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COMMUNICATION

Architectures of Tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ Hierarchical Microspheres and Their Lithium Storage Properties

Gang Zhou, Xiaochuan Duan,* Bin Liu, Qiuhong Li and Taihong Wang

Experimental Section

Materials

1-n-butyl-3-methy-limidazolium dihydrogenphosphate ([Bmim][H_2PO_4]) and 1-n-butyl-3-methyl imidazolium tetrafluoroborate ([Bmim][BF_4]) were obtained from Lanzhou Greenchem ILS, LICP. CAS. China. Other chemicals were purchased and used without further purification. The water used was deionized.

Synthesis of Solid Tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ Microspheres

In the typical synthesis procedure, 0.236 g of [Bmim][H_2PO_4] (1 mmol) and 0.113 g of [Bmim][BF_4] (0.5 mmol) were put into 15 mL of methanol under stirring to form a homogenous solution. Subsequently, 0.404 g of $Fe(NO_3)_3 \cdot 9H_2O$ (1 mmol) was added into the above homogenous solution under continuous stirring. Then 0.0603 g of $LiCl \cdot H_2O$ (1 mmol) was added into the solution and continued to stir for 10 min, the total solution was transferred into a stainless-steel autoclave with a capacity of 20 mL, sealed and heated at 180 °C for 48 h. When the reaction was completed, the autoclave was cooled to room temperature naturally. The resultant product was collected and washed with deionized water and anhydrous ethanol for several times until the solution was neutral. The final product was dried in a vacuum at 80 °C for 3 h. Varying the amount of $Fe(NO_3)_3 \cdot 9H_2O$ and ionic liquid precursors ([Bmim][H_2PO_4] and [Bmim][BF_4]) could produce a series of tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ microspheres with different morphologies. The synthetic conditions for preparing some typical samples are summarized in Table S1.

Synthesis of Hollow Tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ Microspheres

To obtain hollow tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ microspheres, we use inorganic salts, ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and ammonium fluoride (NH_4F), instead of ionic liquid precursors ([Bmim][H_2PO_4] and [Bmim][BF_4]) to serve as phosphate source and fluoride source, while preserving other conditions described above. The detailed data can be found in Table S1.

Characterizations

The products were characterized by XRD, SEM, TEM and HR-TEM measurements. XRD measurements were performed on a Rigaku D/max 2500 diffractometer with Cu Kα radiation (λ= 0.154056 nm) at V= 40 kV and I = 150 mA, and the scanning speed was 8°/min. Morphology observations were performed on a Hitachi S4800 field emission scanning electron microscope (FE-SEM). The composition was analyzed with an Oxford INCA energy-dispersive spectroscopy (EDS) module attached to the SEM microscope. TEM and HR-TEM images were recorded with a Tecnai G2 20S-Twin transmission electron microscope operating at an accelerating voltage of 120 kV. N_2 adsorption/desorption isotherms were collected at liquid nitrogen temperature using a Quantachrome Nova 2000e sorption analyzer. The specific surface areas (SBET) of the samples were calculated following the multipoint Brunauer-Emmett-Teller (BET) procedure.

Electrochemical Test

Electrochemical studies were characterized in CR2016-type coin cell with a multi-channel current static system Arbin (Arbin Instruments BT 2000, USA). The cathode electrode consisted of 80 wt% active material, 10 wt% conductivity agents, and 10 wt% binder polymer binder on a aluminum foil. Test cells were assembled in an argon-filled glove box with water and oxygen contents less than 1 ppm. Li foil was used as counter electrode, polypropylene (PP) film (Celgard 2400) as separator. The electrolyte was 1m $LiPF_6$ (EC/DC/DMC 1:1:1). The cells were discharge-charged between 2.0 and 4.5 V at room temperature.

Table S1. Summary of the Experimental Parameters and Their Corresponding Morphologies of Tavorite Microspheres Obtained under Different Conditions.

No.	n(Fe^{3+}) (mmol)	n([Bmim][H_2PO_4]) (mmol)	n([Bmim][BF_4]) (mmol)	n($NH_4H_2PO_4$) (mmol)	n(NH_4F) (mmol)	Morphology
S1	1	1	0.5	-	-	microspheres composed of irregular particles
S2	2	2	1	-	-	microspheres composed of polyhedra
S3	3	3	1.5	-	-	microsphere composed of nanorods
S4	1	-	-	1	0.5	hollow microspheres

All the reactions were conducted at 180 ºC for 48 h.

