Supporting Information

Rapid One-Pot Synthesis of $LiMPO_4$ (M=Fe, Mn) Colloidal Nanocrystals by Supercritical Ethanol Process

Dinesh Rangappa[1,2]*, Koji Sone[2], Masaki *Ichihara*[3], Tetsuichi Kudo[2] and Itaru Honma[1,2]*.
* dineshrangappa@gmail.com; i.honma@tagen.tohoku.ac.jp

Experimental Section

Synthesis

We have used common and cheap solvent ethanol as SCF medium. All the chemicals were purchased from Wako, chemicals. Firstly, precursor solution was prepared by dissolving $FeCl_2$.$4H_2O$ (0.4 mmol) in 20 ml oleylamine (60 mmol) and 16 ml ethanol at constant temperature of 60 ^oC for 1 hour. Solutions of o-H_3PO_4 (0.4 mmol) and Li acetyl acetonate (0.4 mmol) were prepared by dissolving each compound separately in 2 ml of ethanol. These solutions were slowly added to the above mixture under constant stirring. In a typical synthesis, about 5 ml of precursor solution was charged into 10 cc^3 volume stainless steel reactor and heated up to 250-400 ^oC temperatures and 38 MPa pressure for 4-10 min. Then, the reaction was terminated by quenching the reactor with cold water bath. The resultant $LiFePO_4$ nanocrystals were collected by repeated washing and centrifugation with ethanol, followed by drying in a vacuum dry oven at 120 ^oC for 12 hours.

Materials characterization

The crystal structure was examined by X-ray diffraction (XRD) analysis with a Bruker AXS D8 Advance instrument using Cu Kα radiation. The morphology was observed by high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2010F). Infrared (IR) spectra of the as prepared materials that were recorded by an FT/IR-6200 IR spectrophotometer (JASCO Corp., Tokyo, Japan).

Electrochemical characterization

The electrochemical properties of LiFePO4 nano rods were studied by assembling a beaker type three electrode cell. The samples were dried overnight at 100 ◦C in a vacuum before assembling the cell. The dried LiFePO4 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 cm2 stainless steel SUS sheet (100 mesh) using the doctor-blade method. The cathode loading was 4-5 mg/cm2. Li metal on stainless steel SUS mesh was used as a counter and reference electrodes. The electrolyte consists the solution of 1 M LiClO4 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 potential range of 2.0–4.5V versus Li under different current densities.

Supporting information Figures

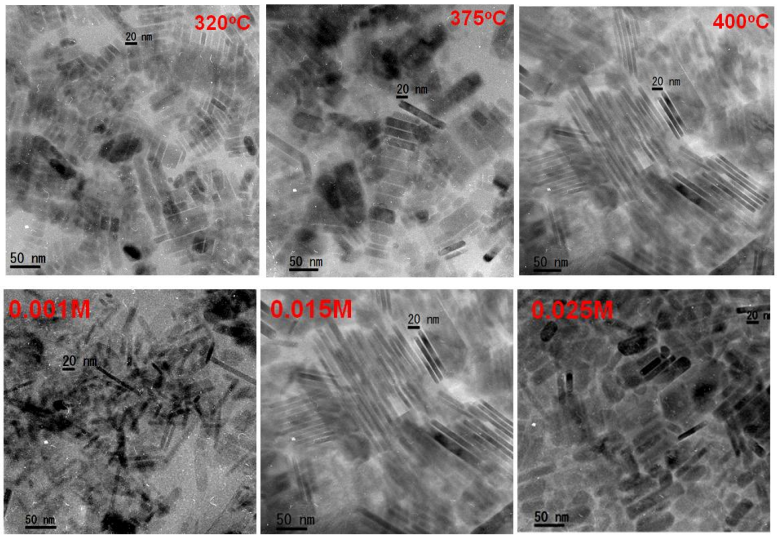

Figure S1. TEM images of $LiFePO_4$ nanocrystals synthesized at different temperature keeping constant precursor concentration 0.015M and at 10 min reaction time (top set). The bottom set images shows the nanocrystals formed at different precursor concentrations keeping reaction at constant reaction temperature 400°C for 10 min.

