LIFEPO$_4$ NANODENDRITES: A PROMISING CATHODE MATERIAL FOR LI-ION MICROBATTERIES

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Abstract: LiFePO$_4$ crystals were synthesized in a novel system of ethylene glycol/water (EG/W), in which dodecyl benzene sulphonic acid sodium (SDBS) was used as soft template to control the particle morphology. The obtained sample displays an interesting hierarchical nanostructure (*i.e.* nanodendrites) which was constructed by nanorods of 3-5 μ in length and ~50 nm in diameter. The EG/W ratio, amount of SDBS added, hydrothermal temperature and duration played the important roles in the assembly of the nanodendrites. It is proposed that the nanodendrites form by the end-to-end self-assembly of nanorods.

Keywords: Nanodendrite; LiFePO$_4$; Self-assembly

INTRODUCTION

LiFePO$_4$ has emerged as a very attractive cathode material for Li ion batteries due to its high thermal stability, long cycling life, environmental friendliness, and abundant availability of the chemical composition [1,2]. In addition to the intrinsic property of a material, the particle morphology or architecture has a great influence on the performances of materials. Currently, nanodendrites have been identified as one of the most promising morphologies for ultrahigh electrochemical/catalytic activity [3]. Various methods have been proposed to synthesize LiFePO$_4$ with nanostructures, such as solid-state reaction, sol-gel, and so forth. The high temperatures, difficulty for structure control, toxic reactants, and high cost, are among the major challenges. Hydrothermal synthesis is an effective method to obtain well-crystallized materials with well-defined morphologies, where no additional high-temperature annealing is needed [4]. Recently, Yang *et al*. [5] synthesized LiFePO$_4$ dumbbell-like microstructures via a solvothermal route, which showed an excellent cycling stability. In their work, nevertheless, expensive benzyl alcohol and LiI were used, and a long reaction time (48 h) was required. Much effort is still needed to develop a more economically efficient route to synthesize LiFePO$_4$ with well-defined morphology.

EXPERIMENTAL

All the chemicals are analysis grade and used as received. Typically, the appropriate quantities of LiOH, FeCl$_2$ ·7H$_2$O, H$_3$PO$_4$, L-Ascorbic acid and SDBS with the molar ratios of 3:1:1:3:1 were dissolved in 35 mL of EG/W mixture (1/1 volumetric ratio) under intensive magnetic stirring to form a homogeneous solution. The solution was transferred into a 50 mL Teflon®-lined stainless steel autoclave and heated to 160 °C to react for 6 h. After being cooled naturally to room temperature, the product was centrifuged, washed with DI water and ethanol, and finally dried at room temperature for 24 h. In order to investigate the effects of preparation conditions on the samples, the volumetric ratio of EG to W, the amount of SDBS added, hydrothermal time and temperature, were varied. The samples were characterized by X-ray diffractometer (XRD), field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED).

DISCUSSION

Influence of hydrothermal temperature and duration The hydrothermal temperature was varied from 140 to 160, 180 and 200 °C, while the other processing parameters were maintained the same. XRD spectra were used to investigate the phase compositions of the as-synthesized samples. After being processed at 140 °C, no single-phase LiFePO$_4$ sample was obtained. Instead, the sample contained significant amounts of impurity crystals (*e.g.*, Li$_3$PO$_4$ and Fe$_4$(PO$_4$)$_3$(OH)$_3$). It could be assumed that the enough energy provision is necessary for the formation of LiFePO$_4$ crystals. Above 160 °C, the diffraction peaks of all the samples can be well indexed to single-phase LiFePO$_4$ with an orthorhombic olivine structure (JCPDS card no. 81-1173). Moreover, the diffraction peaks become stronger and narrower with the increase of temperature. Using Scherrer's equation from the (020) peak, the mean crystallite sizes (D$_{020}$) of the samples prepared at 160, 180 and 200 °C are calculated to be 25.5, 37, and 42 nm, respectively. This result confirms