Table S2. Summary of Refined Cell Parameters of the Samples and JCPDS Card 72-2482.

No.	*a* (Å)	*b* (Å)	*c* (Å)	*α*	*β*	*γ*	volume (Å^3)
Standard	5.138	5.307	7.422	67.48	67.72	81.98	172.99
S1	5.13797	5.30697	7.42213	67.4818	67.7195	81.9801	172.99
S2	5.13790	5.30704	7.42209	67.4783	67.7170	81.9797	172.98
S3	5.13793	5.30698	7.42196	67.4815	67.7201	81.9802	172.98
S4	5.13798	5.30698	7.42204	67.4794	67.7192	81.9793	172.98

Cell parameters indexed using MDI Jade

Architecture of Shell Structure

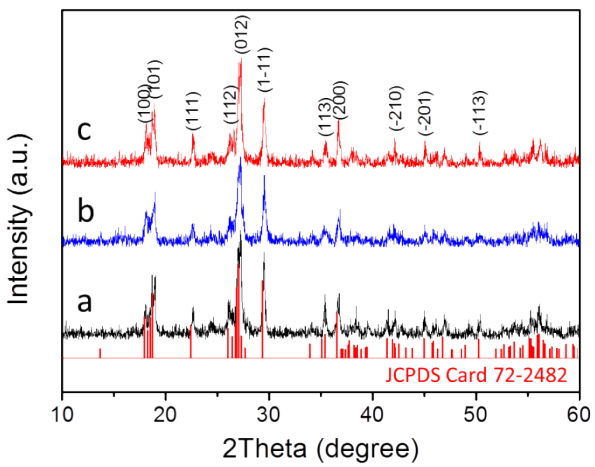

Figure S1. XRD patterns of as-synthesized tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ microspheres with different morphologies from different concentration of $Fe(NO_3)_3{\cdot}9H_2O$ and ionic liquid precursors ([Bmim][H_2PO_4] and [Bmim][BF_4]): (a) S1, microspheres composed of irregular particles; (b) S2, microspheres composed of polyhedra; (c) S3, microspheres composed of nanorods. All of the diffraction peaks can be indexed to the triclinic structure of tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$, which are consistent with the reported values (JCPDS Card 72-2482).

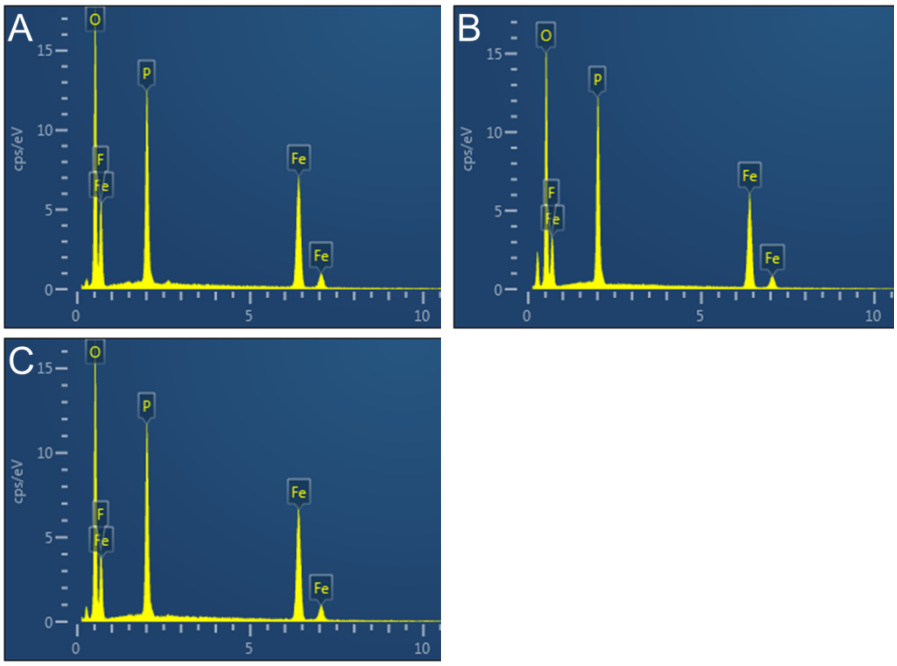

Figure S2. Energy-dispersive X-ray spectrum (EDS) of as-synthesized tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ microspheres: (A) S1, microspheres composed of irregular particles; (B) S2, microspheres composed of polyhedra; (C) S3, microspheres composed of nanorods.

