



Short communication

## Directed growth of nanoarchitected $\text{LiFePO}_4$ electrode by solvothermal synthesis and their cathode properties

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## ABSTRACT

We demonstrate a rapid and one-pot solvothermal synthesis of  $\text{LiFePO}_4$  hierarchical nanorods and flowers like microstructures in a short reaction time (4–10 min) at temperature as low as 300–400 °C, without any high temperature post-annealing. The ethylene glycol was used as a solvent with hexane and oleic acid as co-solvent and surfactant, respectively. Addition of the co-solvent and/or surfactant played a key role in controlling the morphology and microstructures of the  $\text{LiFePO}_4$  nanocrystals. The EG and oleic acid were acted as the size and morphology controlling agents and carbon source when annealed at 600 °C. Sample exhibited about 90% specific capacity at 0.5 °C and showed good cyclic performance. The high-resolution TEM image revealed that these nanorods were self-assembled to form flower like microstructure in presence of oleic acid during the synthesis.

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### 1. Introduction

Among the Li ion battery materials, the  $\text{LiFePO}_4$  has attracted considerable attention because of its potential applications as an cathode material owing to its high stability, non-toxicity, good charge/discharge capabilities and cheap cost [1,2]. Many attempts have been made to improve its intrinsic problems such as poor electronic conductivity and slow Li ion diffusions by coating different conductive materials (conductive carbon or polymers and metal ion doping), controlling morphology and reducing particle size [3–6].  $\text{LiFePO}_4$  nanostructure is of great interest, because, the electrochemical properties of bulk LFP could be significantly improved benefiting from nanometer size effects. Various  $\text{LiFePO}_4$  nanostructures such as irregular nanoparticles, nanorods, nanoplates and porous nanostructures have been synthesized [7,8]. Organization of such nanoscale building blocks into complex hierarchical architectures via self-assembly is of great interest to nanoscience and nanotechnology, because of their size and shape dependent physical and chemical properties for potential applications in electronics, optics, energy and chemical conversion [9–12].

Recently, a few synthetic methods have been used to prepare size and morphology controlled  $\text{LiFePO}_4$ . Ellis et al. have synthe-

sized  $\text{LiFePO}_4$  nanocrystals with tubular morphology by surfactant or polymer assisted hydrothermal method [7]. Dominko et al. reported the porous nanostructures of  $\text{LiFePO}_4$  particles with hierarchically organized pores which can operate up to 50 °C while still preserving a high tap density of  $1.9 \text{ g cm}^{-3}$  [9]. Yang et al. and Saravanan et al. reported  $\text{LiFePO}_4$  with complex hierarchical structures such as nanoplates and dumbbell like microstructures. However, there are few reports on the preparation of  $\text{LiFePO}_4$  hierarchical architectures with well-defined size and morphologies [13,14].

In this report, we demonstrate a rapid and one-pot solvothermal synthesis of  $\text{LiFePO}_4$  nanorods and flower like hierarchical microstructures within a short reaction time (4–15 min) at temperature as low as 300 °C without any high temperature post-annealing. The ethylene glycol was used as a solvent with hexane and oleic acid as co-solvent and surfactant, respectively. Effect of co-solvent and surfactant on the morphology and microstructures of  $\text{LiFePO}_4$  nanocrystals is studied. The plates like nanorods with the lithium diffusion direction along the *b* axis are particularly beneficial to achieve the high-power capability in the lithium ion battery.

### 2. Experimental

#### 2.1. Synthesis

The  $\text{LiFePO}_4$  nanorods were synthesized using  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ , LiOH, and ascorbic acid (all from Aldrich). The starting