that the crystals have grown larger with the increase of hydrothermal temperature. We observed their morphologies by FE-SEM. Most interesting, the as-prepared sample at 160 $^{\circ}$C displays a hierarchical structure, *i.e.* nanodendrites, as illustrated in Fig. 1(a). When observed at a low magnification that the particles displayed a fairly uniform morphology and each particle features a nanodendrite of 4-5 μ in size. Fig. 1(a) reveals that the individual nanodentrite consists of the nanorods of 100 nm in diameter and 2-5μm in length. These nanorods seem to be attached end-to-end to form the ordered architecture. This novel hierarchical architecture of LiFePO$_4$ nanorods has not been reported previously. However, the as-prepared samples at 180 and 200 $^{\circ}$C display irregular morphologies. It is obvious that the hydrothermal temperature has a significant influence on the morphology and structure of the products. We behold that there may exist an appropriate temperature favorable for the nucleation and growth of crystals so as to form the well-defined morphology. Here, an appropriate hydrothermal temperature, *i.e.* 160 $^{\circ}$C, was chosen to synthesize LiFePO$_4$ nanodendrites.
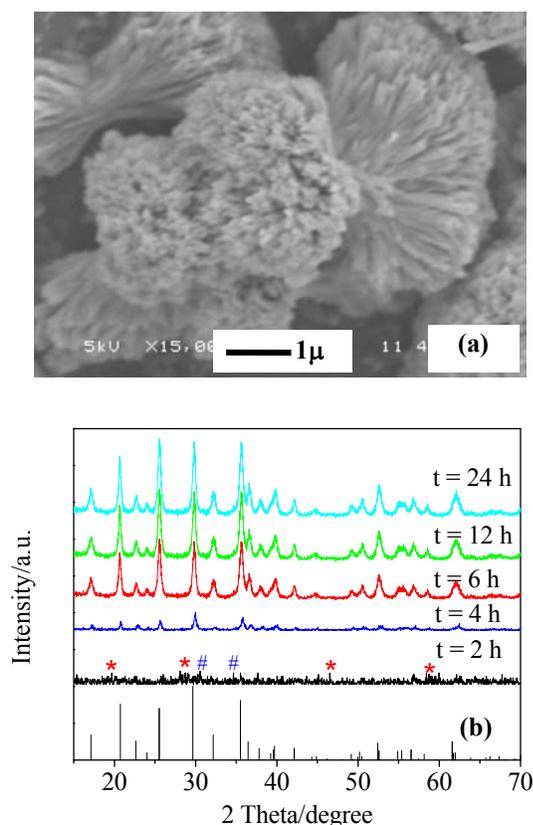

Fig. 1: FE-SEM image (a) of the LiFePO$_4$ sample prepared at 6 h and XRD patterns (b) of the as-samples prepared at different hydrothermal durations.*: Li$_3$PO$_4$, #: Fe$_4$(PO$_4$)$_3$(OH)$_3$

Hydrothermal time was then varied from 2, 6, 12 and 24 h to investigate the effect of reaction time while the hydrothermal temperature was kept at 160 $\circ$C. Fig. 1(b) shows XRD patterns of the as-prepared samples. After being processed for 2 h, no LiFePO$_4$ was evidenced, but the weak peaks of Fe$_4$(PO$_4$)$_3$(OH)$_3$ and Li$_3$PO$_4$ were observed. When the reaction time was extended to 4 h, the peaks of both Li$_3$Fe$_2$(PO$_4$)$_3$ and Li$_3$PO$_4$ disappeared, and all the diffraction peaks, although relatively weak, can be well indexed to LiFePO$_4$. When the reaction time was extended to 6 h, all the diffraction peaks of the sample turned out to be strong, and can be well indexed to high purity LiFePO$_4$ structure. Further increasing reaction time to 12 and 24 h, all the diffraction peaks become stronger. The crystallite size (D$_{020}$) was calculated using Scherrer's equation (D=0.9 λ/βcosθ) from the full-width-at-half-maximum (β) of the strong and well-resolved diffraction peak (020). The calculated mean D$_{020}$ values for the samples prepared at 4, 6, 12 and 24 h are 18.8, 25.5, 27.1 and 27.5 nm, respectively. The results showed that after the processing time was longer than 6 h, the crystals grew at a fairly smaller extent. It is therefore concluded that the crystal growth slowed down after 6 h. An even longer processing time will have a minor influence on the crystal size and morphology of the reported LiFePO$_4$ nanodendrites. Further, HRTEM was performed to investigate the variation of LiFePO$_4$ particle morphology with processing time (Fig. 2). It is revealed that after being processed for 2 h at 160 $^{\circ}$C, the sample was composed of 10-nm-large nanoparticles (Fig. 2a). On the other hand, when the processing time is extended to 4 h, the sample obtained turned out to be LiFePO$_4$ nanorods that are 100 nm in length and 10-20 nm in diameter (Fig. 2b). After being processed for 6 h, the HRTEM images further confirm that the as-obtained sample consists of many well-dispersed nanodendrites with uniform morphology. The length of those structures is again confirmed as of 4-5 μ (Fig. 2c). The results consistently agree with the FE-SEM images presented in Fig. 1a. We also observed that after being processed for 12 or 24 h, the particles maintained the nanodendrite morphologies (not showing here). The spiky structure on the edge of single particle further indicates that the particles are composed of nanorods with a diameter of about 100 nm (Fig. 2d). The inset of ED patterns (Fig. 2e) indicates the single-crystalline nature of the nanorods. A HRTEM image (Fig. 2f) taken on the tip of an individual nanorod displays clear crystal lattices with *d*-spacing of 0.29 nm, corresponding to the (020) plane of orthorhombic LiFePO$_4$ crystals. This result suggests that the crystal

