Characterization of $LiFePO_4$ Nanostructures Synthesized by Solvothermal Method

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Received: September 16, 2016; accepted: June 9, 2017

Abstract

In this work, we have synthesized $LiFePO_4$ particles with the size around 200 nm by solvothermal method. The crystalline $LiFePO_4$ was synthesized from $LiOH.H_2O$, $FeSO_4.7H_2O$ and H_3PO_4 precursors, using ethylene glycol and water as solvents. Ascorbic acid was added to the solution to prevent oxidation of Fe^{2+} to Fe^{3+}. The structure was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). Carbon black is determined to reduce the phase structure of Fe^{3+} remaining in the $LiFePO_4$ composition into Fe^{2+} after the annealing step. The $LiFePO_4$ particles were also mixed with EC 600JD carbon black and followed by the annealing at 550 °C for composite formation. Their electrochemical properties were determined by cyclic voltammetry (CV) and galvanostatic cycling with potential limit (GCPL).

Keywords: $LiFePO_4$, Li-ion battery, Solvothermal.

1. Introduction

$LiFePO_4$ (LFP) is a promising cathode material for lithium ion batteries because of its remarkable electrochemical properties, such as its high theoretical specific capacity (170 Ah/kg), long life cycles, safety with environment, and low cost (Padhi A.K. *et al.,* 1997).

However, $LiFePO_4$ has very low electronic and ionic conductivity at room temperature (~10^{-9} S/cm and 10^{-5} S/cm, respectively) and has only one channel of direction [010], which restricts its rate capability. So, to make $LiFePO_4$ a suitable cathode material for lithium ion batteries, its electronic/ionic conductivity must be increased and its length of [010] channels must be also controlled shorter for facilitation of lithium ion diffusion. To improve the electrochemical properties, various methods have been used by the researchers, ranging from the $LiFePO_4$ particle size control to carbon coating through $LiFePO_4$ composite synthesis or doping with cations superlative to Li^+ (Nan *et al.*, 2013; Padhi *et al.,* 1997; Safronova *et al.*, 2012; Wang *et al*, 2012; Wu *et al.*, 2012; Yang *et al.*, 2013; Zhou *et al.*, 2012).

The obtained $LiFePO_4$ nanocrystals appeared under different shapes, including: spindle, rod, urchin, small-particle, cuboid and flower (Nan *et al.*, 2013). The $LiFePO_4$ nanocrystals with rod shape have the length elongated of [010] prominent for the lithium ion diffusion, that being of great advantage to improve the rate capability performance.

In this study, we report the synthesis of $LiFePO_4$ crystalline size around 200nm by solvothermal method, using $LiOH.H_2O$, $FeSO_4.7H_2O$, H_3PO_4 precursors in a mixture of ethylene glycol (EG) and deionized water (DI water). Moreover, we also used ascorbic acid as an agent for preventing the oxidation of Fe^{2+} to Fe^{3+}.

2. Materials and methodes

2.1. Synthesis procedure

The $LiFePO_4$ nanocrystals were prepared by solvothermal method in a Teflon-lined autoclave at 180°C for 10 hours.

At first, solutions of $FeSO_4$-EG-DI and LiOH-EG-DI was prepared respectively, by adding 0.004 M $FeSO_4.7H_2O$ and 0.01 M $LiOH.H_2O$ in a mixture of EG and DI water (3:2 volume ratio) under ultrasonic dispersion for 20 minutes. Further, the $FeSO_4$-EG-DI solution was added with 0.02 g ascorbic acid and 0.004 M H_3PO_4. Then the solution $FeSO_4$-EG-DI with ascorbic acid, H_3PO_4 and LiOH-EG-DI were mixed in an autoclave.

The grayish green precipitates formed after solvothermal treatment (Fig.1) were filtered and repeatedly washed with DI water and ethanol for several times. The product was then dried in a vacuum furnace at 80°C for 2hours before being

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heated to 550°C for 5 hours in argon atmosphere with the heating rate of 4°C/min.