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precursor solution was prepared in 1:1:1 molar ratio using source materials. First, metal salts ( $0.1 \text{ mol l}^{-1}$ ) were dissolved in 10 ml ethylene glycol. A desired amount of oleic acid or hexane was added to this solution as a surfactant and co-solvent and stirred well in a beaker for 1 h. The amount of hexane used in this solution was about 20 vol%. The surfactant to a precursor molar ratio was 1:10–20. In a typical synthesis, 5 ml of precursor solution was charged in  $10 \text{ cm}^3$  volume stainless steel reactor and heated up to  $400^\circ\text{C}$  temperatures and 40 MPa pressure. After 10 min reaction, the reactor was quenched with cold water to stop the reaction. A pale green colored product was collected by washing the reactor with ethanol followed by the repeated centrifugation with ethanol to remove the unwanted salts. Resultant products were dried in a vacuum dry oven at  $120^\circ\text{C}$  for 6 h in order to eliminate the residual solvent from the particle. Later, this product was heat treated at  $600^\circ\text{C}$  for 4 h in an Ar and  $\text{H}_2$  gas atmosphere to convert organic molecules/carbon on  $\text{LiFePO}_4$  surface to conductive carbon coating for improving the conductivity and electrochemical properties.

## 2.2. Materials characterization

The crystal structure was examined by X-ray diffraction (XRD) analysis with a Bruker AXS D8 Advance instrument using  $\text{Cu K}\alpha$  radiation. The morphology was observed by high-resolution transmission electron microscopy (HR-TEM; JEOL JEM-2010F). Elemental analysis was carried out using the STM attached to HR-TEM (JEOL JEM-2010F). Infrared (IR) spectra of the as prepared materials were recorded by an FT/IR-6200 IR spectrophotometer (JASCO Corp., Tokyo, Japan).

## 2.3. Electrochemical characterization

The electrochemical properties of  $\text{LiFePO}_4$  nanorods were studied by assembling a beaker type three electrode cell. The samples were dried overnight at  $100^\circ\text{C}$  in a vacuum before assembling the cell. The dried  $\text{LiFePO}_4$  sample was mixed and ground with acetylene black and Teflon (poly(tetrafluoroethylene)) binder in the weight ratio of 75:20:5. The prepared paste was spread uniformly on a  $0.1 \text{ cm}^2$  stainless steel SUS sheet (100 mesh) using the doctor-blade method. The cathode loading was  $4\text{--}5 \text{ mg cm}^{-2}$ . Li metal on a stainless steel SUS mesh was used as a counter and reference electrodes. The electrolyte consists the solution of 1 M  $\text{LiClO}_4$  in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1 by volume). The cell assembly was carried out in a glove box filled with high purity argon gas. The charge–discharge tests were performed with a Solartron Instrument Model 1287 controlled by a computer in a potential range of 2.0–4.5 V versus Li under different current densities.

## 3. Results and discussion

### 3.1. Structural analysis

The chemical composition and crystal structure of the  $\text{LiFePO}_4$  nanostructures were confirmed by powder X-ray diffraction, as shown in Fig. 1. These well-resolved diffraction peaks in the range of  $2\theta = 20\text{--}60^\circ$  corresponds to the different crystal planes of  $\text{LiFePO}_4$  with olivine structure indexed in  $Pnmb$  of orthorhombic system (JCPDS no. 40-1499). No second phase is observed. The unit cell parameters that were calculated from observed XRD data ( $d$ -value and  $hkl$  data) for the as prepared  $\text{LiFePO}_4$  nanostructure are  $a = 10.35 \text{ \AA}$ ,  $b = 6.04 \text{ \AA}$ , and  $c = 4.70 \text{ \AA}$  which is in agreement with the previous reports [15]. From Fig. 1, the diffraction peaks of the as prepared  $\text{LiFePO}_4$  nanostructure is relatively broad and short, these peak illustrates that the highly crystalline nature of  $\text{LiFePO}_4$  is achieved by solvothermal process within a short reaction time

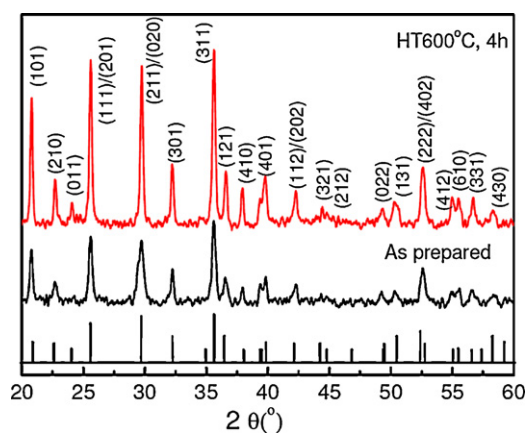


Fig. 1. XRD patterns of  $\text{LiFePO}_4$  flower like microstructure; as prepared (bottom), and heat treated sample at  $600^\circ\text{C}$  (top).

