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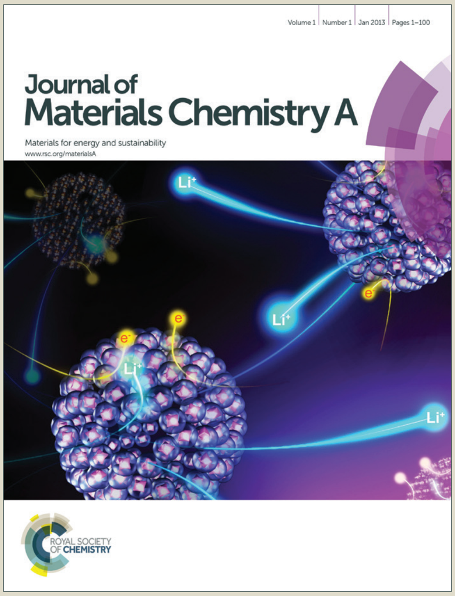

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Maize-like $FePO_4$@MCNT nanowire composite for sodium-ion batteries via a microemulsion technique

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Abstract: In this study, a microemulsion technique was applied to prepare an in-situ self-assembled core-shell $FePO_4$@MCNT nanowire composite as a cathode material for sodium-ion batteries. Multi-walled carbon nanotubes (MCNTs) were uniformly dispersed using Triton X-100 as a surfactant in the microemulsion system. Subsequently, amorphous $FePO_4$ nanoparticles with a diameter of 10-20 nm were loaded onto the surface of MCNTs during the synthetic process, forming an $FePO_4$@MCNT nanowire composite with three-dimensional mixed conducting networks, with a structure resembling maize. The resulting products were collected by centrifugation and washed three times, and sintered under an N_2 atmosphere at 460ºC for 3 h. The discharge specific capacity of $FePO_4$@MCNT was 155.2 mAh g^{-1} in the initial cycle, which was maintained at 157.2 mAh g^{-1} after 70 cycles at 0.1C. The discharge specific capacity at 0.3C, 0.5C, and 1.0C was 133.2 mAh g^{-1}, 122.2 mAh g^{-1}, and 75.3 mAh g^{-1}, respectively, in the range of 1.5–4.2V. The results show that $FePO_4$@MCNT nanowires are a promising candidate as a cathode material in sodium-ion batteries.

Key words: Sodium-ion battery, Cathode material, Microemulsion technique, Iron phosphate, Multi-walled carbon nanotubes

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1. Introduction

In recent years, with an emphasis on environmental protection and increased interest in renewable energy sources, researchers around the world have begun to use lithium-ion batteries as medium- and large-scale energy storage units in electric vehicles, smart grids, solar and wind energy storage systems.[1,2] Lithium-ion batteries have been widely used in mobile phones, tablet PCs, and portable electronic devices due to their high energy density as well as good rate and cycle performance.[3] Li-ion batteries have many advantages, but lithium is not abundant in the earth's crust. Many global lithium reserves and resources are located in remote or politically sensitive areas, so increasing lithium utilization in medium-scale automotive batteries will ultimately push up the price of lithium compounds, thereby making large-scale storage prohibitively expensive.[4,5] For these reasons, the development of rechargeable batteries for large-scale energy systems using abundant resources and cheap raw materials has become inevitable. Sodium has many similar chemical properties to lithium, and sodium is abundant, inexpensive and environmentally friendly. Thus, sodium-ion batteries are considered to be a suitable alternative to lithium-ion batteries in large-scale energy storage systems.[6-8] A considerable number of studies on cathode materials for sodium-ion batteries have been reported recently, such as Na_xCoO_2,[9] $Na_{0.44}MnO_2$,[10,11] $Na_{0.6}MnO_2$,[12] $NaCrO_2$,[13,14] Na_xVO_2,[15] $Na_3V_2(PO_4)_3$,[16,17] $Na_3V_2(PO_4)_2F_3$,[18] $Na_3V_2O_2(PO_4)_2F$,[19] Na_2FePO_4F,[20] and $NaFeF_3$.[21] Like the olivine $LiFePO_4$, the sodium analogue compound, olivine $NaFePO_4$, has also been investigated by researchers; however, olivine $NaFePO_4$ exhibits unsatisfactory electrochemical performance in sodium-ion batteries.[22,23]

As an electrochemically delithiated product of $LiFePO_4$, orthorhombic $FePO_4$ has also been proposed as a cathode material[24], but this cannot be prepared via a direct chemical synthetic route. Researchers have focused on other structures of $FePO_4$ that can be easily synthesized and are electrochemically active.[25-28] Results have shown that amorphous $FePO_4$ has high electrochemical activity and better electrochemical performance than trigonal $FePO_4$ in lithium-ion batteries.[28] The amorphous $FePO_4$ material is considered a conceptually defect-free phase,[29] which benefits the diffusion

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of lithium ions and the electronic conductivity of $FePO_4$ cathode materials. $FePO_4$ has many advantages as an electrode material. First of all, Fe(III) compounds are abundant, inexpensive and easily available raw materials. Moreover, the synthesis process of $FePO_4$ is simple, environmentally friendly, and does not require a protective atmosphere. Finally $FePO_4$ shows a theoretical specific capacity as high as 178 mAh g^{-1}.[30] Nevertheless, $FePO_4$ materials also suffer from poor electronic conductivity and lower diffusion coefficients of lithium ions; therefore, a variety of methods has been used to improve the electrochemical properties of $FePO_4$. For example, the synthesis of nano-sized particles,[28,31] ion doping,[32] the preparation of mesoporous structures,[33] or combination with conductive materials[34,35] has been performed in order to enhance the electrochemical performance of $FePO_4$ in lithium-ion batteries. Carbon coating also is a practical technique which not only improves the electrical conductivity of the electrode, but also increases the stability of the active material through reducing the surface materials with the electrolyte during charge−discharge cycling.[36] However, because of the easy reduction of Fe^{3+} to Fe^{2+} during the carbon-heat reduction process, $FePO_4$ cannot be coated with carbon using the conventional carbon-heat reduction method. As a high-performance carbon material, CNTs have been widely used in studies on Li-ion batteries. Carbon nanotubes can play a variety of roles in electrode materials, i.e. as a sacrificial template,[37] conductive agent,[38] and conductive scaffold.[35,39]

Since the discovery of carbon nanotubes (CNTs) in the 1990s,[40] these materials have attracted enormous interest in recent years due to their excellent electrical, chemical, and mechanical properties, which make them suitable for developing nano-electronics, electrochemical sensors, and biosensors.[41] CNTs exhibit strong van der Waals (vdW) interactions between tubes[42] and high aspect ratios (length to diameter ratio, L/D).[43] The latter feature provides nanotubes with an additional advantage over spherical fillers, evenly be wrapped around with DNA[44] to obtain composites with excellent properties. However, wrapped bundles of carbon nanotubes are generally difficult to disperse, and cannot be uniformly dispersed in water or organic solvents.[45] The agglomeration CNTs limits their applications in many fields.

