Supporting Information Available

Biocarbon-coated LiFePO₄ Nucleus Nanoparticles Enhancing Electrochemical Performances

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Submitted to Chemical Communications

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S1: Biosorption experiments and analyses



Fig. S1. (a) Langmuir adsorption isotherm for Fe^{3+} biosorption at optimum conditions (pH=3, 37 °C, 120 min at 100 rpm). (b) Biosorptions of Fe^{3+} (in percentage) from solution at different Fe^{3+} concentrations, pH=3, by 30 g L⁻¹ yeast biomass as related to the time of contact at 100 rpm. (c) Effect of quantity of yeast biomass on biosorption of Fe^{3+} from solutions at different iron ion concentrations, pH=3 for contact time of 120 min at 100 rpm.

Standard synthetic solutions were prepared in our laboratories using FeCl₃ with concentrations of 1, 2 and 3 g·L⁻¹ Fe³⁺ ions in solution. The factors that affect the biosorption rate were examined in a batch system. Three parameters, i.e., biomass concentration (yeast cell), Fe³⁺ concentration, contact time, were examined regarding their effect on the biosorption of Fe³⁺ ions from solutions. All experiments were carried out with purified yeast cell suspension in flasks in an incubator at 37 ± 0.5 °C with constant shaking to create optimum conditions (contact time, pH, initial Fe³⁺ concentration and yeast dose). The contents of the flasks were thereafter filtered and the filtrates were diluted (10 ml was pipetted into 100 ml volumetric flask and filled to the mark with distilled water). The flame absorption spectroscopy was used to analyze the residual Fe³⁺ concentration. The Fe³⁺ adsorbed by yeast cell biomass was calculated as follows:

$$M = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where *M* is Fe³⁺ adsorbed (mass %) by yeast biomass, C_i and C_f are the initial and final Fe³⁺ concentrations, respectively. The Langmuir model represents a theoretical treatment of non-linear sorption. For the single element category, the Langmuir equation is given by:

$$q = \frac{q_{\max}bC_{eq}}{1+bC_{eq}} \tag{2}$$

where q is iron accumulated per gram of the dry yeast, *Ceq* is the iron ion residual concentration in solution under equilibrium (mg L⁻¹), q_{max} is the maximum adsorption capacity of iron and represents single layer coverage of yeast cell in contact with the iron ion solution, and b is the Langmuir constant (L mol⁻¹) related to energy of sorption and changes with temperature. To draw the Langmuir plots, Eq. (2) is rearranged into the linear expression:

$$\frac{C_{eq}}{q} = \frac{1}{bq_{\max}} + \frac{C_{eq}}{q_{\max}}$$
(3)

The linear plots of Ceq/q versus Ceq show that adsorption follows the Langmuir adsorption model (see Fig. S1a). The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or an equilibrium parameter (R_L):

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

where C_{θ} is the initial concentration of Fe³⁺. The R_L value indicates the shape type of isotherm to be either unfavorable $(R_L>1)$, linear $(R_L=1)$, favorable $(0 < R_L < 1)$ or irreversible $(R_L=0)$.^{1,2} The R_L was found to be 0.74 to 0.16 for the initial concentrations of 1 to 3 g L⁻¹ Fe³⁺, indicating that the adsorption of Fe³⁺ by yeast cells was favorable. The sorption of iron by yeast biomass was very rapid for 1 g L⁻¹ solutions and the equilibrium was achieved within 25 min and the percentage adsorbed is 96%. For 2 and 3 g L⁻¹ solutions, the equilibrium was achieved within 60 min and the percentage of Fe³⁺ adsorbed was 77 and 54%, respectively. In 1 g L⁻¹, the sorption equilibrium was achieved in 120 min and the percentage adsorbed is 95% (Fig. S1b). It is clear from the results that the time required for maximum uptake of Fe³⁺ by yeast was dependent on the initial Fe³⁺ concentrations. This result is interesting, as the equilibrium time is an important parameter for synthetic operations of biocarbon-coated LiFePO₄ nucleus nanoparticles (BC-LFP-NN). The yeast biomass was varied between 8 to 40 g L⁻¹ with the variation in Fe³⁺ concentration to clarify whether the decrease in Fe³⁺ adsorption with increasing the initial Fe³⁺ solutions, the amount of yeast biomass required to adsorb 96% of Fe³⁺ was 12 g L⁻¹ and the amount of yeast biomass required to attain the maximum sorption capacity for 2 and 3 g L⁻¹ Fe³⁺ solutions were 14 and 22 g L⁻¹, respectively. This study has revealed that yeast biomass tends to adsorb more Fe³⁺ ions at high concentrations and for shorter contact periods.