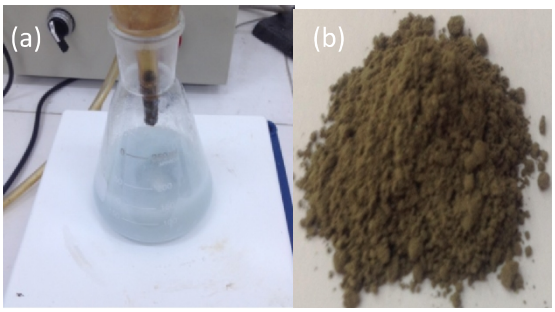

Fig. 1. Images of the compound before (a) and after solvothermal treatment (b).

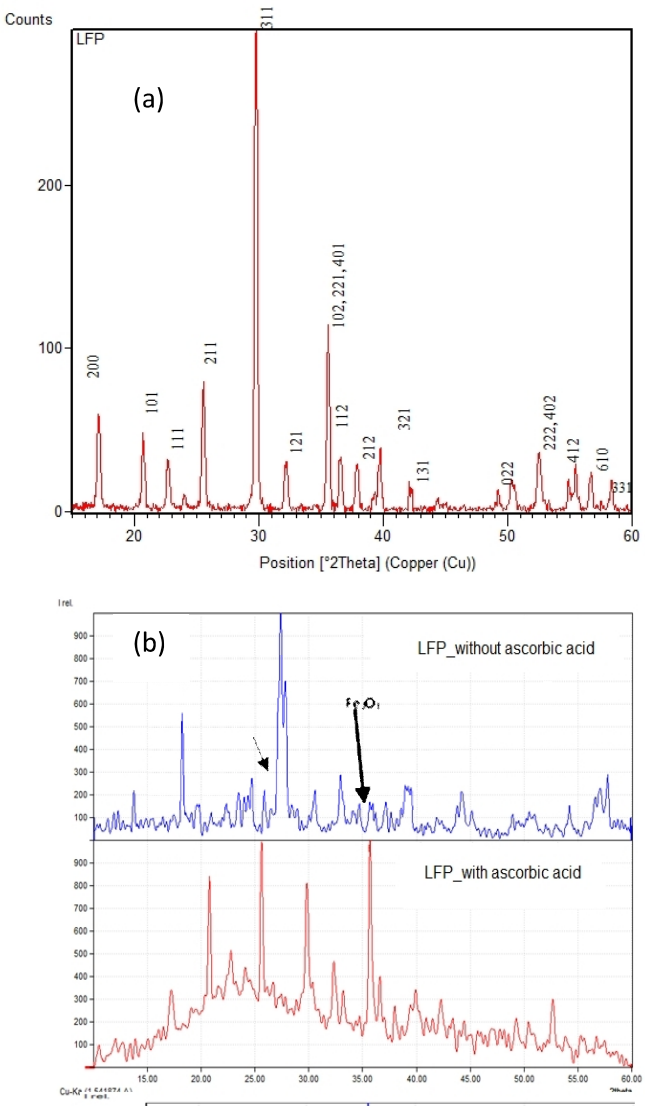

Fig. 2. XRD patterns of olivine $LiFePO_4$ prepared using ascorbic acid (a) and without ascorbic (b)

2.2. Characterization

The $LiFePO_4$ crystalline structure, phase purity and size of the particles were characterized by using a Rigaku/max 2500Pc X-ray diffractometer (XRD) with Cu-Kα radiation (λ=1.5418 Å).. The temperature and time of the crystallization of this compound were revealed by thermal analysis - TG/TDA curves. The morphology of the sample was determined by a LEO -1530 field - emission scanning electron microscopy (SEM).

For electrochemical characterization, the cyclic voltammetry measurements (CVs) were first performed for the synthesized electrode material at room temperature with a Potentio/Galvanostat Autolab 30 (MetrOhm AG) using a three electrode system. The $LiFePO_4$ powder was mixed with acetylene black and polytetrafluoroethylene (PTFE) (weight ratio 80:10:10), pasted on the aluminium foil and cut into pellets. The cell consisted of a working electrode (WE), a Pt wire as a counter electrode (CE) and a reference electrode (RE). The reference electrode consists of a silver wire immersed in 0.1 $mol.l^{-1}$ tetrabutyl ammonium perchlorate (TBAP) solution dissolved in acetonitrile within 10 $mmoll^{-1}$ $AgNO_3$. The potential of this reference electrode is 0.548 V versus a standard hydrogen electrode (SHE). The electrolyte is a 1 M solution of lithium hexafluorophosphate ($LiPF_6$) in a solvent mixture of ethylene carbonate and dimethyl carbonate (EC-DMC) (50:50 volume ratio). The measurement was carried out in a potential window of 2.5 – 4.5 V with a scan rate of about 50 $\mu V.s^{-1}$.