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Much effort has been exerted to develop approaches to provide homogenous dispersions of individual carbon nanotubes. Among these, the surface modification of carbon nanotubes has become a good way to improve the dispersion stability of CNTs. There are two main approaches to the surface modification of carbon nanotubes: non-covalent attachment of molecules and covalent attachment of functional groups to the walls of the nanotubes.[46] Non-covalent functionalization of carbon nanotubes by surface-active agents is particularly attractive, because of the possibility of absorbing various functional groups on the CNT surface without altering the perfect structure of the nanotubes. Thus, the mechanical and electrical properties of CNTs can be preserved. In the last few years, non-covalent surface treatment by surfactants or polymers has been widely used in the preparation of both aqueous and organic solutions to obtain high weight fractions of individually dispersed nanotubes.[45]

In the present work, we considered preparing amorphous $FePO_4$ as spherical nanoparticles, which could be loaded onto the surface of multi-walled carbon nanotubes (MCNTs), and then fabricating an $FePO_4$@MCNT core-shell nanowire composite with a “maize-like” structure. Compared with the considerable body of research on Li-ion batteries, the number of papers published on amorphous $FePO_4$ as a cathode material for sodium ion batteries is considerably less. For example, Liu et al.[47] prepared amorphous porous $FePO_4$ nanoparticles connected by single-walled carbon nanotubes, and used this nanocomposite as the cathode material in Na-ion batteries. However, this involved only a simple physical connection between the $FePO_4$ particles and the single-walled carbon nanotubes.

To our knowledge, maize-like $FePO_4$@MCNT core-shell nanowire composites as cathodes for Na-ion batteries through using non-covalent treatment have not been reported. In the previews study, CNT-amorphous $FePO_4$ core–shell nanowires as cathodes for Li ion batteries were fabricated by functionalizing multi-walled CNTs with carboxylic groups (–COOH) via acid treatment and also by mineralizing them with $FePO_4$ in aqueous phase.[35] These composites are expected to contribute to the facile transport of Na ions and electrons. A simple microemulsion method was applied to produce the $FePO_4$@MCNT nanowire composite. The microemulsion system,

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using Triton X-100 as a non-ionic surfactant, can provide uniform MCNT dispersions through non-covalent surface treatment.[48] Consequently, this composite was successfully fabricated and used as cathode materials for sodium-ion batteries. A high specific capacity and high rate capability were demonstrated by investigating the electrochemical performance of this material.

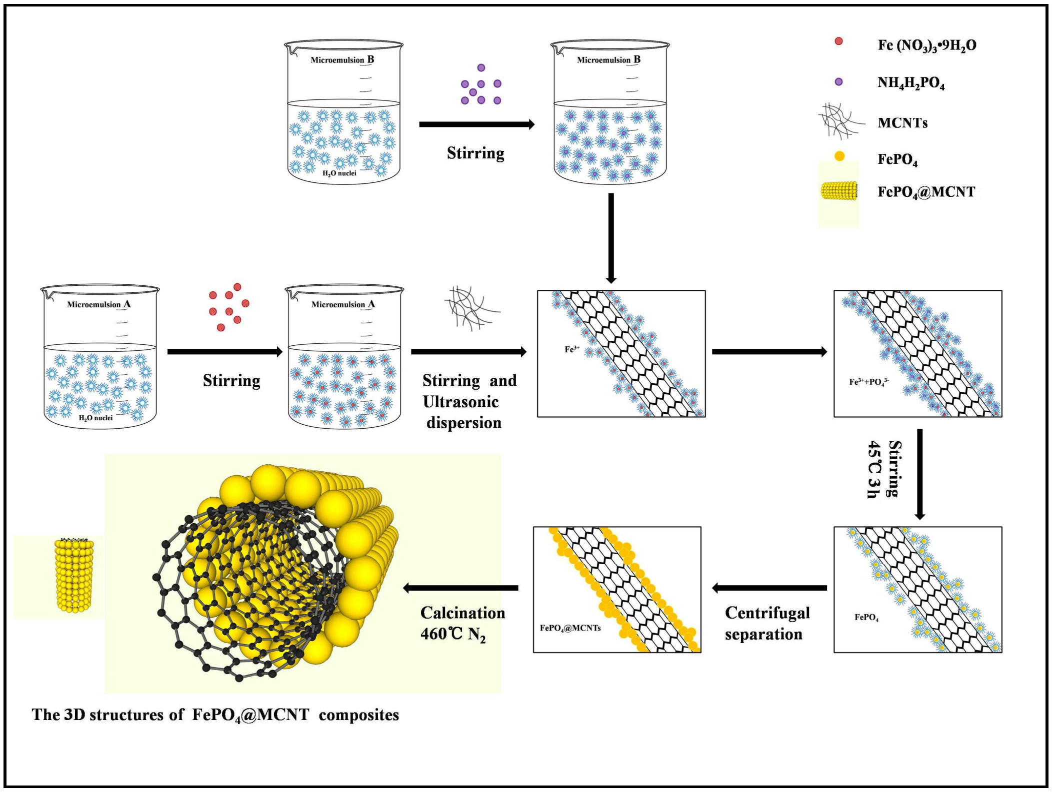

Fig. 1 Synthesis scheme of the $FePO_4$@MCNT composite by a microemulsion technique

2. Experimental

2.1 Material preparation

In the experiment, all the chemicals and reagents used were of analytical reagent grade without further purification. Two 105 ml H_2O/cyclohexane/Triton X-100/n-butylalcohol microemulsion systems were prepared in a volume ratio of 35:25:15:5, designated A and B, differing only in the aqueous phase. The aqueous phase of microemulsion A was a reactant solution with 0.01 mol $Fe(NO_3)_3$•$9H_2O$. The