Fig. S2 (a) XRD patterns for the samples prepared by different addition amount of dry yeast template route and calcined at 750 °C for 8 h, LFP (without yeast); BC-LFP-NN-1 (10 g L^{-1} yeast); BC-LFP-NN-2 (20 g L^{-1} yeast); BC-LFP-NN-3 (30 g L^{-1} yeast). (b) XRD patterns for the samples templated with dry yeast addition amount of 20 g L^{-1} and calcined at different temperatures for 8 h. The peaks are indexed to the pure olivine (LiFePO₄) phase (JCPDS No.83-2092).

In order to discuss influence of an additional amount of the dry yeast template and the heat treatment temperature on structure of BC-LFP-NN sample, we performed structure characterization of samples. **Fig. S2a** shows the XRD patterns of samples synthesized with different additional amounts of dry yeast at 750 °C. The XRD results indicate that LiFePO₄ has orthorhombic olivine-type structure and the residual carbon has an amorphous structure. Fig. S2b compares the XRD patterns of the samples obtained with an additional amount of 20 g L⁻¹ of dry yeast that were calcined at different temperatures for 8 h. The diffraction peaks become narrower and stronger with an increase in the annealing temperature, implying an increase in



Fig. S3. XRD patterns for the BC-LFP-NN samples synthesized with an additional amount of 20 g L^{-1} of dry yeast at 750 °C through the enlargement experiments, the total mass of A-1 sample is 10g, A-2 sample is 100g.

the crystallinity of LiFePO₄ olivine phase. The XRD results indicate that all of samples synthesized through the enlargement experiments have orthorhombic olivine-type structure of pure phase LiFePO₄ and there are no other diffraction peaks of any impurity phase (Fig. S3). Thus, it is facilely for the others to follow this work. The summary of the structural features and performances for the samples synthesized with different additional amounts of dry yeast at at 750 °C is given in Table S1. Along the increase of the dry yeast, the lattice volume of LiFePO₄ in the synthesized samples swells obviously (see Table S1[a]), because the in situ composite structure of active biocarbon with LiFePO₄ nanoparticles leads to a distortion of LiFePO₄ crystal structure during heat treatment. In the range of 0~30 g L⁻¹ dry yeast, the grain size of LiFePO₄ decrease obviously with increase of the additional amounts of dry yeast (Table S1[b]), which is much smaller than those prepared through conventional solid-state reaction.³ This indicates that the biocarbon network obtained by heating yeast cells plays an important role in restraining from the crystal growth of LiFePO₄.

Table S1. Summary of the structural features and performances of the synthesized samples.

Samples	V [a]	D ₂₁₁ [b]	E [c]	C[d]	R₀[e]	S [f]	V _{meso} [g]	D _{pore} [h]
	[Å ³]	[nm]	[×10 ⁻³ S cm ⁻¹]	[wt %]	[g cm ⁻³]	[m ² g ⁻¹]	[cm ³ g ⁻¹]	[nm]
LFP	290.68	38.8	0.011	2.179	3.448	16.76	0.0425	8.951
BC-LFP-NN-1	291.03	35.5	3.727	8.189	3.237	36.22	0.0901	9.441
BC-LFP-NN-2	291.21	34.5	3.986	15.28	3.102	67.53	0.1499	10.45
BC-LFP-NN-3	291.7	30.3	5.245	18.20	3.035	81.84	0.2544	11.86

[a] V: lattice volume of LiFePO₄ in the samples calculated by using Jade 5 XRD pattern-processing software. [b] D_{211} : crystallite size of LiFePO₄ estimated using Scherre's relation $t = 0.9\lambda / \beta_{1/2} \cos \theta$, where λ is the X-ray wave length, θ is the Bragg angle and $\beta_{1/2}$ is the angular full-width-half maximum of the chosen (211) reflection in radian. [c] E: electrical conductivity see text. [d] C: carbon content determined by using Vario EL IIICHN elemental analyzer. [e] R_0 : actual density calculated through pycnometer method. [f] S: specific surface area calculated through BET method. [g] V_{meso} : mesoporous volume. [h] D pore: pore size.