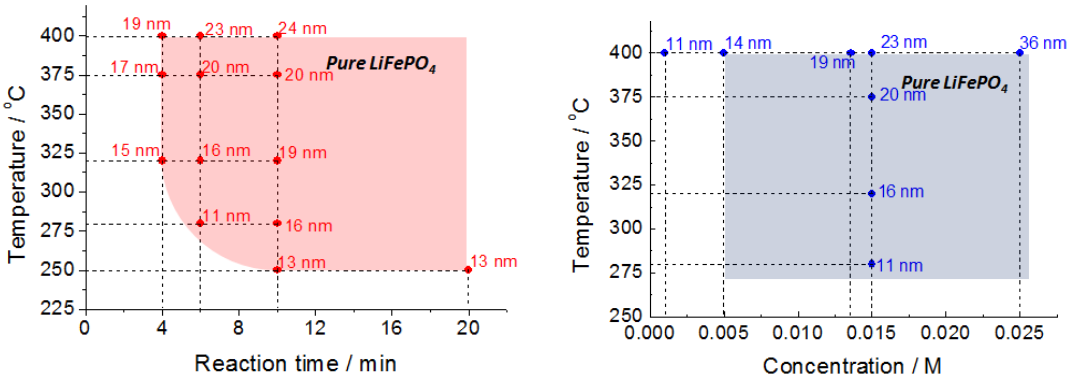

Figure S2. Effect of different reaction temperature and time/ precursor concentration on the particle size of the $LiFePO_4$ nanocrystals.

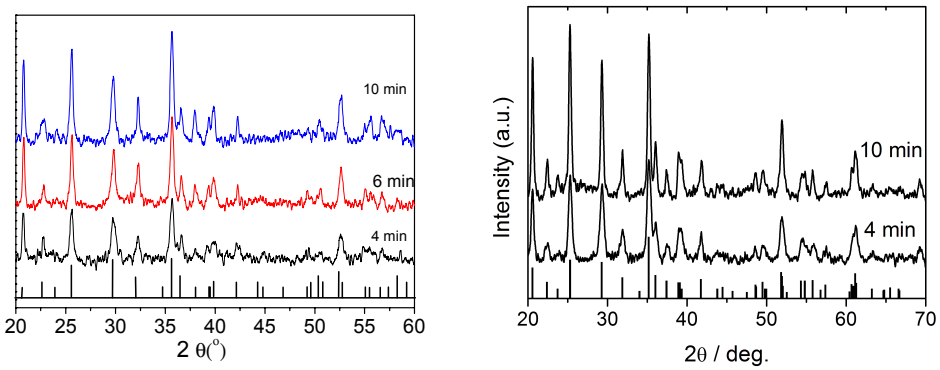

Figure S3 XRD patterns of the $LiFePO_4$ (left hand side) and $LiMnPO_4$ (right hand side) nanocrystals synthesized at different reaction time and at 400 ^oC.

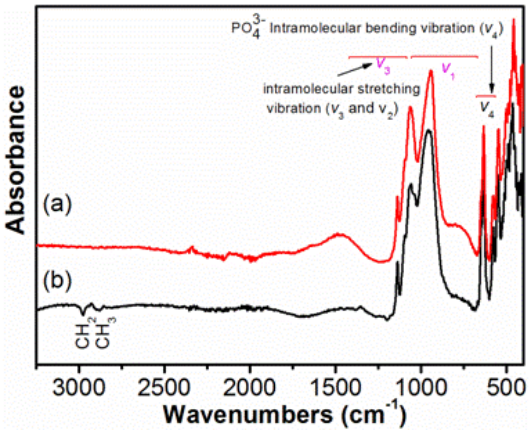

Figure S4. FTIR Spectra of $LiFePO_4$ nanocrystals synthesized in the (a) absence of oleylamine, (b) presence of oleylamine as capping and reducing agent.