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aqueous phase of microemulsion B was a precipitant solution with 0.01 mol $NH_4H_2PO_4$. 30% MCNTs (mass ratio of $FePO_4$ to $FePO_4$@MCNT) were added into microemulsion A. The suspension was vigorously stirred for 30 min and ultrasonically dispersed for 1 h, and then transferred into a glass reaction kettle. Microemulsion B was slowly dropped into microemulsion A under constant stirring at 350 r/min for 30 min (at room temperature), then the solution continued to be stirred at 45°C at pH 2.6 for 3 h, followed by aging for 3 h. The syntheses are outlined in Fig. 1. In the first step, MCNTs were uniformly dispersed in microemulsion A with $Fe(NO_3)_3•9H_2O$ through ultrasonic treatment and hydrophobic microcapsule containing Fe^{3+} ions could be adsorbed onto the surface of the nanotubes. In the second step, microemulsion B with $NH_4H_2PO_4$ was added to microemulsion A to allow for heterogeneous nucleation. In the third step, the $FePO_4$ crystal nuclei grew along the surface of the MCNTs during the synthesis process, forming an in-situ self-assembled $FePO_4$@MCNT nanowire composite. Ultimately, the products were obtained by centrifugal separation, and washed with ethanol several times to remove the microemulsion. The obtained precipitates were dried at 100°C for 12 h, and then calcined at 460°C for 3 h in an N_2 atmosphere.

2.2 Material characterization

The crystal structure and crystalline phases of the samples were identified by powder X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. The diffraction angle (2θ) from 20° to 90° was scanned, at a step size of 0.01° and a rate of 2°/min. For morphological analysis, a scanning electron microscopic (SEM) study of the samples was performed using a Hitachi SU-70 Schottky field emission gun scanning electron microscope.

2.3 Electrode preparation

The composite cathode electrodes were prepared by ball-milling with a mixture of active materials, conductive materials (acetylene black), and a binder (polytetra-fluoroethylene, PTFE) in a weight ratio of 62:30:8. The average mass of

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composite loading on the electrode was 15 mg; then, the electrode sheet was dried in a vacuum oven at 120°C overnight. All the working electrodes were stored in an Ar-filled Mikrouna glove box before use.

2.4 Electrochemical characterization

The characterization of the electrochemical properties of the $FePO_4$@MCNT nanowire composite was accomplished using a CR2016-type coin cell. Na-ion batteries were assembled with sodium foil as the anode electrode, 1 M $NaClO_4$ in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 by volume) as the electrolyte, and a glass fiber mat as the separator. All the test batteries were assembled in a Mikrouna glove box filled with a highly purified argon atmosphere (moisture and oxygen contents lower than 1 ppm). Charge-discharge tests were performed at a voltage in the range of 1.5 V–4.2 V using a Land CT2001A battery test system. The capacity was calculated on the basis of the mass of $FePO_4$, which is the active material of the composite and the mass of MCNT has been deducted. The electrochemical impedance spectrum tests were performed on a Chenghua CHI660C electrochemical workstation. The AC perturbation signal was 5 mV, and the frequency range was from 0.01 Hz to 100 kHz. The EIS parameters were fitted using ZView2 software. All tests were performed at room temperature (25ºC).

3. Results and discussion

Fig. 2 shows the powder XRD patterns of the pure $FePO_4$ samples and as-prepared $FePO_4$@MCNT composite. From the XRD pattern of the $FePO_4$@MCNT composite, it can be seen that there was a broad peak at 26.8° without another observable crystalline Bragg peak. The 26.8° diffraction peak corresponds to the characteristic peak of the (0 0 2) crystal plane of the MCNTs, in good agreement with prior report.[49] Moreover, the result also indicates that the $FePO_4$ particles covered the MCNT core in a fully amorphous structure.

Fig. 3a shows a scanning electron microscopy (SEM) image of the multi-walled carbon nanotubes; the average diameter of the individual nanotubes was about 78 nm.

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Fig. 3b shows an SEM image of pure amorphous $FePO_4$ which followed the same syntheses route without MCNTs, yielding homogenous spherical nanoparticles with an average diameter of about 20 nm. SEM images of the as-prepared $FePO_4$@MCNT nanowire composite observed at different magnifications are shown in Fig. 3c-d. The spherical amorphous $FePO_4$ nanoparticles were closely loaded onto the surface of MCNTs, forming the $FePO_4$@MCNT core-shell nanowire composite with a maize-like structure. In addition, the diameter of the nanowires was estimated to be about 114 nm, which means that the $FePO_4$ nanoparticles adhered to the MCNTs as a single shell. Each MCNT was coated with a layer of $FePO_4$ nanoparticles, and the $FePO_4$@MCNT nanowire composite was uniformly dispersed.

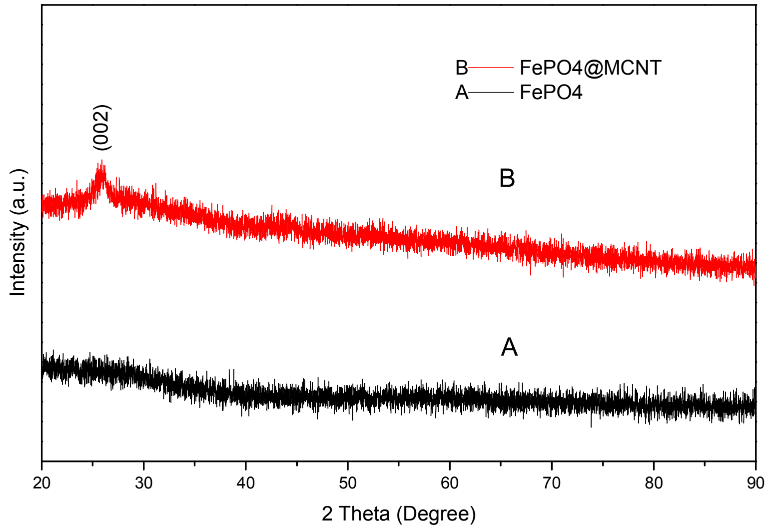
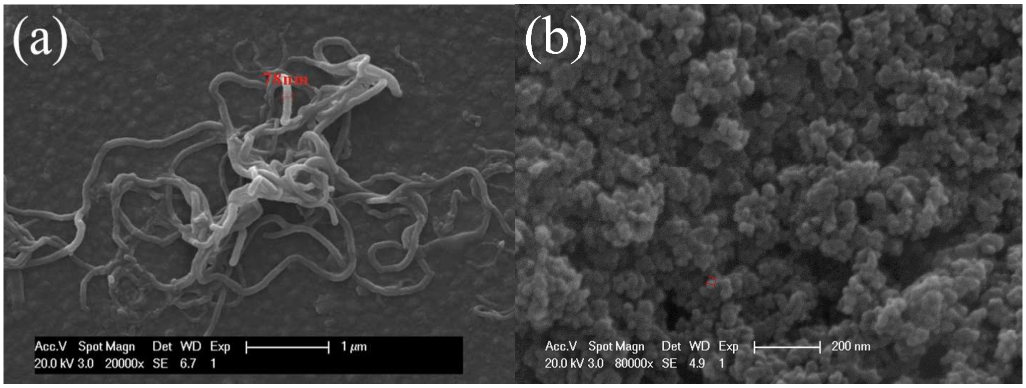