Table S3. Weight Ratio and Atom Ratio of the Elements according to EDS

No.	Fe (wt%)	P (wt%)	F (wt%)	O (wt%)	n(Fe): n(P): n(F): n(O)
S1	34.22	18.29	6.08	41.42	1:0.95:0.52:4.31
S2	35.28	18.61	6.08	40.88	1:0.95:0.51:4.22
S3	34.16	17.98	5.89	42.04	1:0.95:0.51:4.41

According to the stoichiometric ratio of tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$, the standard atom ratio of n(Fe): n(P): n(F): n(O) is 1:1:0.5:4.5.

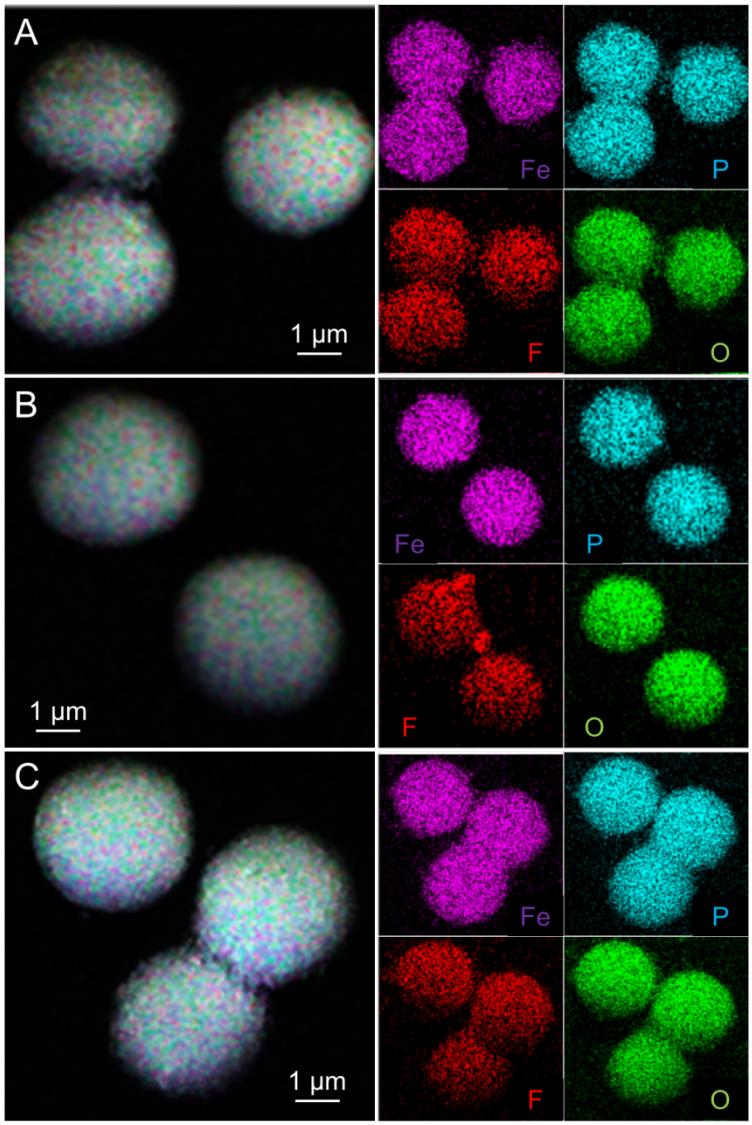

Figure S3. SEM image of as-synthesized tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ microspheres and corresponding elemental mappings of Fe, P, F and O: (A) S1; (B) S2; (C) S3.