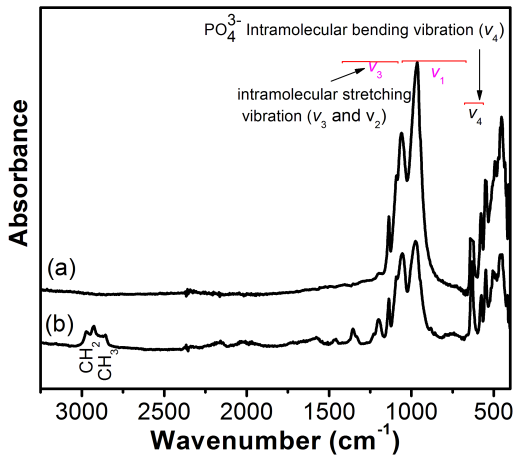

Figure S5. FTIR Spectra of $LiMnPO_4$ nanocrystals synthesized in the (a) absence of oleylamine, (b) presence of oleylamine as capping and reducing agent.

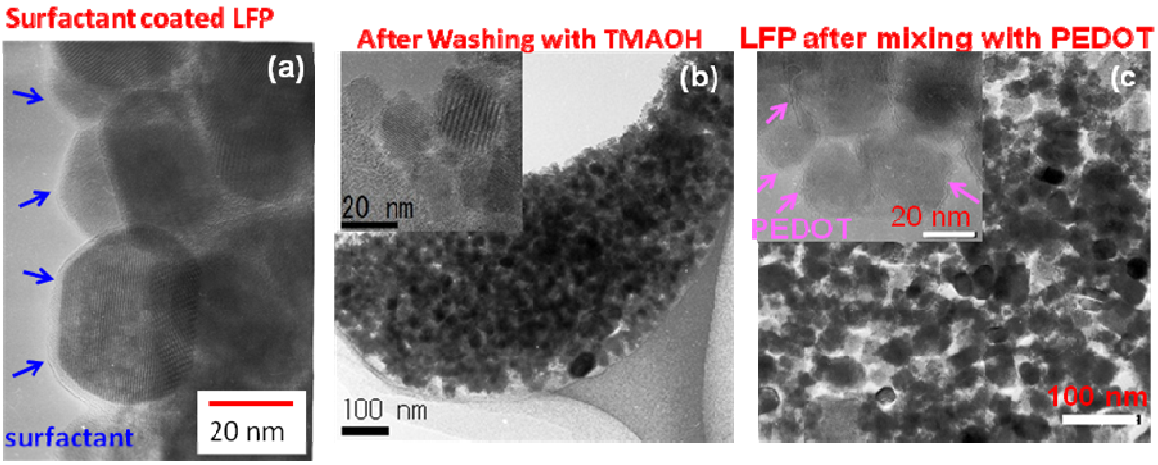

Figure S6. TEM image of (a) surface modified $LiFePO_4$ nanocrystals, (b) after removal of surfactant by washing with tetramethylammonium hydroxide, (c) $LiFePO_4$ nanocrystals surface coated PEDOT.

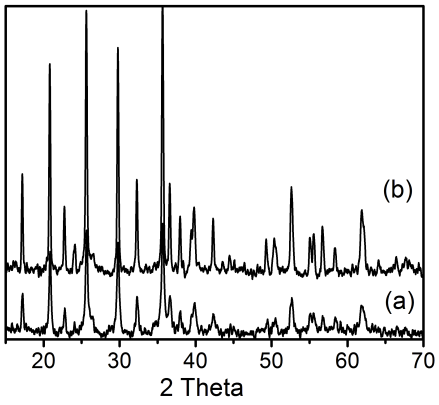

Figure S7. XRD patterns of $LiFePO_4$ (a) after ball milling carbon coating, (b) after heat treatment at 600°C, under Ar and H_2 atmosphere for 4hours.