The amount of $Li_4P_4O_{12}$ impurity in samples synthesized with yeast template is much smaller than that in LFP blank sample (Fig. S2b and Fig. S10a). This can be ascribed to the fact that the present method inhibits $Li_4P_4O_{12}$ crystal growth. The electrical conductivity of the samples increases from 3.727 to 5.245×10^{-3} S cm⁻¹ with an increase in additional amounts of yeast (Table S1[c]), value which are much higher than in pristine LiFePO₄ (1.1×10^{-5} S cm⁻¹). The carbon obtained by heating yeast cells plays an important role in the enhancement of the electrical conductivity. To determine the carbon content of these composites elemental analysis has been performed using VarioEL IIICHN elemental analyzer. The carbon content increased with adding the yeast (Table 1[d]). The carbon content for BC-LFP-NN-2 sample is 15.28 wt %, causes a significant increase in rate capability and energy density (see Fig. S7a), but there is a small decrease in the actual density comparing with that of LFP blank sample (see Table 1 [e]).



Fig. S4. FTIR spectra of the samples. a) Pureyeast. b) FePO₄/yeast mixture precursor. c) BC-LFP-NN-2 sample templated with dry yeast addition amount of 20 g L^{-1} calcined at 750 °C for 8 h. d) blank LFP synthesized at 750 °C for 8 h.

The chemical bond linkages between biomolecules in yeast cells with iron ions and the in-situ nanocomposite linkages between LiFePO₄ nanoparticles with the active biocarbon network were studied by FT-IR (see Fig. S4). The FT-IR spectrum of pure yeast is shown in Fig. S4a. The broad band at 3500 cm⁻¹ is ascribed to the O-H stretching vibration of water. The dominant bands near 1652 and 1534 cm⁻¹ are respectively assigned to amide I and amide II of the proteins in yeast cells. The band at 2920 cm⁻¹ is derived from the CH₂ asymmetry stretching vibration of the protein and carbohydrate in yeast cells. The band at 1047 cm⁻¹ is caused by the C-O stretching of carbohydrates found in the RNA, DNA, and cell membrane of the yeast cell.⁴ Fig. S4b shows the FT-IR spectrum of FePO₄/yeast mixture precursor. By comparing Fig. S4a with Fig. S4b, the following three changes are seen. First, all the amide peaks of the FTIR spectrum have shifted to lower wavenumbers from pure yeast to FePO₄/yeast mixture precursor, implying the existence of chemical interactions between the iron ions and biomacromolecules. Thus, yeast protein molecules interact with iron ions via the amide reductase. Second, the CH₂ vibration peak in yeast cell disappears and a new P-O peak forms, which is ascribed to the protein binding with iron ions through an amine group and phosphating. Finally, the absorption peak at 1045 cm⁻¹ (C–O) is enhanced due to the vibration superposition of the C-O and PO_4^{3-} groups. These results indicate that the carboxyl (COO⁻), hydroxyl (OH⁻) and $-OPO_3^{2-}$ radicals play an important role in the chemical interaction between the protein macromolecules in yeast cells and the iron ions. Fig. S4c is the FT-IR spectrum of BC-LFP-NN-2 sample. The FT-IR spectrum of blank LFP is shown in Fig. S4d. The infrared spectral bands of LiFePO₄ are mainly distributed over two wavenumber ranges from 460–650 cm⁻¹ and 940–1120 cm^{-1.5-7} These bands respectively correspond to the internal stretching, internal bending and external oscillation modes of $PO4^{3-}$. The peak at 2375 cm⁻¹ is due to the P-O stretching mode. The dominant bands from 940 cm⁻¹ to 1040 cm⁻¹ are due to PO_4^{3-} . The bands observed at 500-640 cm⁻¹, correspond to intra-molecular symmetrical stretching vibrations of the Fe–O bond in the FeO₆ unit.⁸ By comparing Fig. S4c with Fig. S4d, two main changes are seen in the FTIR spectra. First, for the BC-LFP-NN sample all the Fe-O peaks have shifted to lower wavenumbers from those of pure LiFePO₄ sample. This result demonstrates an increase of the Fe-O chemical bond length in the LiFePO₄ structure. Second, the vibration transmittance of the PO_4^{3-} peaks weakened. These changes indicate that there are in-situ nanocomposit linkages between the $LiFePO_4$ nanoparticles and the active biocarbon network. Through the FT-IR spectroscopy results, we have verified that the deposition and self-assembly mechanism is feasible for synthetizing BC-LFP-NN sample.



Fig. S5. (a) N_2 adsorption-desorption and (b) pore size distribution of the samples prepared with different addition amount of dry yeast template and calcined at 750 °C for 8 h.