preferentially grow along the {020} direction. The element compositions of this sample were further confirmed by the EDX spectra (not shown here). The peaks of Fe and P can be observed clearly, but the peaks of lithium did not appear in EDX spectra due to the light mass of lithium. The above time-dependent experiments suggest that at the beginning stage, the nucleation process take place under hydrothermal conditions, first leading to the formation of nanoparticles. Then the nanoparticles grow into nanorods through the crystallization-dissolvation-
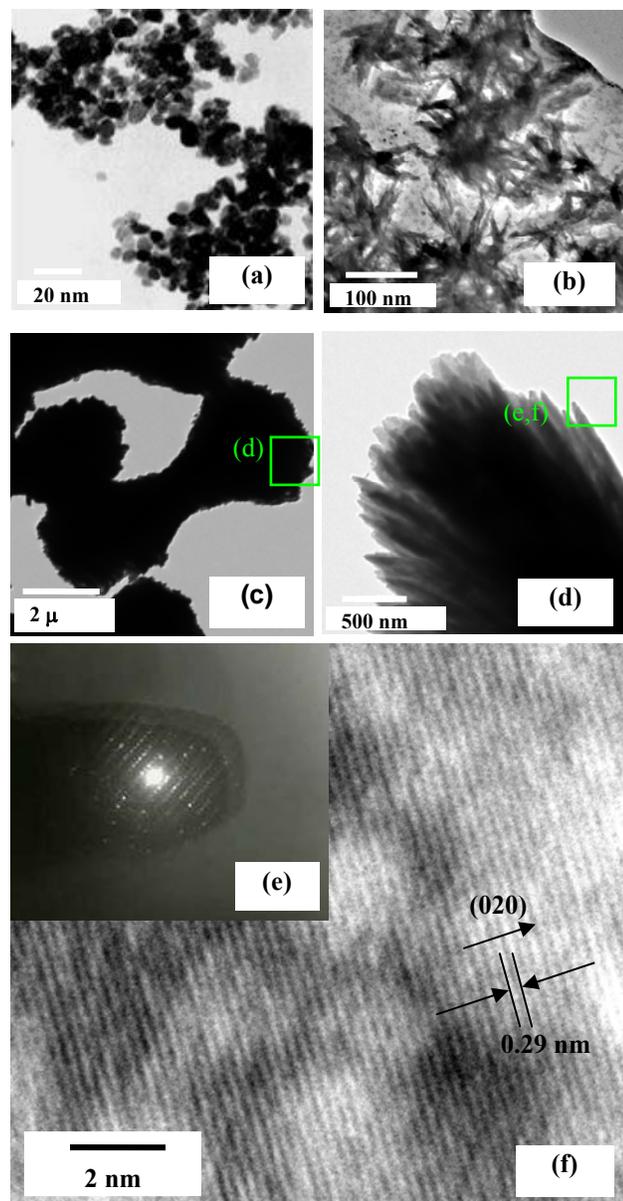

Fig. 2: HRTEM micrographs of the samples at different reaction times: (a) 2 h; (b) 4 h; (c) 6 h; (d) the tip of an individual particle; (e) the inset of SAED image; (f) lattice spacing image for the sample prepared at 6 h

recrystallization processes. Eventually, the nanorods organize into the hierarchical structures through an end-to-end assembly mode.

Influence of the EG/W volumetric ratio The EG/W volumetric ratio was varied from 0/1, 1/1, 2/1, 4/1 and 1/0 while other preparation parameters were maintained the same. The XRD results demonstrated that at the EG/W ratios of 0/1, the sample obtained is mainly composed of $LiFePO_4$ crystals, accompanied by a small amount of $Fe_4(PO_4)_3(OH)_3$ impurity crystals. At 1/1 and 2/1, single-phase $LiFePO_4$ crystals were obtained. However, the FE-SEM observation confirms that the sample obtained at 2/1 shows irregular morphology. At 4/1 and 1/0, pure $LiFePO_4$ samples were not obtained, but a large amount of impurity crystals (Li_3PO_4, $FeFe_3(PO_4)_3(OH)_3$ and unknown phases) formed. It is obvious that the reacting medium composition also has a significant influence on the phase composition and morphology of the products. Two aspects are assumed to be important. First of all, an enough high solubility of the precursor chemicals in the EG/W medium is needed to guarantee the formation of $LiFePO_4$. As the EG content increases, the solubility of the precursor chemicals decreases. For the same amounts of chemicals, the precursor chemicals can not dissolve and mix homogeneously in the EG/W medium of a higher EG content. Consequently, high pure $LiFePO_4$ crystals can not form. Secondly, the mobility or reactivity of ions in the medium has an important influence on the crystal growth. The viscosity (21mPa·s, 20 °C) of EG is much higher than that (1.0087×10^{-3} mPa·s, 20 °C) of water, which will lead to slow mobility or reactivity of different ion species. At an appropriate content of EG (*i.e.* 1/1 volumetric ratio of EG to W), the reactivity of the precursor chemicals may match one another, which does favor to form the final product. This needs further research.