Fig. 2 XRD patterns of $FePO_4$ and the $FePO_4$@MCNT composite.



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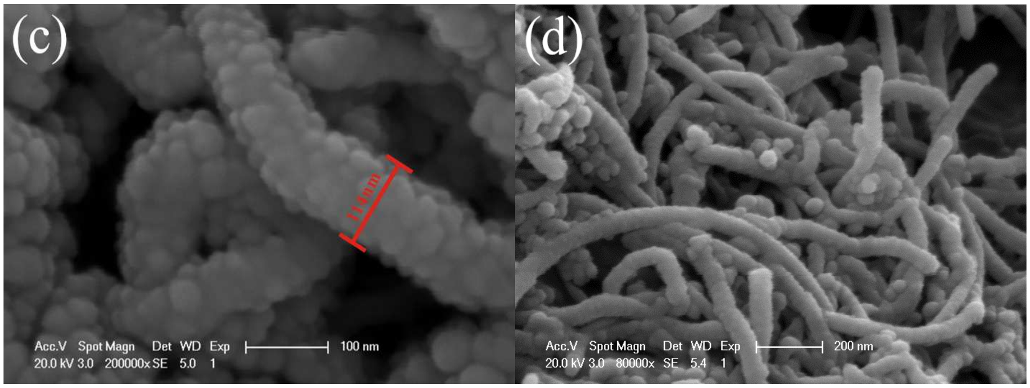

Fig. 3 SEM images of (a) MCNTs, (b) $FePO_4$ and (c, d) the $FePO_4$@MCNT composite.

Fig. 4 shows the discharge specific capacity versus cycle number of $FePO_4$ and the $FePO_4$@MCNT composite at 0.1C. According to the profile, the first discharge specific capacity of pure amorphous $FePO_4$ was 133.6 mAh g^{-1}, which was maintained at 123.3 mAh g^{-1} after 30 cycles, i.e. only 69% of the theoretical capacity (178 mAh g^{-1}). In comparison, the first discharge specific capacity of $FePO_4$@MCNT was up to 155.2 mAh g^{-1}, which was maintained at 150.5 mAh g^{-1} after 30 cycles, i.e. 85% of the theoretical capacity. The results clearly show that the $FePO_4$@MCNT composite, as a cathode material, had an obviously higher discharge capacity than pure $FePO_4$ for sodium-ion batteries; moreover, such a remarkable capacity is higher than most reported value of cathode materials for sodium-ion batteries.[10-18] In addition, the unusual discharge behavior of the two materials was also noted in Fig. 4. The discharge specific capacities of $FePO_4$ and the $FePO_4$@MCNT composite all decreased at first and then increased during the initial few cycles, and gradually stabilized after about 15 cycles. This phenomenon has not been observed or mentioned in study of using amorphous $FePO_4$ for lithium-ion batteries.

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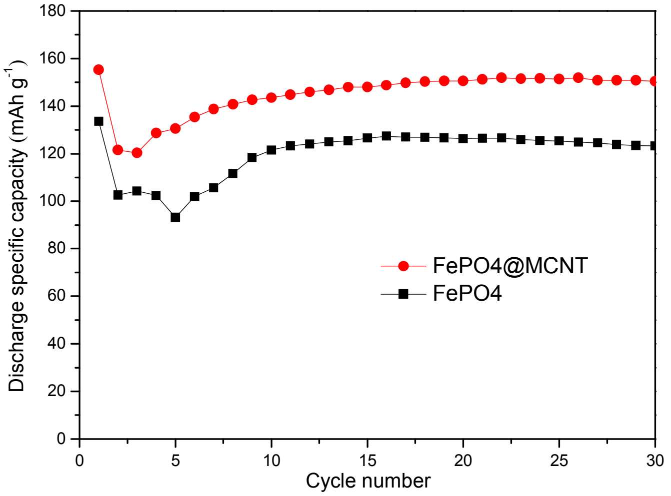

Fig. 4 Discharge specific capacity versus cycle number for $FePO_4$ and the $FePO_4$@MCNT composite at 0.1C.

The 30th charge-discharge profiles of $FePO_4$ and the $FePO_4$@MCNT composite at 0.1C are shown in Fig. 5. Unlike crystalline materials, for instance the olivine $LiFePO_4$ cathode for Li-ion batteries which shows a clear potential plateau near 3.4 V, all of the presented charge-discharge curves show a smooth slope, which is a typical feature of the amorphous structure of $FePO_4$.[47] This feature is also observed in Li-ion batteries, and be considered an advantage in monitoring the state of the charge and discharge process during battery operation.

The cycling stability and coulombic efficiency of the $FePO_4$@MCNT composite at 0.1C is shown in Fig. 6. According to the profiles, the $FePO_4$@MCNT composite delivered discharge and charge capacities as high as 155.2 mAh g^{-1} and 128.7 mAh g^{-1} in the first cycle, corresponding to a coulombic efficiency of 120.6%. The coulombic efficiency of the 30th and 70th cycles was 93.9% and 95.9%, respectively. Meanwhile, the 70th discharge and charge capacities of $FePO_4$@MCNT composite were still remained at 157.2 mAh g^{-1} and 163.9 mAh g^{-1}. The facile sodium ion diffusion through the outer $FePO_4$ single shell and the fast electron transport through the MCNT core were responsible for the observed high Na-storage capacity, good cycling stability and coulombic efficiency.