The mesoporosity was characterized by the adsorption-desorption isotherms and Barret-Joyner Halenda pore-size-distribution curves. According to the International Union of Pure and Applied Chemistry regulations,⁹ all the isotherm shapes of the samples synthesized with different additional amounts of dry yeast are of the type-IV pattern that indicates mesoporous characteristics (**Fig. S5**). The BC-LFP-NN-2 sample shows that hysteresis loop consists of a nonuniform open pore structure (region 1, H3 loop at P/P0 from 0 to 0.89 and the pore-size distribution centered at 4.0 nm) and a homogeneous plugged pore structure (region 2, H4 loop at P/P0 from 0.89 to 0.98 and at 12.0 nm). The pore structure data of the samples see Table S1[f-h]. The BET surface area, pore volume and pore size of the synthesized samples increases with increasing amounts of dry yeast. Because the value of the pore volume and pore size fits well with the lithium diffusion and electrolyte transfer, the BC-LFP-NN-2 shows the best electrochemistry property (see Fig. S7a). Such an open interconnected mesoporous structure can significantly increase the permeability of the electrolyte in the mesoporous microsphere and thus facilitate lithium ion diffusion.



Fig. S6. (a) Raman spectra of the samples prepared by different addition amount of dry yeast template route and calcined at 750 °C for 8 h, LFP (without yeast); BC-LFP-NN-1 (10 g L^{-1} yeast); BC-LFP-NN-2 (20 g L^{-1} yeast); BC-LFP-NN-3 (30 g L^{-1} yeast). (b) Thermogravimetric (TGA) curves of the BC-LFP-NN-2 and LFP samples

Raman spectroscopy is a very sensitive tool for studying the properties and structural features of coated carbon, since

Raman experiments can give chemical signals in the surface region.¹⁰ To detect the surface components of the BC-LFP-NN samples, we measured Raman spectra of these samples, as shown in **Fig. S6a**. The Raman spectra of samples display two intense broad peaks at 1352 and 1585 cm⁻¹, both of which were attributed to the D band (disordered carbon, sp3) and the G band (graphite, sp2) of Raman vibration modes for amorphous carbon, respectively.¹¹ The electronic conductivity of the composite has a complicated correlation with the peak intensity ratio and the band area ratio of the D vs. G band. The peak intensity ratio (ID/IG) calculated is an index of the degree of disordering. An increase in the ID/IG ratio reflects a greater degree of disorder.¹² By comparing these Raman spectra, we can find a distinct difference in the wavenumber range of 300-900 cm⁻¹. Two weak and broad Raman peaks around 600 cm⁻¹ can be detected for LFP sample, which are all assigned to the intramolecular stretching modes of the PO₄³⁻ anion. However, for BC-LFP-NN samples, no Raman signals of LiFePO₄ can be distinguished in the same range, suggesting that the thickly biocoated carbon (13.5 wt %) may screen the deeper LiFePO₄ from being detected. These Raman behaviors are very well in agreement with those already reported for other types of LiFePO₄/C composite.¹³ The degree of disordering for the carbon in the BC-LFP-NN samples increases with the addition of dry yeast template. The ration of ID/IG of the BC-LFP-NN sample is 1.12, indicating that the coated carbon might be amorphous phase.¹⁴ The result is consistent with that of HRTEM (Fig. 2g), which shows that no lattice fringes caused by graphite were found in the carbon surface layer.

Thermogravimetric (TGA) measurement was used to estimate the total amount of carbon coated on the nanoparticles in the BC-LFP-NN-2 sample. Fig. S6b gives the TGA curves of the BC-LFP-NN-2 and blank LFP samples tested in air environment. It is clearly seen that the total weight of the blank LFP sample increases as a result of heating the powder in a dry air atmosphere due to the up-take of oxygen, in the course of the $Fe^{2+} \rightarrow Fe^{3+}$ transformation. However, for the BC-LFP-NN-2 sample, a decrease in the sample weight is observed due to the removal of carbon, which exceeds the weight loss due to oxidation of ferrous iron. In the temperature range of 250 - 600 °C, pure LiFePO₄ is oxidized to Li₃Fe₂(PO₄)₃ and Fe₂O₃, leading to a theoretical weight gain of 5.07%.¹⁵ For the BC-LFP-NN-2 sample, the carbon in the composite is oxidized to CO₂ gas at temperatures higher than 350 °C, leading to a big weight loss. Above 620 °C, the oxidation of both LiFePO₄ and carbon is completed and the weight of the sample keeps constant. Finally, by taking into account the theoretical weight gain (5.07%) of pure LiFePO₄ during TG measurement in oxygen, the amounts of carbon remaining in our blank LFP and BC-LFP-NN-2 samples were calculated to be ~1.77% and ~15.27% from the TGA data, respectively.¹³ The tiny carbon content appeared in our blank LFP sample, possibly due to residual carbon resulting from pyrolyzed ascorbic acid, which serves as a reducing agent in the synthesized reaction. In contrast, the BC-LFP-NN-2 sample could be well-prepared with an appropriate biocarbon content of ~13.5 wt % by carbonization of yeast cells in subsequent calcination processes. These observations are in agreement with our Raman measurements.

