Batteries[†]

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Methods.

Synthesis: In a typical synthesis of 1D $LiFePO_4$ nanostructures, 300 mg of $FeCl_2·4H_2O$ (97%, Sigma Aldrich) and 18 mg of ascorbic acid (97%, Sigma Aldrich) was dissolved in 10 mL of TetraEG (anhydrous $HO(CH_2CH_2O)_3CH_2CH_2OH$, 99%, Sigma Aldrich) under strong magnetic stirring forming a light-green and homogeneous **solution A**; 94.5 mg of $LiOH·H_2O$ (99.99%, Sigma Aldrich) was dissolved in 5 mL of TetraEG under sonication forming a yellow-brown and homogeneous **solution B**; 152 mg of LiH_2PO_4 (anhydrous, 99.9%, Sigma Aldrich), was dissolved in 0.2 mL distilled water forming **solution C**. Afterwards, solution B was slowly added into solution A under strong magnetic stirring, forming the homogeneous suspension. After 30 mins' strong magnetic stirring, solution C was drop-by-drop added into the mixed suspension. The preparation of the precursor solution should be carried out under Ar atmosphere protection with the presence of traces of L-ascorbic acid (Acros, 5% with respect to the weight of $FeCl_2·4H_2O$) to avoid the oxidation of Fe^{2+}. Then the precursor solution was transferred into a glass vial which was directly put into the Teflon pot. Finally, the Teflon pot was put into the stainless steel autoclave and kept at 200 °C for sufficient time. Typically, solvothermal treatment for 24 hours yields light greenish white, phase pure 1D $LiFePO_4$ nanostructures. After 24 hours solvothermal treatment, the samples were washed with ethanol for several times till the solution was transparent and colorless. Then, the samples were dried up at the vacuum oven under 80 °C.

Different adding sequence of solution A, B and C will result in different assemblies of the 1D nanostructure. When the adding sequence of the solution is A, B and C, the 1D nanostructures show an inter-connected structure, which is not open for the electrolyte penetrations. The carbon coating of the samples was conducted in a typical way by using the sucrose as the carbon source. 0.1 g of glucose and 1 g of the as-synthesized 1D $LiFePO_4$ nanostructures (m/m=0.10) were dispersed in proper amount of deionized water and mechanically mixed in Thinky centrifugal mixer (ARE-310) for 30 min and dried in vacuum oven under 90 °C. The samples were first heated at 350 °C for 4 h and then at 650 °C for 9 h in a tube furnace with Ar/H_2 (90/10, v/v) atmosphere in order to carbonize the glucose and increase the crystallinity of the $LiFePO_4$ samples.

Electrochemical Measurements: For the carbon-coated samples, 15 wt % of carbon black (Super P, TIMCAL), 5 wt % of binder (PVDF, Aldrich), and 80 wt % of the 1D $LiFePO_4$ nanostructures were uniformly mixed in N-methyl-2-pyrrolidinone (NMP, Fluka) under mechanical stirring in Thinky centrifugal mixer (ARE-310) for 30 min. The resulting paste was either transferred onto doctor-bladed onto Al foil. After drying at 115 °C overnight under vacuum, circular electrodes with diameters of 13 mm were punched out and assembled into a standard CR2032 coin cell in an argon-filled glovebox in the case of doctor-bladed films.

Lithium metal (99.9%, Alfa-Aesar) served as both reference and counter electrodes. A fiberglass separator was soaked with electrolyte (1 M $LiPF_6$ in 1:1 wt % ethylene carbonate and diethyl carbonate (BASF Corp.) as the electrolyte). All electrochemical measurements (galvanostatic cycling, cyclic voltammetry, and impedance spectroscopy) were performed using a Biologic instrument (VMP3) at room temperature. The electrodes were cycled between 2.0 and 4.5 V vs Li/Li^+ for varying specific current rates (1 C = 170 mA/g). The typical loading amount (~0.8-1 mg) for nanostructured $LiFePO_4$ and commercial $LiFePO_4$ is similar.

Characterization: X-ray powder diffraction patterns were performed on a Philips X-ray diffractometer (APD 3520) equipped with Cu Kα radiation. SEM and TEM observations were carried out on Hitachi S-5500 scanning electron microspcope (S-5500) and JEOL transmission electron microscope (2010F), respectively. BET surface area was tested with a NOVA® surface area analyzer (Quantachrome Instruments NOVA4000). Electrochemical characterization was performed on LANHE battery cycler (CT2001A) and Bio-logic potentiostat (VMP3) equipped with impedance modules.

