Supplementary Information

Maize-like FePO₄@MCNT nanowire composite for sodium-ion batteries via a microemulsion technique

Shuojiong Xu,¹ Shiming Zhang,⁵,⁶ Junxi Zhang,*¹ Tian Tan,¹ Yao Liu¹

¹Electrochemical Research Group, Shanghai University of Electric Power, Shanghai, 200090, People’s Republic of China.

⁵State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province & Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People’s Republic of China.

* Corresponding author. Tel./Fax: +86-21-65700719.

E-mail address: zhangjunxi@shiep.edu.cn.
Fig. S1 TGA curves of FePO$_4$ and the FePO$_4$@MCNT. The samples were tested by TA Q500 Thermogravimetric Analysis. The remaining weight of FePO$_4$ is 72%, the first weight loss observed below 100°C is about 5~10%, which could be ascribed to the release of adsorbed water on the surface of the sample. The next weight loss from 100°C to 450°C is approximate 20%, which corresponds to the elimination of crystal water. The remaining weight of FePO$_4$@MCNT is 80%, which is consistent with the presence of 70% FePO$_4$ in FePO$_4$@MCNT.
Fig. S2 TEM image of FePO$_4$ @ MCNT were acquired on a Philips CM200 FEG transmission electron microscope operated at 200 KV, showing the MCNT was covered with amorphous spherical FePO$_4$ nanoparticles.

The BET surface areas of samples were measured using Quantachrome Nova Station A by nitrogen sorption at 77K. The surface areas of FePO$_4$ and FePO$_4$@MCNT are 117.691 m$^2$/g and 114.927 m$^2$/g, respectively. The lower value of FePO$_4$@MCNT should be ascribed to one side of amorphous FePO$_4$ nanoparticle loaded on the MCNT.

Fig. S3 The charge and discharge Curves of the initial two cycles of FePO$_4$@MCNT at 0.1 C. The composite delivered discharge and charge capacities of 155.2 mAh g$^{-1}$ and 128.7 mAh g$^{-1}$ in the first cycle; 120.4 mAh g$^{-1}$ and 141.5 mAh g$^{-1}$ in the second cycle.
FEPOMCN-650℃
FEPOMCN-460℃
FePO4-650℃
FePO4-460℃

Intensity (a.u.)

2 Theta (Degree)

(a)
Fig. S4 (a) XRD patterns of FePO$_4$ and the FePO$_4$@MCNT composite at different calcination temperatures (460°C, 650°C). (b) The charge-discharge Curves of FePO$_4$ at different calcination temperatures. (c) The charge-discharge Curves of the FePO$_4$@MCNT composite at different calcination temperatures. As shown in Fig. S4 (a), amorphous FePO$_4$ completely changes to crystalline trigonal FePO$_4$ at 650°C in air. From Fig. S4 (b), the amorphous FePO$_4$ delivered discharge and charge capacities of 133.6 mAh g$^{-1}$ and 102.3 mAh g$^{-1}$ in the first cycle, but the trigonal FePO$_4$ just delivered discharge and charge capacities of
69.2 mAh g\(^{-1}\) and 50.7 mAh g\(^{-1}\), which is consistent with the poor electrochemical behavior in Li-ion batteries.\(^{28}\)

It can be seen from Fig. S4 (a) that the FePO\(_4\)@MCNT composite also shows the 26.8° diffraction peak of the MCNTs at 650°C in N\(_2\). But the other peaks should be ascribed to the carbon thermal reduction of Fe\(^{3+}\) to Fe\(^{2+}\), owing to the MCNTs and organic residues calcined at high temperature in N\(_2\). As shown in Fig. S4 (c), the FePO\(_4\)@MCNT (650°C) composite only delivered discharge and charge capacities of 71.7 mAh g\(^{-1}\) and 76.7 mAh g\(^{-1}\) in the first cycle. It is demonstrated that FePO\(_4\)@MCNT (460°C) composite has better electrochemical performance than FePO\(_4\)@MCNT (650°C).