S3 : Electrochemical property characterizations of the samples prepared by yeast template route

The influence of the additional amounts of dry yeast template and sintering temperature on the electrochemical performance of various samples is shown in **Fig. S7**. In comparison with blank LFP sample, the samples synthesized with different additional amounts of dry yeast template have longer initial charge-discharge curves, higher capacity, lower electrochemical polarization and better reversibility at a current rate of 0.2 C (Fig. S7ab). The first discharge specific capacity for BC-LFP-NN-2 sample is 160.4 mA h g⁻¹, and the discharge capacity declines more slowly during cycling. At 100th cycle, it has 0.9% capacity loss from the initial value, while the capacity loss value for L blank LFP sample is 11.14 % at the 50th cycle (Fig. S12a). Fig. S7c exhibits the charge-discharge cycling life of the BC-LFP-NN-2 sample at higher current rates, and this sample has a rate capacity of 119.5 mA h g⁻¹ at 10 C. Fig. S7d shows the charge-discharge profile at a current rate of 0.2

C for samples synthesized with an additional amount of 20 g L^{-1} of dry yeast at different temperatures. The sample calcined at 750 °C delivers the highest discharge capacities of 160.4 mA h g⁻¹ at 0.2 C, this attributes to excellent morphology of nano-sized, mesoporous spherical LiFePO₄ particles with carbon coating that is formed in situ on surface of particles.



Fig. S7. Electrochemical property characterizations of BC-LFP-NN samples. (a) The initial charge-discharge curves and (b) the cycle performances between 2.5 and 4.4 V at 0.2 C rate (1C=170 mA h g⁻¹) for the samples prepared with different addition amount of dry yeast template and calcined at 750 °C for 8 h. (c) The charge-discharge curves of BC-LFP-NN-2 sample prepared at 750 °C for 8 h at different current rates. (d) The charge-discharge curves at 0.2 C for the samples synthesized with dry yeast addition amount of 20 g L⁻¹ at different temperatures.



Fig. S8. Cycle performances between 2.5 and 4.4 V at different current rates. (1C=170 mA h g^{-1}) for th BC-LFP-NN-2 sample synthesized with dry yeast addition amount of 20 g L⁻¹ and calcined at 750 °C for 8 h.

The cycle stability of th BC-LFP-NN-2 electrodes at high current ratio was investigated in terms of cycle stability during

constant current (CC) cycling tests. All electrodes were subjected to 100 cycles at different current rates at room temperature in the voltage of 2.5–4.4V. As shown in Fig. S8, all electrodes displayed excellent cycling stability. The BC-LFP-NN-2 electrode delivers the highest initial discharge capacities of 145 mA h g⁻¹ at a current rate of 1 C, and maintains the most impressive discharge capacity of 139 (95.9% of its initial value) after 100 cycles. This cathode displays a capacity of about 120 mAhg⁻¹ at a current rate of 5 C, and maintains the discharge capacity of 110 (91.7% of its initial value) after 100 cycles, This could be attributed to the appropriate morphology of biocarbon-coated LiFePO₄ nucleus nanoparticles, nanocomposite structure of the LiFePO₄/C particles, high electrical conductivity and high tap density. By considering the larger cycle number that we applied, our method can indeed lead to the improvement of the already commercialized cathode material.



Fig. S9. (a) Nyquist plots and (b) the plots of impedance as a function of the inverse square root of angular frequency in the Warburg r of samples synthesized with different amounts of yeast template. The cyclic voltammogram profiles (c) of the LFP and BC-LFP-NN-2 at low scan rate of 0.1 mV s-1 and (d) high scan rate of 0.5 mV s-1 between 2.3 and 4.3V.

Electrochemical impedance spectroscopy (EIS) is an important method used to evaluate the diffusion coefficient of lithium ions. This is because the Warburg impedance at low frequency is directly related to the lithium-ion diffusion process in an electrode material.¹⁶ Fig. S9a shows the Nyquist plots of the samples synthesized with different amounts of yeast template at 750 °C. All plots exhibit a semicircle in the high-frequency region, which is attributed to the charge transfer process. The diameter of the semicircles decreases with the increase of additional amounts of dry yeast template. This tendency means that the charge transfer resistance R_{ct} decreases with increasing amounts of yeast. The real axis intercept at Z_{real} in the very high frequency region identifies the ohmic resistance (R_e) of the electrolyte and electrodes. The slope of the line at low frequency represents the Warburg impedance (W), which is associated with lithium-ion diffusion in the LiFePO₄ cathode (see inset figure in Fig. S9a). The BC-LFP-NN-2 sample calcined at 750 °C has the lowest charge transfer resistance, which can be attributed to the mesoporous structure of the nanocomposite microspheres. The diffusion coefficient of the lithium ion can be calculated from the plots in the low frequency region using the following equation:¹⁷