Morphologies of the 1D $LiFePO_4$ nanostructures with different assemblies

Different adding sequence of solution A, B and C will result in different assemblies of the 1D nanostructure. When the adding sequence of the solution is A, B and C (ABC), the 1D nanostructures show an inter-connected structure, which is not open for the electrolyte penetrations.

Label.	$FeCl_2{\cdot}4H_2O$	TetraEG	Ascorbic acid	$LiOH{\cdot}H_2O$	TetraEG	LiH_2PO_4	H_2O
ABC	**300 mg**	**10 mL**	**18 mg**	**94.5 mg**	**5 mL**	**152 mg**	**0.2 mL**
ACB	**300 mg**	**10 mL**	**18 mg**	**94.5 mg**	**5 mL**	**152 mg**	**0.2 mL**

Tab. S1 Recipes and the adding sequences to obtain the single crystalline 1D $LiFePO_4$ nanostructures. The ABC and ACB sequences are both used to obtain the 1D $LiFePO_4$ nanostructures with different assemblies. The samples obtained from the ACB sequence have the superior electrochemical performances, which are shown in the maintext.

1. Branched nanowires on the $LiFePO_4$ nanoarchitectures

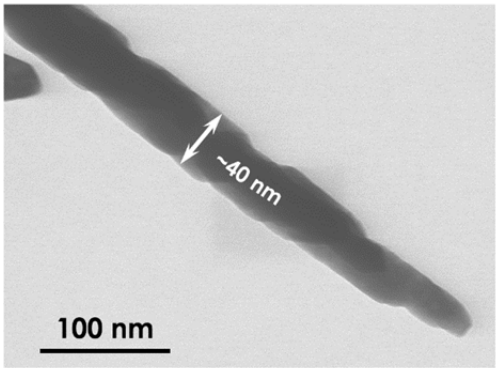

Fig. S1 STEM image of a single $LiFePO_4$ nanowire with the diameter of ~40 nm.

2. Structure characterizations of the ABC_1D $LiFePO_4$ nanostructures.

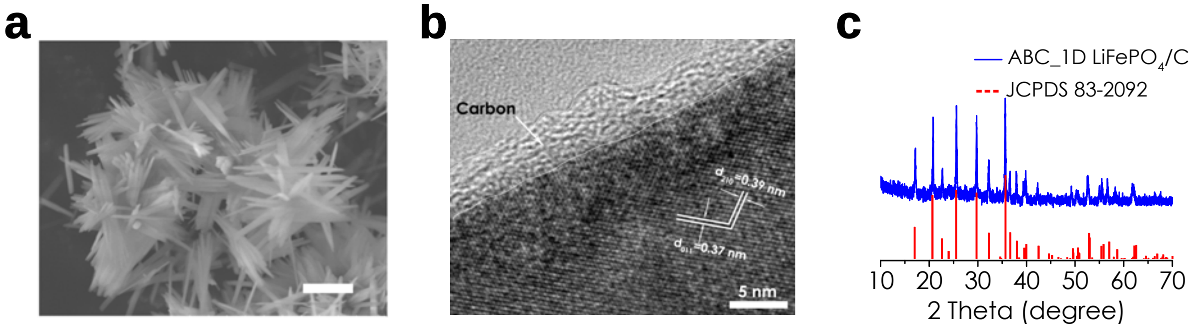

Fig. S2 Structure characterization of the ABC_1D $LiFePO_4$ nanostructures. (a) SEM images of the ABC_1D $LiFePO_4$ nanostructures with an inter-connected structure. Scale bar: 3 μm (b) HRTEM of the ABC sample taken on an individual $LiFePO_4$ nanorod showed clear crystal planes. The amorphous outer layer with a thickness of ~ 3 nm was due to the formation of carbon coating on the samples. (c) XRD pattern of the as-prepared ABC_1D $LiFePO_4$. The diffraction peaks correspond well to the standard pattern of orthorhombic $LiFePO_4$ (JCPDS 83-2092), without any other impurity phase detected.