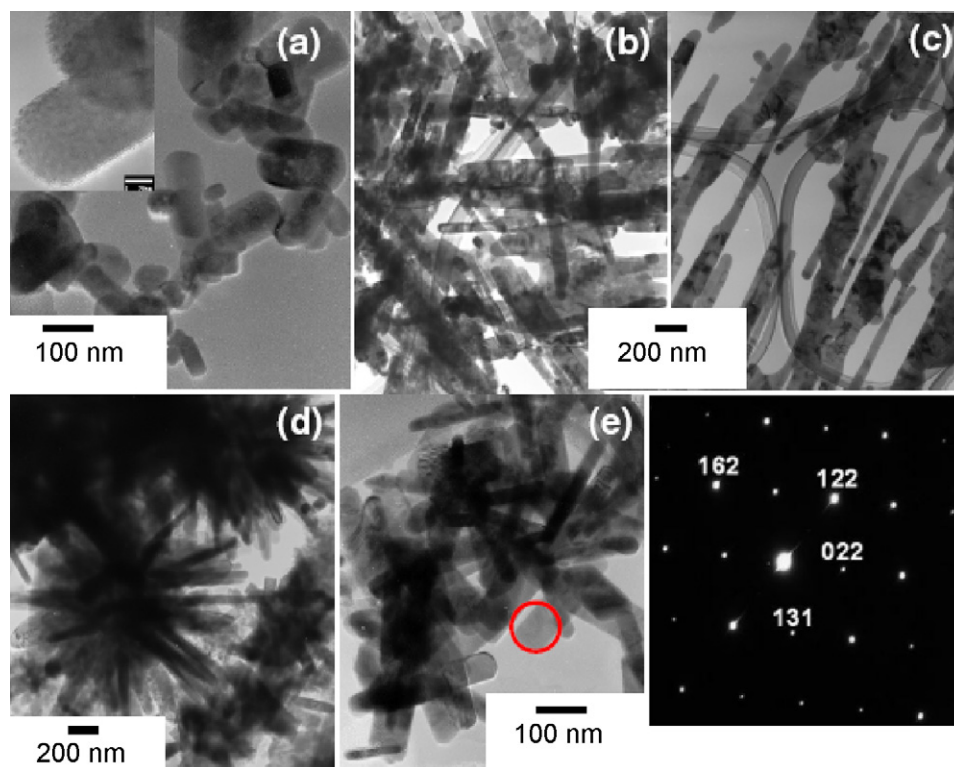
without post-annealing at elevated temperatures. The diffraction peaks became more intensive and narrower by additional heat treatment indicating that the crystallinity of nanostructures was further improved without any change in crystal structure. As it can be seen from Fig. 1, the intensities of (1 0 1), (1 1 1/2 0 1), (2 1 1/0 2 0) and (3 1 1) peaks are almost constant, which is similar to that reported by other researchers [7,9,15].