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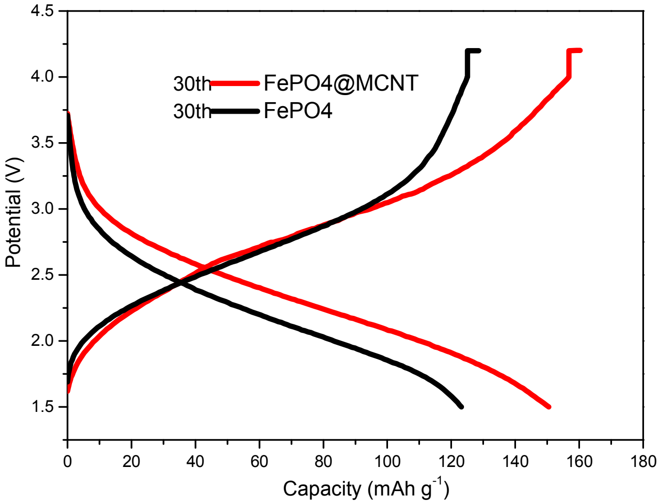

Fig. 5 The 30th charge-discharge profile of $FePO_4$ and the $FePO_4$@MCNT composite at 0.1C.

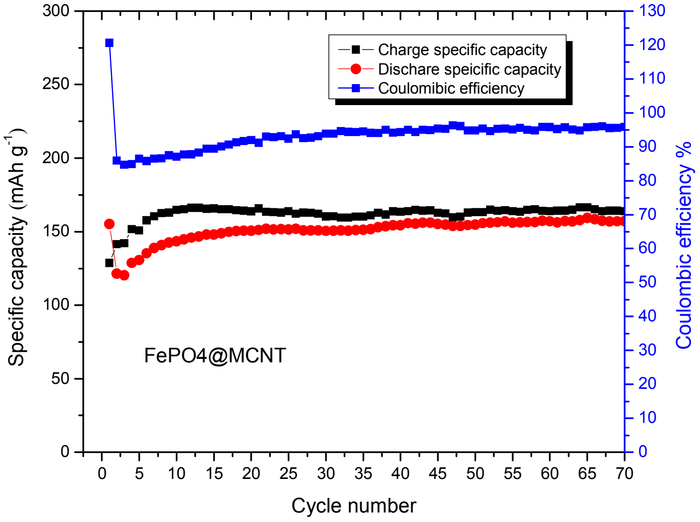

Fig. 6 The cycling stability and coulombic efficiency of $FePO_4$@MCNT at 0.1 C.

The rate performance of electrodes for sodium-ion batteries has been rarely mentioned or unsatisfactory in previous studies. For instance, Jian et al.[16] prepared carbon-coated $Na_3V_2(PO_4)_3$ with an initial discharge capacity of 93 mAh g^{-1} at 0.05C, but this was only 29 mAh g^{-1} at 1C in the range of 2.7-3.8V. Kawabe et al.[20] investigated carbon-coated Na_2FePO_4F, with an initial discharge capacity of 110 mAh

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g^{-1} at 1/20C, but delivered approximately 55 mAh g^{-1} at 1C in the range of 2.0-3.8V. Therefore, we also studied the rate capability of $FePO_4$ and the $FePO_4$@MCNT composite in Na-ion batteries. Fig. 7 shows the discharge specific capacities of the $FePO_4$ and the $FePO_4$@MCNT composite at 0.1C, 0.3C, 0.5C, and 1C, respectively. The reversible capacity of $FePO_4$ was 123.2 mAh g^{-1}, 105.2 mAh g^{-1}, 64.1 mAh g^{-1}, and 38.1 mAh g^{-1} at 0.1C, 0.3C, 0.5C, and 1C, respectively. In stark contrast, the reversible capacity of the $FePO_4$@MCNT composite was 150.5 mAh g^{-1}, 133.2 mAh g^{-1}, 122.2 mAh g^{-1}, and 75.3 mAh g^{-1} at 0.1C, 0.3C, 0.5C, and 1C, respectively. Accordingly, the outstanding rate performance of the $FePO_4$@MCNT composite as a cathode material for sodium-ion batteries was strongly indicated by the data. In order to explain these experimental results, we provide a diagram to describe the transition process of electrons and sodium ions in the $FePO_4$@MCNT composite during Na-ion battery discharge.

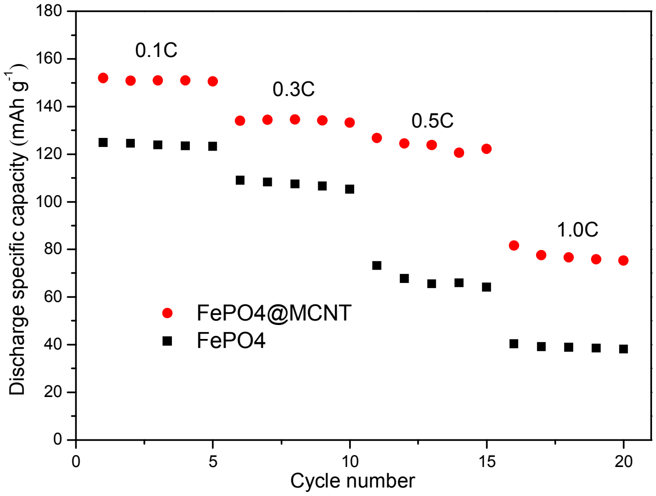

Fig. 7 Rate capability curves of $FePO_4$ and the $FePO_4$@MCNT composite.