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}$$
(5)

where *R* is the gas constant, *T* is the absolute temperature, *A* is the surface area of the cathode, *n* is the number of electrons per molecule during oxidization, *F* is the Faraday constant (96,486 C mol⁻¹), *C* is the lithium-ion concentration, and σ is the Warburg factor. The latter obeys the following relationship:

$$Z_{real} = R_e + R_{ct} + \sigma \omega^{-1/2} \tag{6}$$

where R_e is the resistance between the electrolyte and electrode, R_{ct} is the charge transfer resistance, and ω is anglar frequency.

Fig. S9b shows the linear fit of Z_{real} vs. $\omega^{-1/2}$, from which the slope σ can be obtained. It is possible to calculate the lithium diffusion coefficient in the material by using σ . The results show that the D_{Li} values for the LFP, BC-LFP-NN-1, BC-LFP-NN-2 and BC-LFP-NN-3 samples are 1.44×10^{-17} cm² s⁻¹, 2.67×10^{-15} cm² s⁻¹, 2.65×10^{-14} cm² s⁻¹ and 5.31×10^{-15} cm² s⁻¹, respectively. These values of the samples indicate that electrochemical kinetics of BC-LFP-NN is easier than that of the blank LFP regarding Li⁺ extraction.

Cyclic voltammogram (CV) profiles of the blank LFP and BC-LFP-NN-2 samples, collected at a scanning rate of 0.1 mV s⁻¹ and 0.5 mV s⁻¹ between 2.3 and 4.3 V are shown in Figs. S9c and d. From Fig. S9c we can see one pair of the anodic and cathodic peaks at 3.6 V and 3.3 V, respectively. The BC-LFP-NN-2 has more high current than the LFP sample. Both of the two curves have well symmetric performance, which correspond to the electrochemical intercalation and deintercalation reactions of lithium-ion. It is also agreed with the galvanostatic charge-discharge curve (see Fig. S9b). In the reduction scan, Li⁺ insertion occurs on octahedral sites upon the two-phase reduction of Fe²⁺/Fe³⁺ redox couple, otherwise in the oxidation scan.¹⁸ Fig. S9d shows the CV curves of the LFP and BC-LFP-NN-2 samples collected at a scanning rate of 0.5 mV s⁻¹. It is obvious that both the intensity and area of the redox peaks increase with increasing the scan rate. Due to the phase-transition processes between LiFePO₄ and FePO₄, the Li⁺ cannot completely extract/insert from/into the bulk during the time interval of a higher rate scan, and this causes the irreversible behaviors. The appearance of kinetic effects depends on the scan rates, implies that the electrochemical lithium-ion deintercalation–intercalation processes could change from being kinetically quasi-reversible to irreversible when scanning rate increases from being low to high.¹⁹ The Randle-Sevcik formula was used to determine the Li⁺ ion diffusion coefficient around the three pairs of charge-discharge platforms. Since the intercalation of Li⁺ ions in particles is a diffusion process, the electrode reaction can be assumed to be under a condition of semi-infinite diffusion. The formula can be written as:

$$I_p = 2.69 \times 10^5 A n^{3/2} C_p D^{1/2} v^{1/2}$$
⁽⁷⁾

where I_P is the peak current (A), A the surface area of the electrode (cm²), D the diffusion coefficient of the Li⁺ ion (cm² s⁻¹), C_o the concentration of Li⁺ (mol cm⁻³), v the CV scanning rate (V s⁻¹), and n the number of electrons transferred in the electrode reaction. In this paper, n is equal to 1, and A is assigned to be 1.77 cm², and D and Co are defined with respect to the Li⁺ ion per unit cell.

The lithium-ion concentration (C_o) can be calculated in the following way. Li⁺ ions are present in each unit cell in the lattice of LiFePO₄, and the value of the cell volume(V) of LFP is 2.91755366×10⁻²⁸, Accordingly, the value of *Co* is about 2.29×10⁻² mol cm⁻³. Based on Eq. (7), the apparent diffusion coefficients *Dc* (c peak) of LFP and BC-LFP-NN-2 collected at the scanning rate of 0.1 mV s⁻¹ between 2.3 and 4.3 V are calculated to be 1.3×10^{-9} cm² s⁻¹ and 1.0×10^{-9} cm² s⁻¹, respectively,

In contrast, they are calculated to be 1.1×10^{-9} cm² s⁻¹ 4.0×10^{-10} cm² s⁻¹ at the scan rate of 0.5 mV s⁻¹. It is found that the diffusion coefficient decreases as the scanning rate increases, confirming that the Li⁺ extraction of LFP demands more energy at the higher scanning rate.