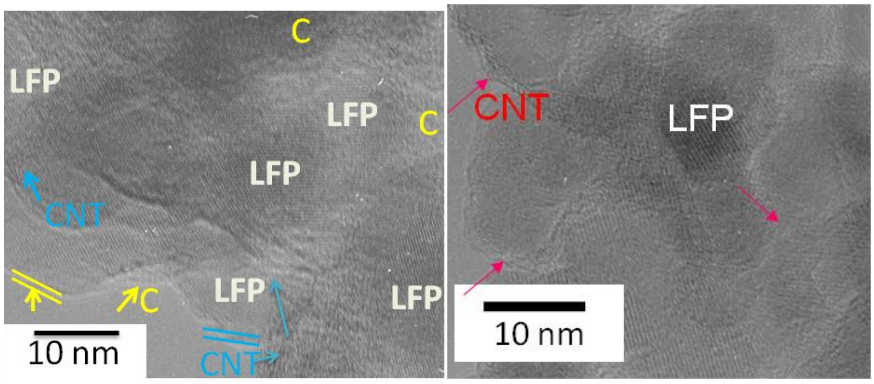

Figure S8. HR-TEM images of $LiFePO_4$ after ball milling carbon coating and heat treatment.

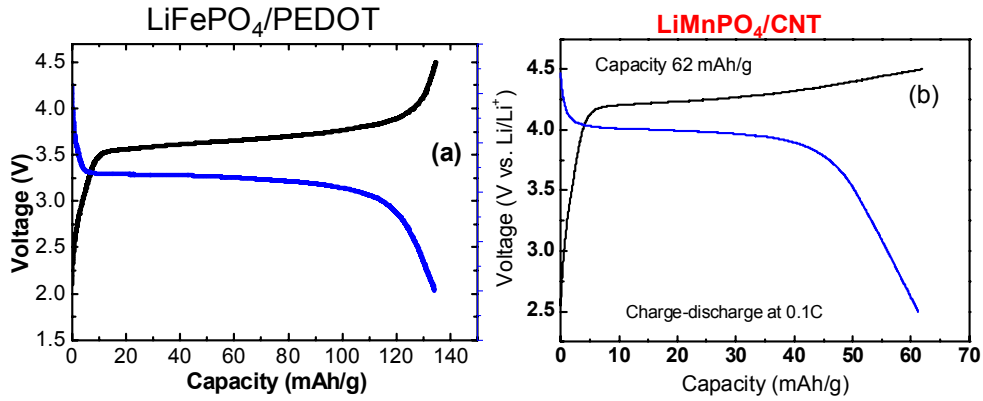

Figure S9. Charge-discharge profile of (a) $LiFePO_4$/PEDOT nanoelectrode prepared without any additional heat treatment, (b) the $LiMnPO_4$/CNT nanocrystals electrode prepared with carbon coating under ball milling followed by heattreatment at 600°C, under Ar and H_2 atmosphere for 4 h. The current density for charge-discharge measurement was 0.1C.

Table S1. The list of the comparative information of experimental parameter and products

Sample	Reaction time (min)	Temperature (°C)	Precursor Concentration	Morphology	Particle size	Electrochemical Properties
$LiFePO_4$	6	275-320	0.015 M	Spherical & plate	11-19 nm	good
	10	250	0.015-0.025 M	Nano plate	11-13 nm	
	10-15	400	0.015-0.025 M	Nano rods	11-36 nm	
$LiMnPO_4$	4	280	0.015 M	Spherical	7 nm	medium
	6	275-400	0.015-0.025 M	Spherical &plate	7-13 nm	
	10-20	400	0.015	plate	12-24	