Fig. 8 shows an image of the transition process in this unique core-shell maize-like composite. In the core area, a fast electron conduction path of the composite was obtained because of the specific three-dimensional (3D) electron conductive network of MCNTs. It has been reported that the effective electrical

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conductivity of MCNT films in the longitudinal and transverse directions is $\sigma_{\square} = (1\sim4) \times10^4\ \Omega^{-1}\ m^{-1}$ and $\sigma_{\perp} = (5\sim25) \times10^2\ \Omega^{-1}\ m^{-1}$, respectively.[50] In addition, the close adhesion between MCNTs and amorphous $FePO_4$ could ensure that electrons transmit through the interface efficiently. Thus, electrons can quickly move into each low electrical conductive amorphous $FePO_4$ nanoparticle along the sidewall of MCNTs by means of an area-to-point transition before the charge transfer reaction. In the outer shell, sodium ions insert into the surface of $FePO_4$ particles at almost the same time. The facile sodium ion diffusion through the outer $FePO_4$ single shell occurs for two main reasons. On the one hand, the nano-scale size can effectively increase the specific surface area, which ensures a high electrode−electrolyte interface area and enhances the interface reaction; on the other hand, nanoparticles benefit from the movement of sodium ions along the diffusion direction and shorten the pathway for sodium ion diffusion in the active materials.[51] Furthermore, spherical particles, unlike other shapes such as cubic,[52] have a higher specific surface and volumetric specific capacity than irregular particles;[53] this is beneficial to electrochemical performance.[54] Consequently, the unique structure of the $FePO_4$@MCNT composite effectively improves the sodium ion and electron diffusion rates in Na-ion batteries. A high specific capacity and high rate capability of this cathode material was obtained, as expected.

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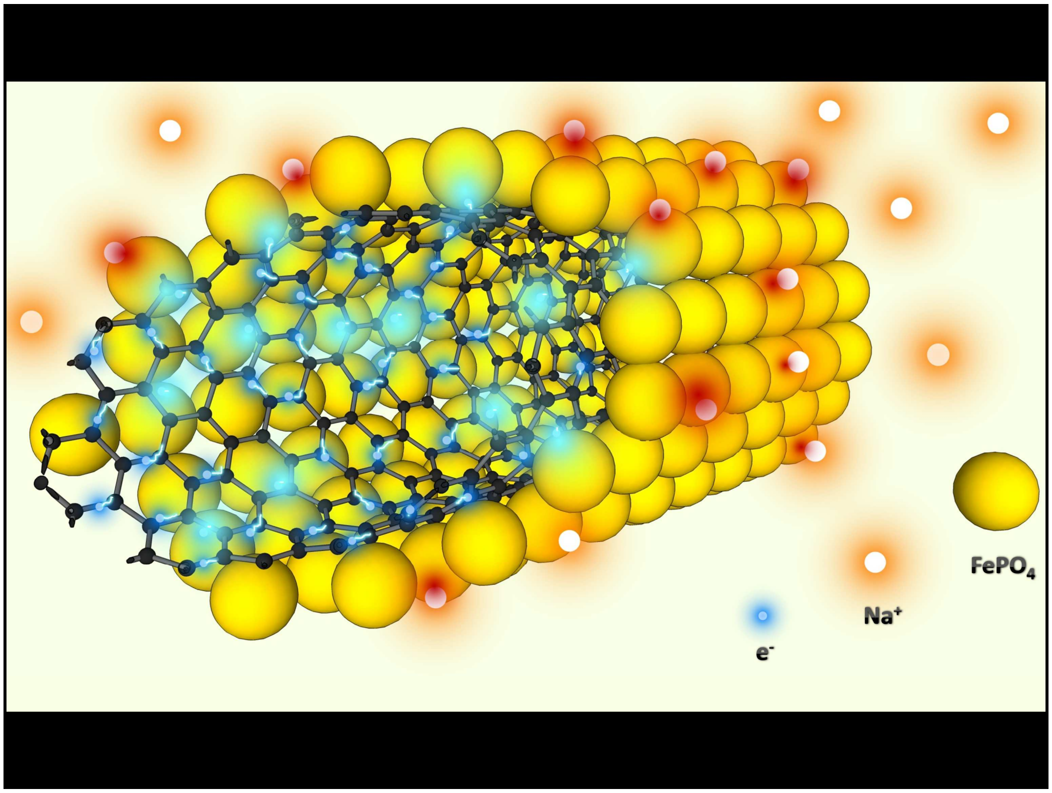

Fig. 8 The scheme of the transition processes of electrons and sodium ions in the FePO$_4$@MCNT composite during sodium ion insertion into FePO$_4$

In order to further illustrate the effect of MCNTs on the improved electrochemical performance of the cathode material, electrochemical impedance spectroscopy (EIS) experiments were carried out in coin cells. Fig. 9(a) shows the electrochemical impedance spectroscopy (EIS) spectra of FePO$_4$ and the FePO$_4$@MCNT composite. The Nyquist plots of the two cathodes in this figure include a depressed semicircle at high and medium frequencies, which relates to the charge transfer process on the electrode surface, followed by a linear section at low frequencies, which relates to the diffusion of sodium ions in the electrode. Fig. 9(b) shows the corresponding equivalent circuit. Rs represents the electrolyte resistance; CPE and Rct represent constant phase element and charge transfer resistance, respectively. The charge transfer resistance can be calculated according to the depressed semicircle; Zw represents the diffusion controlled Warburg impedance.[55] The fitted impedance parameters, according to the equivalent circuit, are presented in Table 1. It can be seen in Table 1 that the Rct values of FePO$_4$ and the FePO$_4$@MCNT

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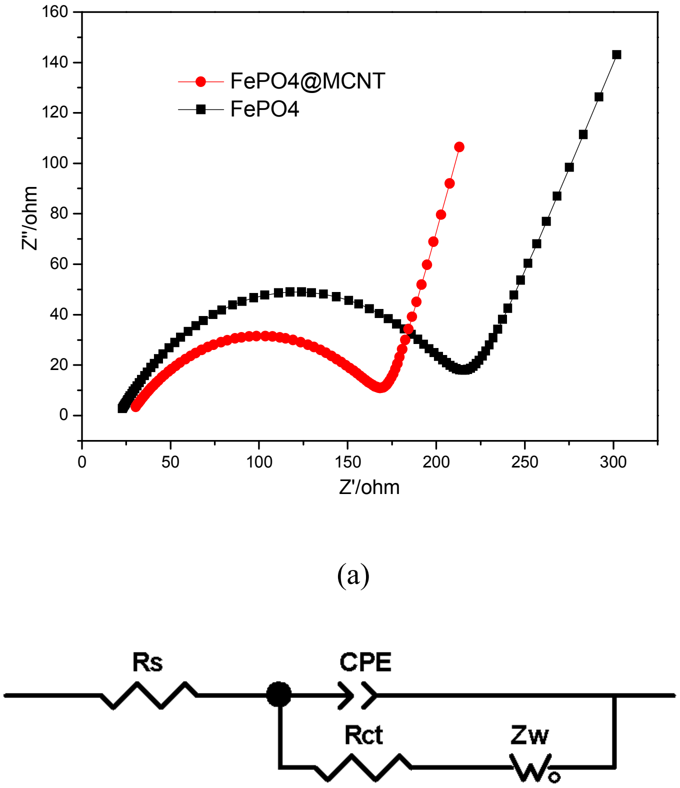
composite were 199.3 Ω and 147.8 Ω, respectively. Thus, the EIS results demonstrate that the Rct value of the $FePO_4$@MCNT composite was far lower than that of pure $FePO_4$, implying a smaller charge transfer resistance and higher electronic conductivity due to the influence of MCNT hybridization with $FePO_4$.