S4: Structure and electrochemical property characterizations of LFP blank sample

Fig. S10a shows the XRD patterns of the LFP blank samples synthesized at different temperatures. The sample calcined at 450 °C shows no detectable peaks of LiFePO₄, suggesting the amorphous nature, only some minor peaks of Li₄P₄O₁₂ can be observed. The XRD patterns of powders annealed at 550, 650 and 850 °C demonstrate the appearance of olivine LiFePO₄ phase. The diffraction peaks become narrower and stronger with increasing the annealing temperature, implying an increase in crystallinity of the olivine LiFePO₄ phase. Fig. S10b compares the XRD patterns of LFP and BC-LFP-NN-2 calcined at 550 °C. The widening of X-ray diffraction peaks implies that the in-situ nanocomposited linkages between LiFePO₄ nanoparticles with the active biocarbon network induce strong lattice distortions and volume expansion of unit cell of the LiFePO₄ crystallite, and restrain from the crystal growth of LiFePO₄.



Fig. S10. (a) XRD patterns for the LFP blank samples calcined at different temperatures for 8 h. (b) XRD patterns for the LFP and BC-LFP-NN-2 samples calcined at 550 °C. The peaks are indexed to the pure olivine (LiFePO₄) phase.



Fig. S11. TEM images with different amplification factor in different area for the LFP blank sample.



Fig. S12. (a) The charge and discharge curves of the LFP blank sample cathode after cycling different cycle number at a rate of 0.1 C. (b) The charge-discharge curves of the LFP blank sample cathode at different current rates.

The cycling performances of the LFP blank sample cathode after cycling different cycle number at a rate of 0.1 C are displayed in **Fig. S11a**, where the discharge capacities decline during cycling. At the 50th cycle, it keeps 121.1 mA h g⁻¹ between 2.5 and 4.4 V at 0.1 C and it has 11.14% capacity loss of the initial value. In Fig. S11b it can be observed that the LFP blank sample cathode presents an discharge capacity of 133.2, 115.5, 104.0 and 92.0 mA h g⁻¹ between 2.5 and 4.4 V at 0.1, 1.0, 2.0, 5.0 C rate, respectively. The rate performance of the LFP is even worse than the BC-LFP-NN.

S5: Details of experimental procedures

The reagents used in this work include FeCl₃ (99%, Tianjin Kermel Chemical Reagent Co., Ltd.), CH₃COONa and ascorbic acid (99.5%, Tianjin Bodi Chemical Co., Ltd.), (NH₄)₂HPO₄ (99%, Tianjin Bodi Chemical Co., Ltd.), LiOH (97%, Tianjin Damao Chemical Co., Ltd.), and yeasts (Instant dry yeast, Angel Yeast Co., Ltd.). The BC-LFP-NN materials were prepared by the biotemplate method. The general procedure of this experiment is described as follows, quantitative instant dry yeast (0, 10, 20, and 30 g) was cultivated in 1000 mL glucose aqueous solution for 30 min at 30 °C . After 30 minutes of stirring, a uniform bio-emulsion was formed. The purified yeast cells were obtained by centrifuging and washing with distilled water. The FeCl₃ was dissolved in deionized water and added to the purified yeast cell solution with magnetic stirring at room temperature for 3 h. Then (NH₄)₂HPO₄ and CH₃COONa were added to the Fe/yeast cell mixture solution in a stoichiometric ratio of Fe:P:Na=1:1:1.5. A yellow colored solution with deposited FePO₄ was formed (Eq. 8). After stirring vigorously for 1 h, the deposited FePO4 was centrifuged and washed several times with distilled water and ethanol, and then dried in an oven at 80 °C for 8 h. The dry FePO₄/yeast products were mixed with LiOH and ascorbic acid on the basis of the same molar ratios for 6 h through a dry ball-milling process. Here, the ascorbic acid is the carbon source (Eq. 9). Then, the mixtures were pressed into pellets, the resulting pellets were annealed at 300 °C for 2h, and then sintered at various temperatures (450, 550, 650, 750 and 850 °C) in N₂ atmosphere for 8 h for the synthesis of LiFePO₄ powder (Eq. 10). The heating rates were kept relatively low, at 5 °C min⁻¹, to avoid structural collapse from fast crystallization. The final product obtained was in the form of black powder or pellets, and the samples sintered at 750 °C were marked as LFP (without yeast), BC-LFP-NN-1(10 g L^{-1} yeast), BC-LFP-NN-2 (20 g L^{-1} yeast), BC-LFP-NN-3 (30 g L^{-1} yeast). (0)

$$FeCl_3 + (NH_4)_2 HPO_4 + CH_3 COONa \rightarrow FePO_4 + CH_3 COOH + NaCl + 2NH_4Cl$$

$$C_6H_8O_6 \rightarrow 4H_2O + 4C + 2CO$$
(9)