A charge/discharge cycling test for Swagelok-type battery was carried out in liquid electrolyte at room temperature. Cathodic paste was prepared by mixing the $LiFePO_4$ powder with carbon black and PTFE emulsion in the weight ratio of 80:10:10. This paste was then rolled down to 0.1 mm thickness, cut into pellets of 10 mm diameter and dried 130°C under a vacuum. Typical active material masses used were 15 – 20 $mg.cm^{-2}$. The electrolyte was a 1 M solution of $LiPF_6$ in EC-DMC 1:2 (Merk Co.), negative electrodes were 200 µm thick lithium foil (Metel Ges., Germany). Cells were assembled in a glove box under argon atmosphere with <2 ppm H_2O. Electrochemical studies were carried out using a MacPile Controller (Bio-Logic, France) in the potential window 2.8 – 4.2 V versus Li/Li^+ in the galvanostatic mode at the C/10 regime.

3. Results and discussion

3.1. Effect of ascorbic acid on the $LiFePO_4$ crystalline structure

Figure 2 shows X-ray diffraction patterns of two $LiFePO_4$ samples after solvothermal treatment with

and without using ascorbic acid. The comparison with published spectra of Li, Fe, P and O reveal that both XRD patterns of the as-prepared $LiFePO_4$ samples are indexed to be the orthorhombic olivine-type $LiFePO_4$ (space group Pnma, JCPDS 96-400-1849) with its characteristic main peaks at the diffraction angles 2θ = 36°, 30°, 26°, 15° correspondent with the crystal planes of {311};{211},{202};{111}{200}.

However, the $LiFePO_4$ sample without ascorbic acid contains not much olivine material $LiFePO_4$ phase due to the very low intensities of the characteristic peaks. In the XRD pattern, $Fe_3(PO_4)_2.3H_2O$ phase was clearly observed at the remarkable position peaks at 17°, 27° and 28°. There is also the presence of Fe_2O_3phase at 2θ = 24°, 33°, 35° and FeO_2 phase at the characterictic peak of 21°. In this case, the sample is partially oxidized. The $LiFePO_4$ sample with ascorbic acid is clearly identified and the typicalolivine structure of $LiFePO_4$ is indicated by the strong and intense peaks. Meanwhile, the $Fe_3(PO_4)_2.3H_2O$ phase was not observed in this pattern. The presence of FeO_2 and Fe_2O_3structures were not clearly observed due to very weak intense peaks. The grain size (D) of single phase $LiFePO_4$ was calculated by the Scherrer formula with $\beta \cos\theta = k\lambda/D$, where β is the full-width-at-half-maximum length of the diffraction peak on a 2θ scale and k is a constant here close to unit. The calculated mean value of D was approximately 200 nm.

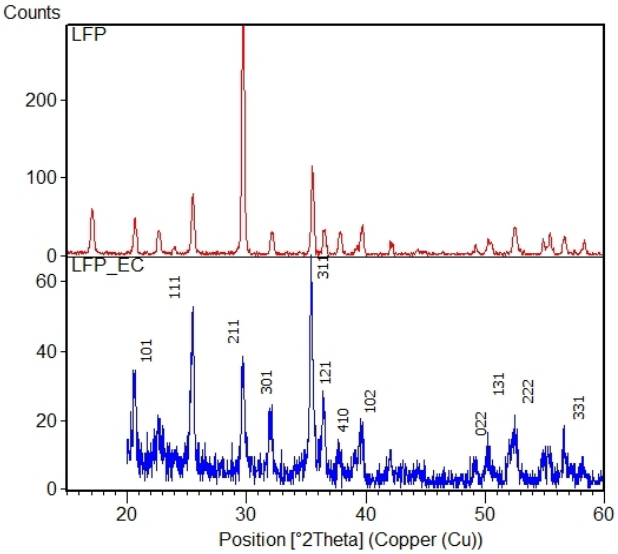

Fig. 3. XRD patterns of olivine $LiFePO_4$ prepared without carbon black Ketjen EC 600 JD (K-carbon) by solvothermal method and with K-carbon followed an annealing of 550°C

3.2. Effect of carbon on the $LiFePO_4$ crystalline structure

In order to determine the electrochemical properties of materials, we mixed $LiFePO_4$ synthesized with using ascorbic acid with carbon black. The carbon black using here is the type of Ketjen EC 600 JD (K-carbon) due to its high conductivity. The $LiFePO_4$/K-carbon composite was annealed at the temperature of 550°C for 5 hours in argon atmosphere to form a connection between the carbon and $LiFePO_4$ particles.