### 3.2. Size and morphology

The size and morphology of the  $\text{LiFePO}_4$  nanostructure were examined by HR-TEM. Fig. 2 shows the HR-TEM images of the as prepared  $\text{LiFePO}_4$  samples. Solvent has a crucial role to play in the morphology of  $\text{LiFePO}_4$ . The  $\text{LiFePO}_4$  formed in the ethylene glycol solvent displayed rectangular nanoplate like morphology with particle size ranging from 50 to 100 nm width as seen in Fig. 2a. When the solvent was changed from ethylene glycol to ethylene glycol and hexane, long nanorods like morphology were obtained with a particle diameter of  $\sim 100\text{--}150 \text{ nm}$  and length of  $\sim 500\text{--}700 \text{ nm}$  as shown in Fig. 2b and c, respectively. In case of ethylene glycol and oleic acid as a solvent and surfactant, short nanorods were obtained. Fig. 2d and e shows the sample obtained in the presence of oleic acid for 10 and 15 min reaction time. It can be clearly seen that the sample is mainly composed of nanorods and nanoflower like microstructures with length ranging from 200 to 400 nm. From these images, clearly by increasing reaction time individual  $\text{LiFePO}_4$  nanorods were hierarchically organized into flower like microstructure via a self-assembly process. The SAED pattern in Fig. 2f with bright spots of well-defined diffraction pattern of olivine phase suggests that the good crystalline  $\text{LiFePO}_4$  nanostructures were formed under solvothermal conditions. We further confirmed by STEM image and corresponding STEM maps of oxygen, iron and phosphorous that the flower like microstructures are  $\text{LiFePO}_4$  (Fig. 3). STEM maps confirmed that the oxygen, iron and phosphorous in  $\text{LiFePO}_4$  homogeneously distributed in to the flower like microstructure. It should be noted that so far not many people are succeeded in synthesizing the  $\text{LiFePO}_4$  hierarchical architectures with well-defined flower like morphologies. The reported literatures mainly involve tubular particles, irregular nanoparticles and porous nanostructures, except the recent hierarchically dumbbell like microstructures reported by Yang et al.

### 3.3. FTIR spectra

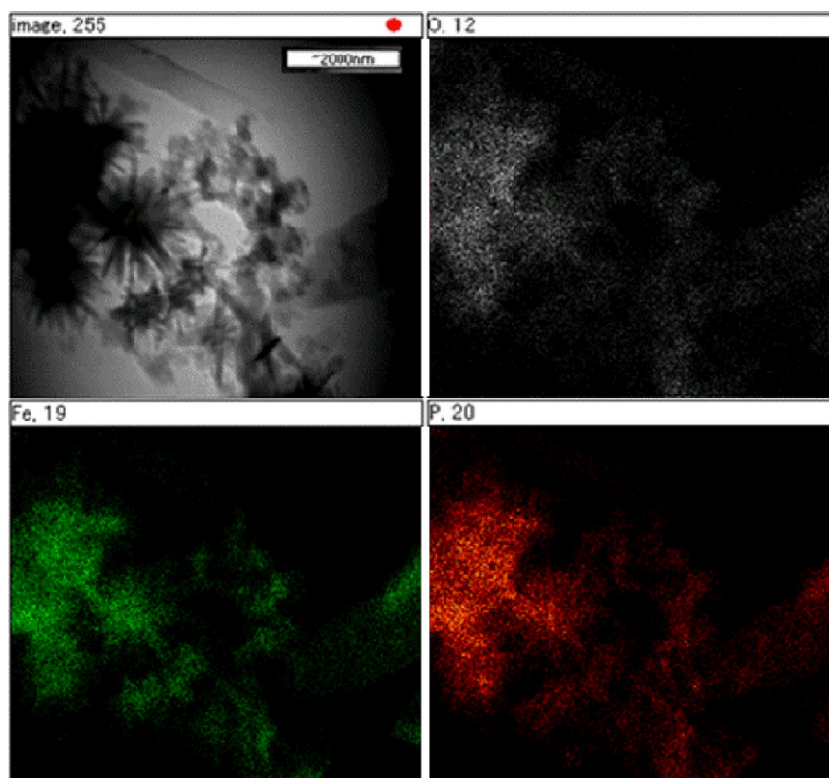
The FTIR absorption spectra of the as prepared  $\text{LiFePO}_4$  with different solvents are shown in Fig. 4. The  $\text{LiFePO}_4$  has two classes of vibrational modes as reported by Christopher and Roger [16].



**Fig. 2.** HR-TEM images LiFePO<sub>4</sub> nanostructures prepared by different solvents and co-solvents; (a) EG, (b & c) EG and hexane, and (d & e) EG and oleic acid. The last image shows the ED pattern of selected area of a nano-rod shown in (e).