(a)

(b)

Fig. 9 Electrochemical impedance spectra (a) and equivalent circuit (b) of $FePO_4$ and the $FePO_4$@MCNT composite.

Table 1 Fitted EIS parameters of $FePO_4$ and the $FePO_4$@MCNT composite.

Sample	$FePO_4$	$FePO_4$@MCNT
Rs(Ω)	20.81	26.88
CPE-T	0.00012728	0.00021465
CPE-P	0.57954	0.51277
Rct(Ω)	199.3	147.8

4. Conclusions

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A new type of maize-like $FePO_4$@MCNT composite to be used as the cathode material in sodium-ion batteries was synthesized via a microemulsion processing route. Using Triton X-100 as a non-ionic surfactant, MCNTs were uniformly dispersed and successfully covered with amorphous $FePO_4$ nanoparticles through non-covalent functionalization. The unique structure of the core-shell nanowires and the 3D electron conductive network of the MCNT core contributed to the facile transport of Na ions and electrons. Consequently, the $FePO_4$@MCNT composite showed excellent electrochemical performance with discharge specific capacities as high as 155.2 mAh g^{-1}, which was sustained at 157.2 mAh g^{-1} after 70cycles at 0.1C; 75.3 mAh g^{-1} was obtained at 1C. The high specific capacity, high rate capability and good stability demonstrate that these $FePO_4$@MCNT nanowires are a promising cathode for Na-ion batteries. Especially, because of the low cost and environmentally benign synthesis, this kind of carbon-based composite material has good commercial prospects in large-scale energy storage systems.

Acknowledgments

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References

[1] M. Armand and J. M. Tarascon, *Nature*, 2008, 451, 652–657.

[2] B. Dunn, H. Kamath and J. M. Tarascon, *Science*, 2011, 334, 928–935.

[3] J. M. Tarascon and M. Armand, *Nature*, 2011, 414, 359–367.

[4] A. Yaksic and J. E. Tilton, *Resour. Policy*, 2009, 34, 185–194.

[5] B. L. Ellis and L. F. Nazar, *Curr. Opin. Solid State Mater. Sci.*, 2012, 16, 168–177.

[6] S. W. Kim, D. -H. Seo, X. Ma, G. Ceder and K. Kang, *Adv. Energy Mater.*, 2012, 2, 710–721.

Journal of Materials Chemistry A Accepted Manuscript

[7] V. Palomares, P. Serras, I. Villaluenga, K. B. Hueso, J. C. Gonzalez and T. Rojo, *Energy Environ. Sci.*, 2012, 5, 5884–5901.

[8] M. D. Slater, D. Kim, E. Lee and C. S. Johnson, *Adv. Func. Mater.*, 2012, 23, 947–958.

[9] R. Berthelot, D. Carlier and C. Delmas, *Nat. Mater.*, 2011, 10, U73–U74.

[10] F. Sauvage, L. Laffont, J. M. Tarascon and E. Baudrin, *Inorg. Chem.*, 2007, 46, 3289–3294.

[11] E. Hosono, T. Saito, J. Hoshino, M. Okubo, Y. Saito, D. N. Hamane, T. Kudo and H. S. Zhou, *J. Power Sources*, 2012, 217, 43–46.

[12] A. Caballero, L. Hernán, J. Morales, L. Sánchez, J. S. Peña and M. A. G. Aranda, *J. Mater. Chem.*, 2002, 12, 1142–1147.

[13] S. Komaba, C. Takei, T. Nakayama, A. Ogata and N. Yabuuchi, *Electrochem. Commun.*, 2010, 12, 355–358.

[14] J. J. Ding, Y. N. Zhou, Q. Sun and Z. W. Fu, *Electrochem. Commun.*, 2012, 22, 85–88.

[15] D. Hamani, M. Ati, J. M. Tarascon and P. Rozier, *Electrochem. Commun.*, 2011, 13, 938–941.

[16] Z. L. Jian, L. Zhao, H. L. Pan, Y. S. Hu, H. Li, W. Chen and L. Q. Chen, *Electrochem. Commun.*, 2012, 14, 86–89.

[17] J. W. Kang, S. Baek, V. Mathew, J. Gim, J. J. Song, H. Park, E. Chae, A. K. Rai and J. Kim, *J. Mater. Chem*., 2012, 22, 20857-20860.

[18] J. Barker, R. K. B. Gover, P. Burns and A. J. Bryan, *Electrochem. Solid-State Lett.*, 2006, 9, A190–A190.

[19] F. Sauvage, E. Quarez, J. M. Tarascon and E. Baudrin, *Solid State Sci.*, 2006, 8, 1215–1221.

[20] Y. Kawabe, N. Yabuuchi, M. Kajiyama, N. Fukuhara, T. Inamasu, R. Okuyama, I. Nakai and S. Komaba, *Electrochem. Commun.*, 2011, 13, 1225–1228.

[21] Y. Yamada, T. Doib, I. Tanaka, S. Okada and J. Yamaki, *J. Power Sources*, 2011, 196, 4837–4841.

[22] P. Moreau, D. Guyomard, J. Gaubicher and F. Boucher, *Chem. Mater.*, 2010, 22, 4126–4128.

[23] K. Zaghib, J. Trottier, P. Hovington, F. Brochu, A. Guerfi, A. Mauger and C. M. Julien, *J. Power Sources*, 2011, 196, 9612–9617.