The XRD diagrams of the obtained samples with and without K-carbon were shown in Fig. 3: the one without K-carbon before heating and the other with K-carbon followed a heating at 550°C. The XRD results indicate that the $LiFePO_4$ sample with K-carbon after the heating gives the only crystalline phase of an olivine structure (JCPDS 96-210-0917); meanwhile, the sample without K-carbon before the heating beside a main olivine structure, shows a signal of two crystalline phases of Fe_2O_3 with the main peaks at 24°, 29°, 33°, 35° and FeO_2 at 21°, 37^0 with weak intensity despite of their unclear presence.

3.3. Effect of acid ascorbic reduce Fe^{3+}

$$2Fe^{3+} + C_6H_8O_6 => 2Fe^{2+} + 2H^+ + C_6H_6O_6 \text{ (Eq.1)}$$

From Fig. 2 and (Eq.1) analysis show that using acid ascorbic as an agent in solvents to remove impurity phases. Moveover, it supported control pH between 3.0 and 5.0 which oxidation stage from Fe^{2+} to Fe^{3+} was significantly reduced. Actually, by volumetric titration method detetimined the percentage of Fe^{2+} compare to without acid ascorbic. The rults displayed that only 3-8% of Fe^{3+} contents in solvents before solvothermal.

3.4. Effect of Thermal on the $LiFePO_4$ phase

Thermal gravimetric analysis (TGA) was used to determine thermal stability of $LiFePO_4$ phase. TGA plot illustrated that Less than 20 % of weight loss was observed in temperature range of 80 – 220°C. The first weight loss (10%) started at 70°C related to the residual water molecules in the composite structure. At around 200°C, most residual water was totally released. The second weight loss (~7%) started at 190°C could be a decomposition of organo-phosphonate excess

Between 550 and 800°C, a negligible weight loss was observed, which thereby indicated the small amount of carbon free non-bonded to the $LiFePO_4$ particle. At 860°C, the oxygen loss from $[PO_4]$ group can be occurred with negligible amount. Hence, $LiFePO_4$ composite can be annealed at 500 – 750°C to obtain well – crystallized phase(Fig. 4).

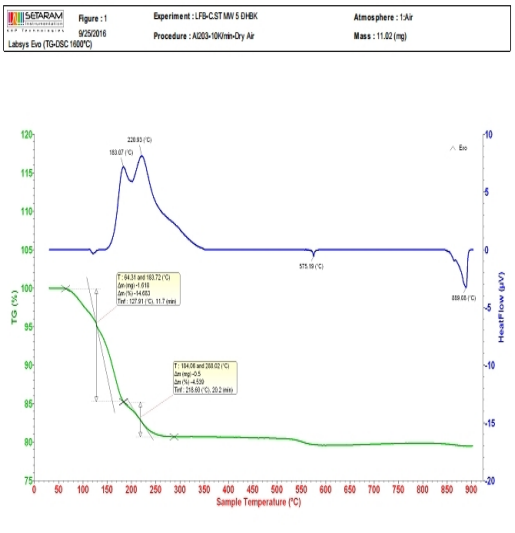

Fig. 4. Thermal analysis of $LiFePO_4$ composite conducted at heating rate of 5 °C/min.