Influence of the surfactant amount added When the molar ratio of SDBS/Fe was varied from 0:1, to 1/1, 2/1 and 4/1, the XRD results confirm that all the as-prepared samples are high pure $LiFePO_4$ crystals. However, the FE-SEM results demonstrated that the $LiFePO_4$ nanodendrites can only obtained at the 1/1 ratio of SDBS/Fe. Without SDBS, the sample obtained consists of the particles with irregular morphology. As shown in Fig. 3, the crude spindle- and bone-like particles are obtained at 2/1 and 4/1, respectively. These observations clearly establish that the amount of SDBS is a crucial factor for the control of the particle morphology. We conjecture that an appropriate amount of SDBS may act as a soft

template to direct the growth of nanoparticles into nanorods at the early stage of the process through a preferentially bonding to certain crystal planes. Later on, these nanorods are further aligned tightly and assembled by an end-to-end mode under the guidance of the soft template to form hierarchical forms (*i.e.* nanodendrites).
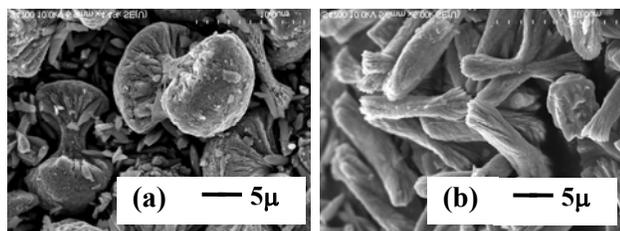

Fig. 3: FE-SEM images of the samples at different molar ratios of SDBS to Fe: (a) 2/1, (b) 4/1

Formation mechanism of the nanodendrites
First of all, at an optimal EG content (EG/W=1/1 in our experiment), the reactivity of all the precursor chemicals in this mixture medium will match each other, which favors to form the desired olive-structure crystal. On the other hand, the chemicals in this mixture medium will have a higher degree of supersaturation than they do in water if the same amounts of precursors are used. Consequently, the EG/W system would favor the nucleation and growth of crystals. At too high EG content, the precursors can not be mixed homogeneously due to the lower solubility of the precursors. In short, we conclude that this EG/W mixture medium is critical for the formation of the LiFePO$_4$ crystals. For the process reported herein, the mixture system turns out to be a promising reaction medium to improve the purity of the final products and provide well-controlled crystallization, which overcomes the drawbacks of the pure aqueous system. The time-dependent experiment results reveal that SDBS, an anionic surfactant, is used to both guide the growth of the LiFePO$_4$ nanorods and template their further self assembly. During the crystal growth, the surfactant acted as strong coordinating agents by selectively binding to some crystal faces and accordingly inhibited their growth. At the early stages, SDBS directs crystals to grow along the crystal direction whose crystal plane weakly bonds with the surfactant molecules. As a result, the nanorods are formed. In addition, it is conjectured that the SDBS molecules also act as a soft template to template the nanorod building blocks into the final hierarchical structures through the end-to-end self-assembly. We believe that this assembly mode results from the Van der Waals attraction of

hydrophobic interaction of the surfactant molecules bonded to the end of the nanorods. Since surfactant molecules preferentially and strongly adsorbed on the nanorod side, the stronger electrostatic force exist on the nanorod side than that on the end. It seems that there is a balance between electrostatic repulsion interaction and hydrophobic attraction interaction. Hence the electrostatic repulsion interaction on side is stronger than that on end between nanorods, which refrains the side-by-side attachment. The long hydrophobic chains of the SDBS molecules boned on the nanorods will attracted one another through hydrophobic interaction. As a result, the nanorods are attached with each other by their ends to form hierarchical structure (Fig. 4).
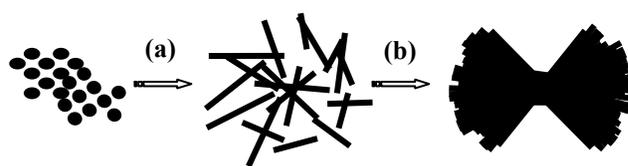

Fig. 4: Formation mechanism of Nanodendrites: (a) growth (b) assembly by an end-to end mode

CONCLUSION

The hierarchical LiFePO$_4$ nanodendrites has been successfully synthesized in the EG/W system using SDBS as the surfactant. The hierarchical structures are formed through the self-assembly of nanorod building blocks by their end-to-end attachment. The synthesized LiFePO$_4$ nanodendrites are expected to be a promising cathode material for lithium-ion batteries and supercapacitors.

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