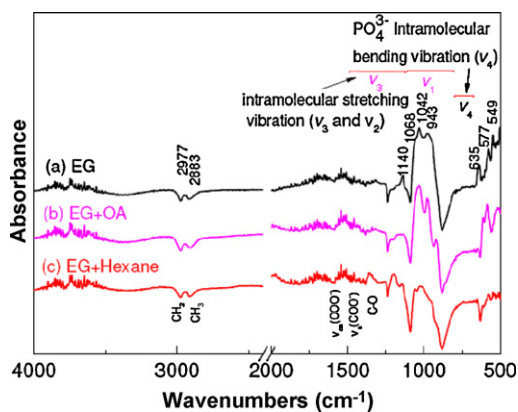
First one is intramolecular stretching vibration mode of PO<sub>4</sub><sup>3-</sup> anion (V<sub>1</sub> and V<sub>3</sub>) and second one is intramolecular bending vibration mode (V<sub>4</sub>) of phosphate anions. In Fig. 4, the intramolecular stretching (V<sub>1</sub> and V<sub>3</sub>) motions of each PO<sub>4</sub><sup>3-</sup> anion is correlated

to those of the other PO<sub>4</sub><sup>3-</sup> ions in the unit cell, which produces a rich vibrational multiplet structure as observed at 943 cm<sup>-1</sup> and 1042 cm<sup>-1</sup>, 1068 cm<sup>-1</sup> and 1140 cm<sup>-1</sup>. The bands in the region of 643–633 cm<sup>-1</sup> can be assigned to the bending modes (V<sub>4</sub>) of



**Fig. 3.** STEM image and corresponding STEM maps of oxygen, iron and phosphorus in LiFePO<sub>4</sub> synthesized by EG and oleic acid as solvent and surfactant at 400 °C for 10 min reaction.





**Fig. 4.** FTIR absorption spectra of nanostructure LiFePO<sub>4</sub> synthesized by solvothermal method at 400 °C for 10 min; (a) EG, (b) EG and oleic acid, and (c) EG and hexane.

phosphate anions. The bands in the region of 500–665 cm<sup>-1</sup> can be assigned to the lithium ion motion. As we can see in the FTIR spectra, there is not much difference in the vibrational modes (region 500–1150 cm<sup>-1</sup>) of LiFePO<sub>4</sub> synthesized with different solvent and surfactant. The bands in the region of 2800–2960 cm<sup>-1</sup> can be attributed to the CH<sub>2</sub> stretching mode of methyl and methylene groups, which indicates that the solvent and surfactant molecules bonded to the surface of the LiFePO<sub>4</sub> nanostructures (Fig. 4b). The bands at 1532 and 1445 cm<sup>-1</sup> correspond to the stretching frequency of the carboxylate group, which indicate a complex reaction between the hydroxyl groups on the surface of the LiFePO<sub>4</sub> nanocrystals and the carboxylate group of the oleic acid. The –C=C group of oleic acid was characterized by band at 1068 cm<sup>-1</sup>. Absorption at 1140–1200 cm<sup>-1</sup> due to the associated hydroxyl groups indicated the existence of EG. This result suggested that the LiFePO<sub>4</sub> nanoparticles surface was coated with organic molecules during the solvothermal synthesis. These organic molecules on the LiFePO<sub>4</sub> nanoparticles surface played an important role in the directed growth and self-assembly of LiFePO<sub>4</sub> microstructure. In addition, they act as carbon source during the heat treatment and forms conductive carbon coating on the surface of the LiFePO<sub>4</sub> nanoparticles.