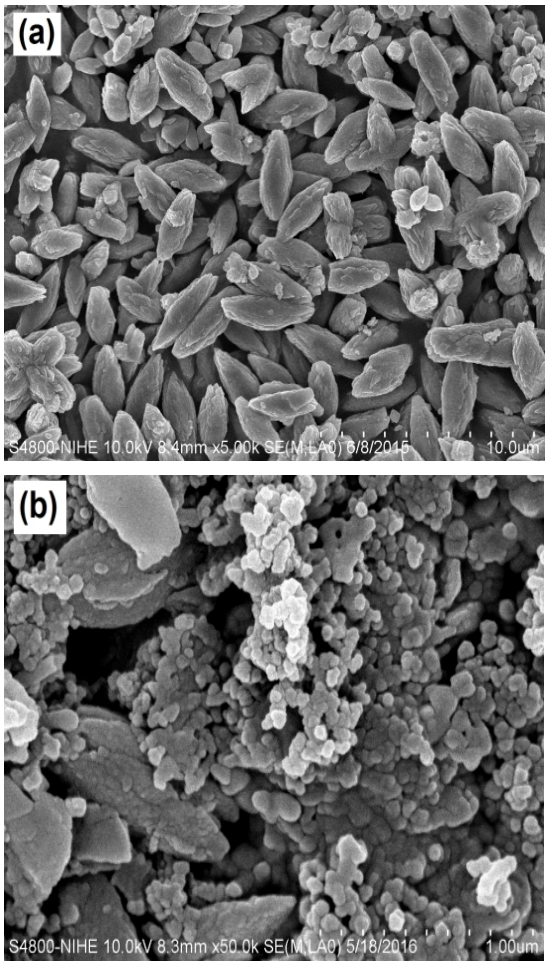

Fig. 5. SEM images of crystalline $LiFePO_4$ obtained (a) after solvothermal treatment and (b) by heating with K-carbon at 550°C for 5 hours in argon atmosphere.

The free carbon of ogarnic agent content in the composite material was difined aproximately 2-3%(over 900°C)

3.5. SEM image analysis

The morphology, size and shape of the $LiFePO_4$ particles after solvothermal treatment were examined by SEM as shown in Fig. 5. The image reveals that the crystalline sizes have an elongated rod like shape with a size about 200 nm.

3.6. Electrochemical characterization

The electrochemical properties for the synthesized electrode materials were characterized by cyclic voltammetry measurements (CVs).

The CV characterization was performed in nonaqueous 1M $LiPF_6$/EC:DMC (2:1) solution in the range 2.5 – 4.2 V. Fig. 6 shows two oxidation-reduction peaks symmetric at 3.4 – 3.5 V (vs Li^+/Li) that confirms the reversible intercalation of Li^+ ions into the host $LiFePO_4$, corresponding to the redox reaction Fe(II) ⇔ Fe(III). The redox reaction Fe^{3+}/Fe^{2+} releases Li^+ ion from $LiFePO_4$ by the folowing reaction:

$$LiFe(II)Fe(III)PO_4 \Leftrightarrow Li^+ + e^- + Fe(III)PO_4.$$

It was observed from Figure 5 that the first cycle of CV curve is irreversible, which presents two oxidation-reduction peaks unsymmetrical. This seems to be due to the unstable system for first second of measurement

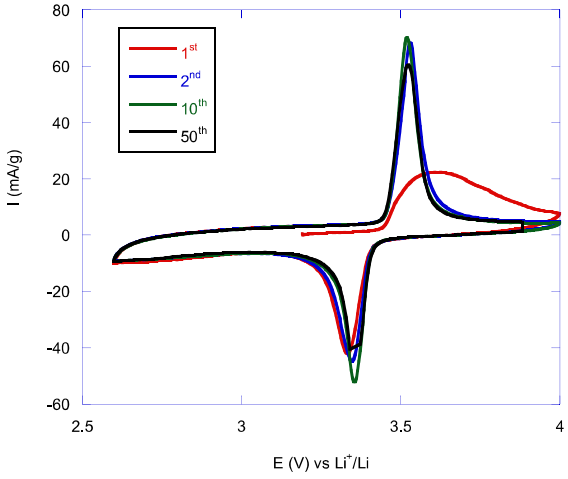

Fig. 6. Cyclic voltammetry measurements (CVs) of $LiFePO_4$/K-carbon composite for 50 cycles at scan rate 50 $\mu V.s^{-1}$.

The charge/discharge characteristics of the cathode material $LiFePO_4$/K-carbon were determined by cycling test in the potential range 2.5 – 4.2 V versus Li/Li^+ and in galvanostatic mode in the C/10 regime. The discharge specific capacity Q_s in Fig. 6 was estimated by the formula:

$$Q_S = \frac{1000}{m}\int i.dt = -\frac{26802}{M}.x \text{ [2]}$$

where M is the molar mass of $LiFePO_4$ (157.75 $g.mol^{-1}$), x is the number of intercalated Li^+ ions per formula (number of transferred electrons per intercalated ion) and 26802 is the Faraday number in mAh.