3. BET tests of the single-crystalline 1D $LiFePO_4$ nanostructures

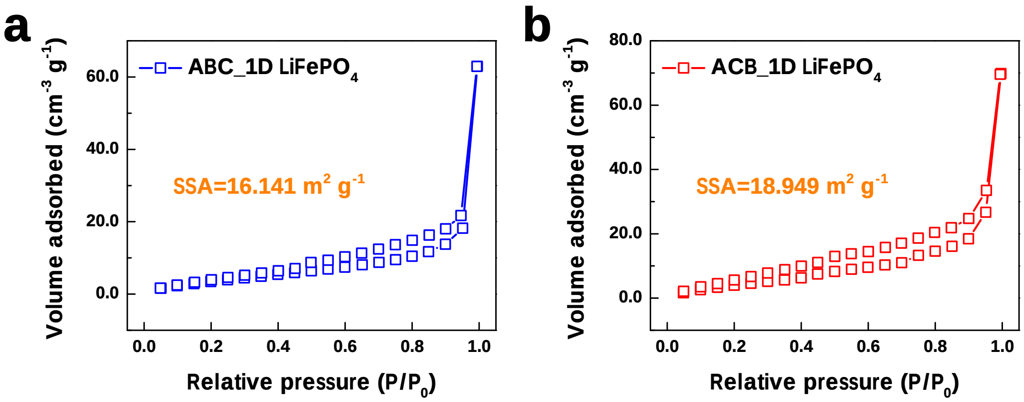

Fig. S3 BET analysis of the ABC and ACB samples: (a) Isotherms of ABC_1D $LiFePO_4$ samples, (b) Isotherms of ACB_1D $LiFePO_4$ samples. The specific surface areas (SSA) of the ABC and ACB_1D $LiFePO_4$ samples are 16.141 m^2 g^{-1} and 18.949 m^2 g^{-1}, respectively.

4. CV profiles of the commercial $LiFePO_4$/C powders.

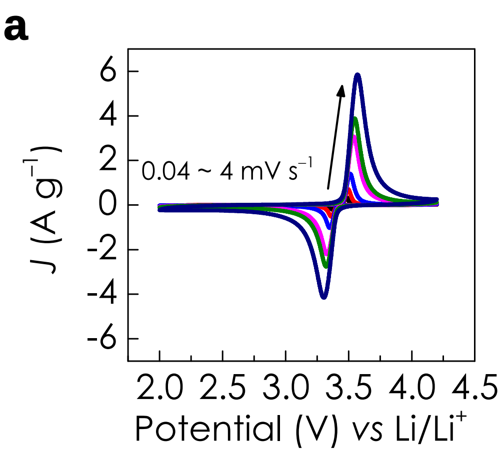

Fig. S4. Cyclic voltammetric profiles of the commerical $LiFePO_4$ powders at various sweeping rates of 0.04, 0.1, 0.4, 1, 2, and 4 mV s^{-1}.

To determine the lithium ion diffusion coefficiency, the CV profiles at various scanning rate were conducted. The peak current rate (J_{pc}) is in linear response to the square root of scanning rate (v) as shown above, from which the average lithium ion diffusion coefficient of the commercial $LiFePO_4$ powders could be further estimated. According to the Randles-Sevcik equation:[1]

$$J_{pc} = 2.69 \times 10^5 n^{3/2} D^{1/2} C v^{1/2}$$

Where J_{pc} is peak current rate, n is number of electrons transferred in the half-reaction for the redox couple (for $LiFePO_4$, n = 1), D is Li–ion diffusion coefficient ($cm^2\ s^{-1}$), C is molar concentration of Li ions in $LiFePO_4$ (2.28×10^{-2} mol cm^{-3}), and v is sweeping rate (V s^{-1}). The Li–ion diffusion coefficient of the commercial $LiFePO_4$ powders was calculated to be (~ 1.10×10^{-14} during charge and ~ 5.62×10^{-15} $cm^2\ s^{-1}$, which were consistent with previous reports.[2]

5. Electrochemical impedance spectroscopy (EIS) of the single crystalline 1D $LiFePO_4$ nanostructures.

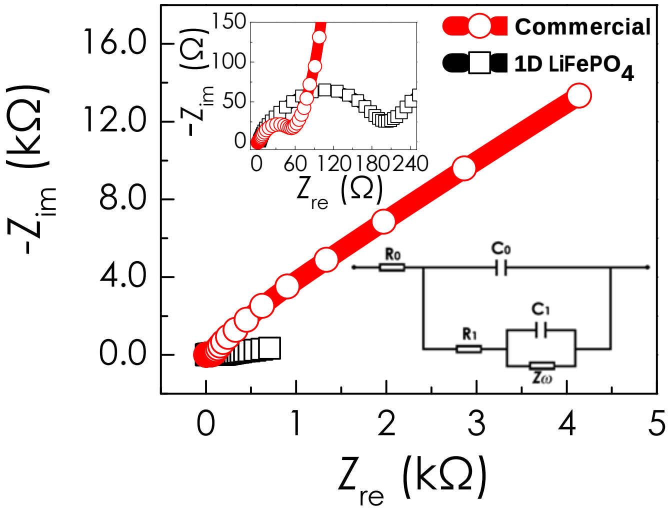

Fig.S5 Nyquist plots of 1D $LiFePO_4$/Li metal (black) and commercial $LiFePO_4$/Li metal (red) half-cells measured in the frequency region of 10^6–0.01 Hz. Inset: simplified-contact-Randles equivalent circuit for the simulation of the Nyquist plots.