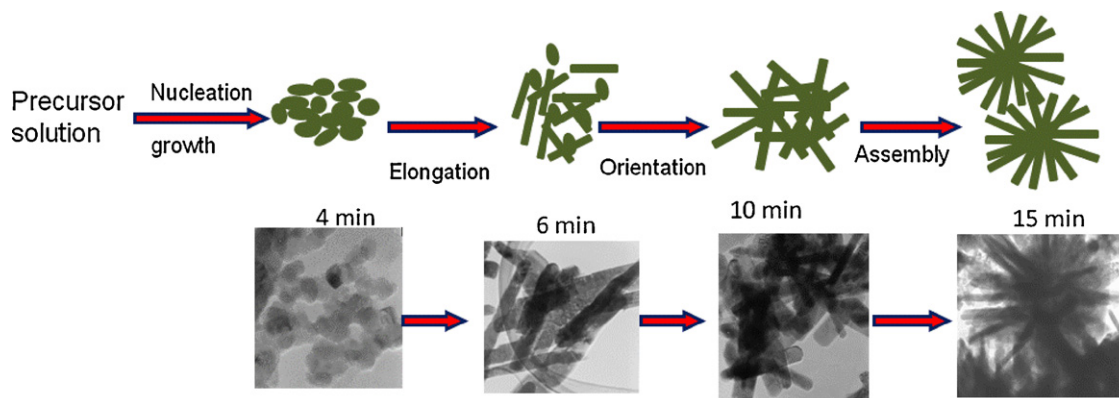
#### 3.4. Formation mechanism

In order to understand the formation process of the LiFePO<sub>4</sub> hierarchical flower like microstructure, we carried out detailed time dependent experiments under solvothermal conditions. At first, formation of sphere like LiFePO<sub>4</sub> nanoparticles occurred rapidly at 400 °C temperature within 4 min of reaction time as

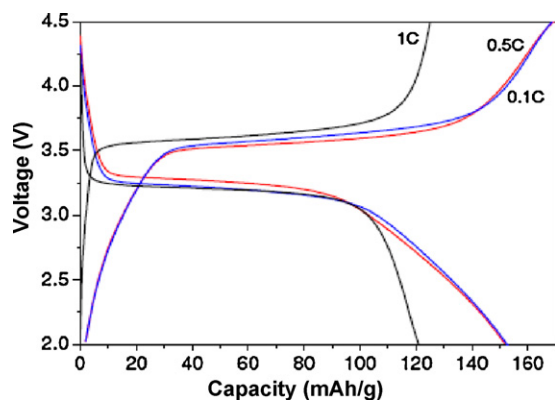
shown in Fig. 5. By increasing the reaction time up to 6 min, the nanoparticles continued to grow via elongation into 1D rod like structure. There are two morphologies coexisting at this crystal formation stage, namely, sphere and nanorods like structure. Zhou et al. have successfully prepared highly hierarchical plate like FeWO<sub>4</sub> microcrystals by a simple solvothermal route using ethylene glycol as a capping agent [17]. They suggest that ethylene glycol plays an important role in directing the growth and self-assembly of such unique structures along certain growth direction. It appears that the ethylene glycol and oleic acid acts as a soft template in directing the growth of nanoparticles to nanorods at the early stages through forming hydrogen bonds, and these nanorods further aligned by orientation to form flower like hierarchical structure when the reaction time was prolonged to 10–15 min in the presence of oleic acid. As it is well known, oleic acid acts as a surfactant and capping agent, which may greatly affect the size, morphology and microstructure of the products. Thus, the oleic acid molecules may adsorb onto the surface of these nanorods. It is the interaction of this adsorbed oleic acid molecules that lead to the decrease in the rods length and finally forms hierarchically flower like microstructure with prolonged reaction time.