Creation of Interior Space

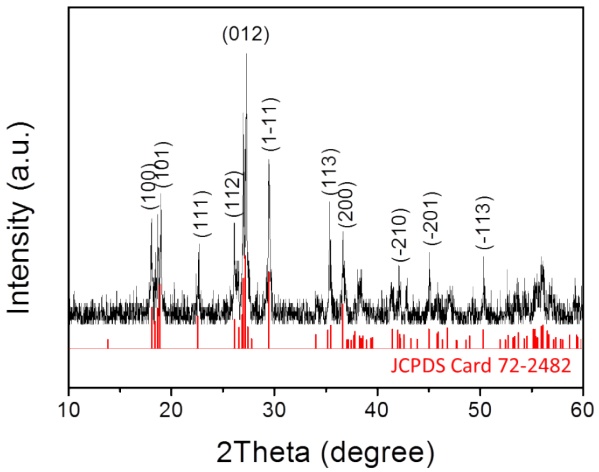

Figure S4. XRD patterns of as-synthesized tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ hollow microspheres. All of the diffraction peaks can be indexed to the triclinic structure of tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$, which are consistent with the reported values (JCPDS Card 72-2482).

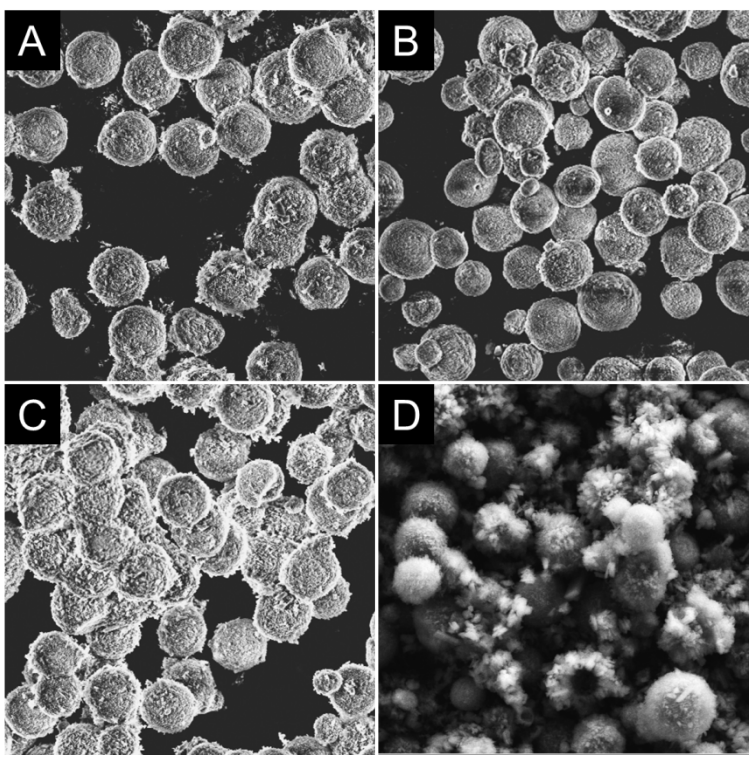

Figure S5. SEM image of as-synthesized tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ electrodes before galvanostatic discharging/charging: (A) S1; (B) S2; (C) S3; (D) S4.

Electrochemical Property

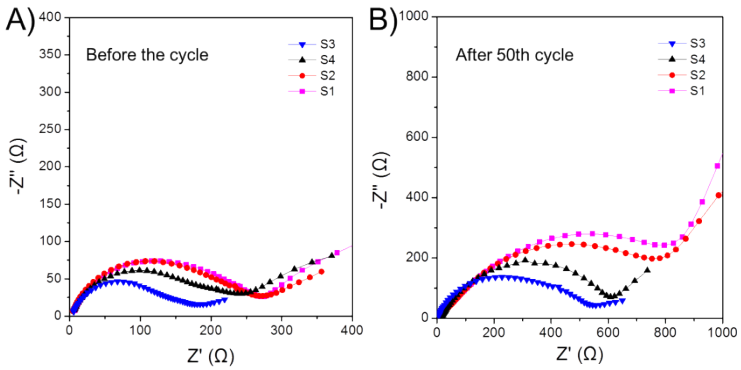

Figure S6. Impedance spectra (Nyquist plots) of tavorite $LiFe(PO_4)(OH)_{0.5}F_{0.5}$ electrode materials collected in charged state after different cycles: (A) before the cycle; (B) after 50th cycle.