6. Charge-discharge curves of the commercial $LiFePO_4$/C powders at various current rates.

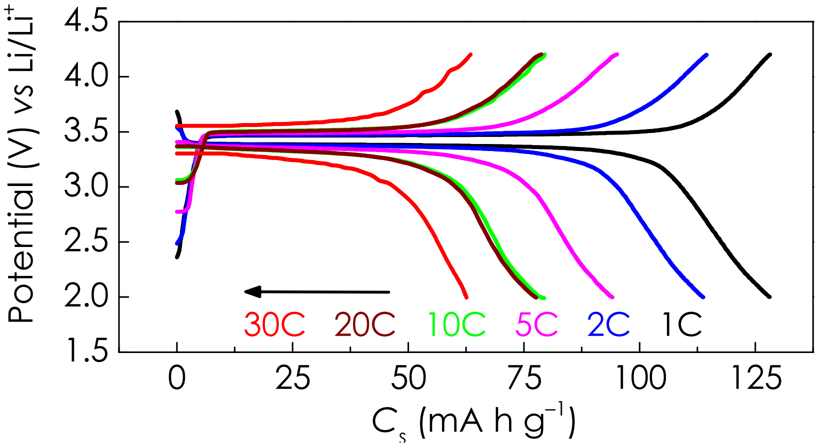

Fig.S6 Charge/discharge profiles of the commerical $LiFePO_4$ powders at various current rates from 1C to 30C. The electrode delivers a specific capacity (C_s) of ca. 130 and 63 mA h g^{-1} at 1 and 30 C, respectively.

7. Rate performance comparison among the reference papers.

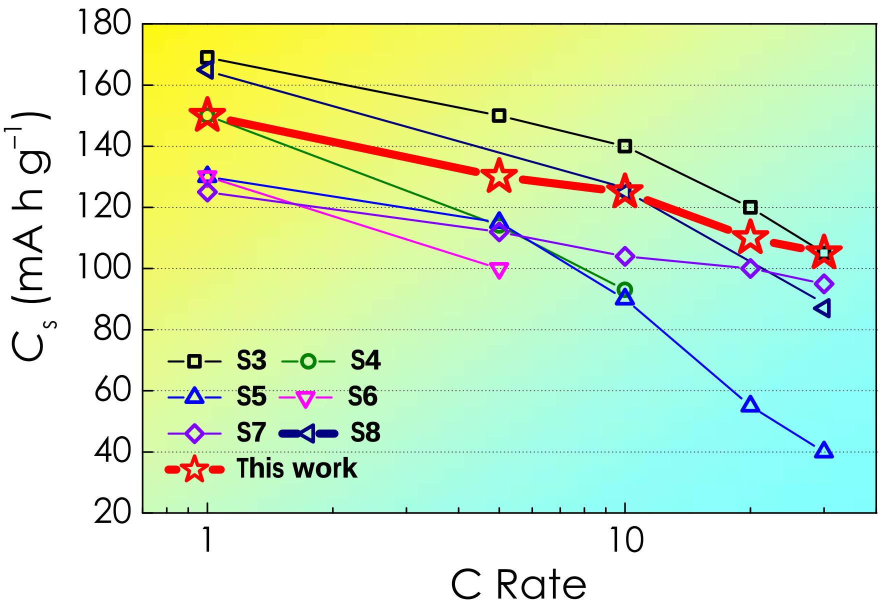

Fig.S7 Rate performance comparison between the current work and other reported works with different morphologies obtained by different methods. The rate performance of our nanoarchitectured $LiFePO_4$ was comparable to recently reported high-rate $LiFePO_4$ nanosheets with the nanometer thickness[3] and $LiFePO_4$ nanowires prepared by electronspinning,[4] but superior to those $LiFePO_4$ particles with microporous structure,[5-7] and $LiFePO_4$ nanoparticles prepared via other hydro/solvothermal or solid reaction methods.[8]

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