#### 3.5. Electrochemical properties

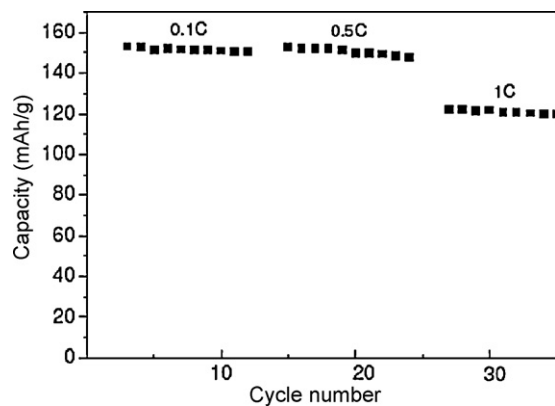
The electrochemical properties of the LiFePO<sub>4</sub> hierarchical microstructures were investigated by Li insertion/extraction. Before the electrochemical measurements, the LiFePO<sub>4</sub> sample was heated up to 600 °C in Ar and H<sub>2</sub> atmosphere for 4 h. As we know from FTIR spectra, the surfactant remains more or less on the surface of the final product, even after being washed several times with ethanol. Considering this, the product was annealed to remove the left surfactant from the surface. In addition, annealing can transform the surfactant into carbon to enhance the electronic conductivity. Therefore, ethylene glycol and oleic acid can be considered not only as solvent and surfactant to control the size and morphology, but also as a carbon source. Fig. 6 displays the charge and discharge curves of the sample at the current density of 0.1–1 C in the potential range from 2 to 4.5 V. LiFePO<sub>4</sub> hierarchical nanorods and flower like microstructures showed a flat discharge voltage at approximately 3.4 V, which represents the typical electrochemical action of Li<sup>+</sup> insertion into FePO<sub>4</sub>. The charge–discharge plateaus of LiFePO<sub>4</sub> hierarchical microstructures is shorter than LiFePO<sub>4</sub> bulk spherical particles that reported in literature. The sloping region for the synthesized sample is longer ~39% in comparison with reported value ~10–20%. As it is well known, the LiFePO<sub>4</sub> charge discharge plateau represents a two phase region, where the FePO<sub>4</sub> and LiFePO<sub>4</sub> coexist during the Li insertion. There are different explanations about the slope of charge–discharge capacity curves.



**Fig. 5.** Schematic illustrations of the directed growth of LiFePO<sub>4</sub> nanorods and 3D hierarchical nanoflower by nanorods self-assembly.



**Fig. 6.** The discharge profiles of LiFePO<sub>4</sub> nanostructures at different discharge rates ranging from 0.1 to 1 C. The sample was synthesized at 400 °C in 10 min by solvothermal under EG and OL followed by heat treatment at 600 °C.



**Fig. 7.** Cyclic performance of the LiFePO<sub>4</sub> nanostructure electrode measured at 0.5 C charge and discharge rates.

One is the formation of solid solution of Li<sub>x</sub>FePO<sub>4</sub> below certain critical size, for example 40 nm [18]. The second explanation is that pseudo-capacitive effect, which means the charge storage of Li ions from faradaic processes occurring at the surface of the materials. Presently, the LiFePO<sub>4</sub> hierarchical flower like microstructures is probably showing the pseudo-capacitive behavior as this structure is formed by self-assembly of 200–400 nm nanorods. Recently, pseudo-capacitive effect has been observed for LiFePO<sub>4</sub> dumbbell like microstructures hierarchically constructed with nanoplates [13]. However, they report small capacity for such microstructure, which they attributed to the low electronic conductivity and

slow lithium ion diffusion. In contrast, the present hierarchical constructed LiFePO<sub>4</sub> flower like microstructures offers capacity as high as 154 mAh g<sup>-1</sup> at 0.1–0.5 C with good power capability. This material retains about 70% capacity at 1 C with a very good cyclic ability and no noticeable fade as seen in Fig. 7. Therefore, the electrochemical performance of the LiFePO<sub>4</sub> flower like microstructure shows promising results that was observed for the LiFePO<sub>4</sub> hierarchical microstructures prepared by different synthetic routes [7,8].

#### 4. Conclusions

In summary, hierarchical flower like LiFePO<sub>4</sub> nano-microstructures were synthesized by a facile and rapid solvothermal method. Solvent played a crucial role in controlling the size and morphology of LiFePO<sub>4</sub> nanostructure. Long rods like structure were obtained using EG and hexane as the solvent and co-solvents. When ethylene glycol and oleic acid were used as a solvent and surfactant, short nanorods and hierarchical flower like LiFePO<sub>4</sub> nanostructures were obtained. The EG and oleic acid played a role of size and morphology conducting agents and acted as a carbon source, when annealed at 600 °C. Sample exhibited about 90% specific capacity at 0.5 C and showed good cyclic performance.

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