[24] S. F. Yang, Y. N. Song, P. Y. Zavalij and M. S. Whittingham, *Electrochem. Commun.*, 2002, 4, 239–244.

[25] C. Masquelier, P. Reale, C. Wurm, M. Morcrette, L. Dupont and D. Larcher, *J. Electrochem.*

Journal of Materials Chemistry A Accepted Manuscript

Soc., 2002, 149, A1037–A1044.

[26] Y. N. Song, S. F. Yang, P. Y. Zavalij and M. S. Whittingham, *Mater. Res. Bull.*, 2002, 37, 1249–1257.

[27] Y. B. Xu, Y. J. Lu, P. Yin, L Yan, Z. Y. Yang and R. D. Yang, *J. Mater. Process., Technol.*, 2008, 204, 513–519.

[28] S. M. Zhang, J. X. Zhang, S. J. Xu, X. J. Yuan and B. C. He, *Electrochimica. Acta*, 2013, 88, 287–293.

[29] B. Abeles and T. Tiedje, *Phys. Rev. Lett.*, 1983, 51, 2003–2006.

[30] C. Gerbaldi, G. Meligrana, S. Bodoardo, A. Tuel and N. Penazzi, *J. Power Sources*, 2007, 174, 501–507.

[31] H. J. Yang, H. J. Song, H. J. Shin and H. C. Choi, *Langmuir*, 2005, 21, 9098–9102.

[32] X. Yang, S. M. Zhang, J. X. Zhang, M. Y. Xu, P. Ren and X. C. Li, *Funct. Mater. Lett.*, 2011, 4, 323–326.

[33] Z. C. Shi, Y. X. Li, W. L. Ye and Y. Yang, Electrochem. *Solid-State Lett.*, 2005, 8, A396–A399.

[34] Y. Yin, Y. Hu, P. Wu, H. Zhang and C. Cai, *Chem. Commun.*, 2012, 48, 2137–2139.

[35] S. W. Kim, J. Ryu, C. B. Park and K. Kang, *Chem. Commun.*, 2010, 46, 7409–7411.

[36] X. F. Zhang, K. X. Wang, X. Wei and J. S. Chen, *Chem. Mater.*, 2011, 23, 5290–5292.

[37] W. Tang, Y. Y. Hou, F. X. Wang, L. L. Liu, Y. P. Wu and K. Zhu, *Nano Lett.*, 2013, 13, 2036–2040.

[38] Y. K. Zhou, J. Wang, Y. Y. Hu, O'Hayre. R and Z. P. Shao, *Chem. Commun.*, 2010, 46, 7151–7153.

[39] Z. Chen, D. Q. Zhang, X. L. Wang, X. L. Jia, F. Wei, H. X. Li and Y. F. Lu, *Adv. Mater.*, 2012, 24, 2030–3026.

[40] S. Ijima, *Nature*, 1991, 354, 56–58.

[41] M. Nagaraja, H. M. Mahesh, J. Manjanna, K. Rajanna, M. Z. Kurian and S. V. Lokesh, *J. Electron. Mater.*, 2012, 41, 1882–1885.

[42] T. Yamamoto, S. Noda and M. Kato, *Carbon*, 2011, 49, 3179–3183.

[43] E. T. Thostenson, C. Y. Li and T. W. Chou, *Compos. Sci. Technol.*, 2005, 65, 491–516.

[44] Q. H. Yang, Q. Wang, N. Gale, C. J. Oton, L. Cui, I. S. Nandhakumar, Z. P. Zhu, Z. Y. Tang, T. Brown and W. H. Loh, *Nanotechnology*, 2009, 20, 195603–195607.

[45] L. Vaisman, H. D. Wagner and G. Marom, *Adv. Colloid Interface Sci.*, 2006, 128–130, 37–46.

Journal of Materials Chemistry A Accepted Manuscript

[46] A. Eitan, K. Y. Jiang, D. Dukes, R. Andrews and L. S. Schadler, *Chem. Mater.*, 2003, 15, 3198–3201.

[47] Y. L. Liu, Y. H. Xu, X. G. Han, C. Pellegrinelli, Y. J. Zhu, H. L. Zhu, J. Y. Wan, A. C. Chung, O. Vaaland, C. S. Wang and L. B. Hu, *Nano Lett.*, 2012, 12, 5664–5668.

[48] B. Wu, L. Bai, Q. M. Gong and J. Liang, *Acta Phys. –Chim. Sin.*, 2009, 25, 1065–1069.

[49] A. K. Schaper, M. S. Wang, Z. Xu, Y. Bando and D. Golberg, *Nano lette.*, 2011, 11, 3295–3300.

[50] D. J. Yang, S. G. Wang, Q. Zhang, P. J. Sellin and G. Chen, *Phys. Lett. A*, 2004, 329, 207–213.

[51] N. Rajic, R. Gabrovsek and V. Kaucic, *Thermochim. Acta*, 2000, 359, 119–122.

[52] X. H. Liu, L. B. Zhou, R. Yi, N. Zhang, R. R. Shi, G. H. Gao and G. Z. Qiu, *J. Phys. Chem. C.,* 2008, 112, 18426–18430.

[53] A. Guerfi, S. Sévigny, M. Lagacé, P. Hovington, K. Kinoshita and K. Zaghib, *J. Power Sources*, 2003, 119-121, 88–94.

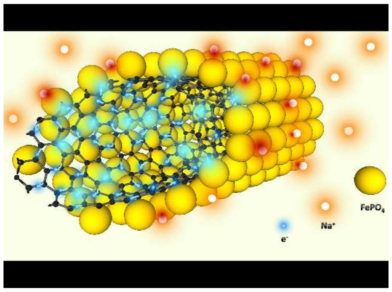
[54] T. H. Cho, S. M. Park, M, Yoshio, T. Hirai and Y. Hideshima, *J. Power Sources*, 2005, 142, 306–312.

[55] J. S. Huang, L. Yang, K. Y. Liu and Y. F. Tang, *J. Power Sources*, 2010, 195, 5013–5018.

Journal of Materials Chemistry A Accepted Manuscript

Table of contents entry (Graphic Abstract)

A maize-like $FePO_4$@MCNT composite was prepared through non-covalent surface treatment and used as a cathode for sodium-ion batteries.



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