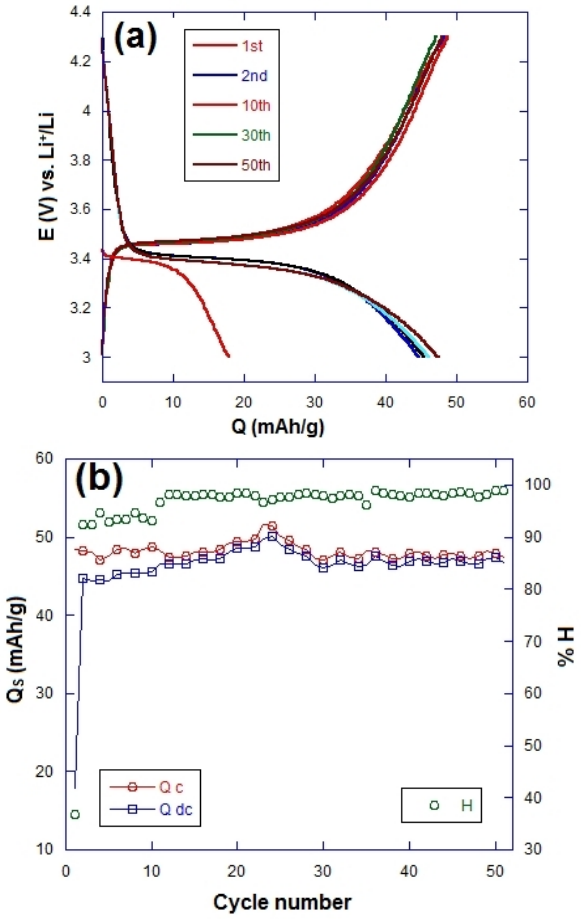

Fig. 7. (a) Initial fifty cycles of charge/discharge performance and (b) Energy storage performance of $LiFePO_4$/K- Carbon at C/10 rate between 2.5 and 4.2 V (vs. Li^+/Li).

For the first cycle of charge-discharge performance, the measurement system is not yet stable related to the asymmetric charge-discharge curve. For the second cycle, this material could intercalate 0.30 ion lithium in the structure for the Li content per formula (for one mole of the material), corresponding to the capacity ~ 50 mAh/g at C/10 regime. The sample exhibited stable performance after 50 cycles. This result is still low in comparison with the references which reported that the composite LFP/C exhibited the discharge capacity of 100 – 130 mAh/g at a C/10 rate (Nan *et al.*, 2013; Wu *et al.*, 2012; Yan *et al.*, 2012; Zhou *et al.*, 2012). This difference could be explained that the prepared $LiFePO_4$ sample is not a totally crystalline structure and a partially amorphous phase is still occurred. In addition, the conductivity of $LiFePO_4$/K-carbon material owing to a connection between $LiFePO_4$ and K-carbon is also affected on the electrode material capacity. The SEM image in Figure 4 clearly showed the weak connection between $LiFePO_4$ material and K-carbon. In fact, the electrochemical properties of the electrode depend on several factors, such as the specific surface area, the material conductivity and the adsorption capacity, which determined the electron transfer process.

4. Conclusion

By solvothermal method, we have successfully synthesized the $LiFePO_4$ crystal phase in the form of elongated rod like shape with the crystalline size around 200 nm, using ascorbic acid and K-carbon like reduction agents preventing the oxidation of Fe^{2+} to Fe^{3+}.

Cathode materials based on the $LiFePO_4$/K-carbon composite was used for rechargeable cell assembly. This $LiFePO_4$/K-carbon material exhibits good cyclability, alongside with low discharge capacity, which is due to insufficient crystallinity of $LiFePO_4$ phase and poor connection between $LiFePO_4$ and K-carbon, limiting its conductivity.

Acknowledgements

This work was financially supported by Ho Chi Minh City University of Technology and Vietnam National University – Ho Chi Minh through the Science and Technology Funds granted for T-CNVL-2015-08 and C2015-20-25 projects respectively.

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