$4FePO_4 + 4LiOH + C \rightarrow 4LiFePO_4 + 2H_2O + CO_2$

(10)

X-ray diffractometry (XRD) was employed to identify the structure of the synthesized materials. The XRD measurement was carried out on a PANalytical X'Pert PRO X-ray diffractometer (Netherlands) with Cu Ka radiation ($\lambda =$ 0.15418 nm). XRD patterns were collected by a step-scanning mode in the range of 10~80°, with an acquisition time of 12.0 s at 0.02° step size. Transmission electron microscopy (TEM) (JEM-100X, Japan) operating at 100 KV was employed to characterize the morphologies of the samples. High-resolution transmission electron microscopy (HRTEM) was carried out on a Philips Tecnai 20U-TWIN microscope, working at 300 kV. Fourier transform infrared spectroscopy (FT-IR) was performed using a Nicolet Nexus spectrometer (Nicolet, NEXUS 470, USA) by using a KBr wafer technique in order to study the composition and structure of the samples. Infrared spectra were recorded in the region 4000-450 cm⁻¹, with a resolution of 4.00 cm⁻¹. The BET specific surface areas were measured by a Micromeritics apparatus (ST-08A, Beijing Huapu Analytic Instrument Co., Ltd, China) after the samples were dried at 150 °C for 5 h. The nitrogen (N₂) adsorption-desorption isotherms and Barrett-Joyner-Halenda pore size distributions were carried out at 77 K using a computer-controlled sorption analyzer (Micromeritics, Gemini V2380, USA) operating in the continuous mode. Before measurement, the samples were degassed in vacuum at 150 °C. The carbon content in the samples was determined by a Vario EL IIICHN elemental analyzer. Ramanspectra were measured in a back scattering configuration using a FT-IR & Raman spectrometer NEXUS 670 (Thermo Nicolet, USA), with a He-Ne laser (excitation line 632.8 nm) in the range of 100-2000 cm⁻¹. Thermogravimetric measurements (TGA) were conducted on a TGA Q500 thermogravimetric analyzer (TA Instruments, U.S.A.) in air at a scan rate of 10 °C /min from room temperature to 700 °C.

The electrical conductivities of the synthesized pellet samples were calculated by measuring the diameter and thickness of the pellets with the ZL10 LCR instrument (Shanghai Instrument Research Institute, China). The Charge-discharge cycling performances were performed with LR2032 coin-type cells. The cathode materials were prepared by mixing the LiFePO₄ sample with acetylene black and polytetrafluoroethylene in a weight ratio of 8:1:1 in ethanol to ensure homogeneity. After the ethanol evaporated, the mixture was rolled into a sheet. The obtained sheet was pressed into a piece onto an Al-foil with about 0.02 mm in thickness, dried under the vacuum atmosphere at 120 °C for 8 h and cut into circular strips of 15 mm in diameter. The mass calculation of active materials was carried out based on the 80% of difference between the mass of BC-LFP-NN materials coated Al foil and the mass of pristine Al foil. The cells were assembled in a glove box filled with high-purity argon, where lithium metal was used as an anode, polypropylene film as separator, and 1M LiPF₆ in an electrolyte consisting of ethylene carbonate/dimethyl carbonate/ethylene methyl carbonate in a volume ratio of 1:1:1. The Charge-discharge cycling performances of LiFePO₄ were tested on Channels battery analyzer (CT3008W) at different current densities between 2.5 and 4.4 V cut-off voltage using the coin-cells. The electrochemical impedance (EIS) and Cyclic voltammetry (CV) measurements were performed on a PARSTAT 2263 electrochemical workstation. EIS was also recorded with the frequency ranging from 100 KHz to 10 mHz and AC signal of 5 mV in amplitude as the perturbation. The voltage range of the CV measurements was 2.3–4.3 V and the scanning rate was from 0.1 mv s⁻¹ to 0.5 mv s⁻¹. All the tests were performed at room temperature.

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