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**3D graphene aerogel framework enwrapped LiFePO<sub>4</sub>  
submicron-rods with improved lithium storage performance**

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1 **Abstract**

2       The three-dimensional (3D) graphene aerogel (GA)-wrapped LiFePO<sub>4</sub>  
3 submicron-rod composite (LFP@GA) has been prepared successfully through a  
4 solvothermal method followed with rapid freeze-drying. Monodispersed LiFePO<sub>4</sub>  
5 submicron-rods are well-enwrapped with the graphene sheets and which further forms  
6 a highly porous and conductive 3D structure, leading to the overall rapid electron  
7 transport of the composite electrode and affording many interwoven pores for fast  
8 supply of Li<sup>+</sup> and storage of electrolyte. Moreover, the combination of the rod-shaped  
9 LFP and porous 3D structure can effectively relieve the stress resulted from the  
10 structural change during the insertion/deinsertion of Li<sup>+</sup>. Owing to these particular  
11 structure and characteristics, the LFP@GA composite presents a high discharge  
12 capacity (162.7 mAh g<sup>-1</sup> at 0.1 C), a remarkable rate capacity (119.9 mAh g<sup>-1</sup> at 5 C)  
13 and an excellent long-term cycle stability after 1000 cycles at 1 C (86.5% capacity  
14 retention), which is potential for use in Li-ion batteries.

15 **Keywords:** LiFePO<sub>4</sub> submicron-rod; graphene aerogel; solvothermal method; cathode;  
16 Li-ion battery

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## 1 **1. Introduction**

2 Li-ion batteries (LIBs) have been the prominent energy suppliers of the high-tech  
3 portable electronic equipments for decades. However, for the forthcoming widespread  
4 applications (electric vehicles, hybrid vehicles, etc), further improving energy/power  
5 density, safety, durability and cost of LIBs are highly required [1-6]. The LiFePO<sub>4</sub>  
6 (LFP) with olivine structure is widely accepted as a potential cathode candidate of  
7 LIBs owing to the high operating voltage ( $\sim 3.4$  V vs Li/Li<sup>+</sup>) and theoretical specific  
8 capacity ( $\sim 170$  mAh g<sup>-1</sup>), excellent thermostability and safety, lowcost and  
9 environmentally benign [7-10]. Nevertheless, the intrinsically low electron  
10 conductivity and Li<sup>+</sup> diffusion are still the main barriers for obtaining high  
11 gravimetric/volumetric power density of this material, which significantly limit its  
12 broad use in EVs and HEVs [11]. To date, enormous achievements have been made to  
13 conquer the electron and ion transmission restrictions for LFP, such as electronically  
14 conductive agents coating [12-16], atomic substitution [17,18], optimizing the size  
15 and morphology [1,19], and constructing the three-dimensional conducting network  
16 [20,21]

17 Among these strategies, the nanosized LiFePO<sub>4</sub> can effectively decrease the  
18 kinetic barrier, reduce the migration path for Li<sup>+</sup> and electrons and increase the  
19 specific surface area, thus improving the reaction dynamic during charge/discharge  
20 processes [22,23]. However, the nanoscale materials tend to agglomerate, resulting in  
21 the poor thermal and cycling stability during long-term use [24,25]. In contrast,  
22 materials with intermediate particle sizes sometimes display the best performance [26].

1 Recently, optimizing the size and morphology of  $\text{LiFePO}_4$  has attracted widespread  
2 attention. The one-dimensional micro/nano structured material can effectively reduce  
3 the transport path for  $\text{Li}^+$  and electrons, enlarge the contact region between electrode  
4 material and electrolyte, alleviate the strain caused by  $\text{Li}^+$  and improve the structural  
5 passability during the repeated insertion/deinsertion processes [27, 28].

6 Meanwhile, the carbonaceous materials have been considered as one of the most  
7 effective materials for coating the  $\text{LiFePO}_4$  particles, which makes the surface of the  
8 material more conductive and relieves the electrode polarization [29]. Nevertheless,  
9 the carbon material introduced into the  $\text{LiFePO}_4/\text{C}$  composites is usually amorphous,  
10 and the content, dispersion and coating layer thickness of carbon material are difficult  
11 to control during the preparation process. In recent years, graphene has attracted  
12 unprecedented attention owing to its ultrahigh specific surface area, outstanding  
13 electronic conductivity, superior mechanic strength and structural flexibility, and  
14 excellent chemical/thermal stability [30-34]. Compared to the amorphous carbon  
15 coating modification, the graphene coating possesses better conductive properties,  
16 more uniform and complete surface coverage. Nevertheless, graphene is generally  
17 derived from graphene oxide (GO) synthesized via the Hummers method, which is  
18 liable to cause the re-stack of graphene sheets via the  $\pi$ - $\pi$  interactions, resulting in the  
19 loss of specific surface area [35]. Recently, the porous graphene aerogel (GA) has  
20 been constructed to effectively prevent graphene sheets from re-stacking and  
21 significantly accelerate the diffusion of electrons and ions due to its extraordinary

1 three-dimensional porous cross-linked structure and the excellent electrical  
2 conductivity of graphene [36,37].

3       Herein, we have proposed a facile two-step route for preparing the 3D porous  
4 GA-wrapped LiFePO<sub>4</sub> submicron-rods composite (LFP@GA) by a solvothermal  
5 method followed with a rapid freeze-drying process. To the best of our knowledge,  
6 this is the first report on the 3D structural porous graphene aerogel wrapped LiFePO<sub>4</sub>  
7 submicron-rod composite materials. On one hand, the obtained intermediate LiFePO<sub>4</sub>  
8 submicron-rods can shorten the Li<sup>+</sup> diffusion distance, relieve the agglomeration of  
9 the particles and alleviate the stress of material resulted from the Li<sup>+</sup> insertion and  
10 deinsertion to some degree. On the other hand, the formed 3D porous GA-wrapped  
11 LiFePO<sub>4</sub> submicron-rods composite by the rapid freeze-drying method can effectively  
12 prevent the re-stack of graphene sheets and agglomeration of the LiFePO<sub>4</sub>  
13 submicron-rods, which largely increase the utilization efficiency of graphene and  
14 LiFePO<sub>4</sub>. The unique porous conductive structure can not only effectively shorten the  
15 Li<sup>+</sup> and electron transport distance, provide plenty of space for storing the electrolyte,  
16 but also act as Li<sup>+</sup> diffusion channels and accommodate the stress of material resulted  
17 from the Li<sup>+</sup> insertion/deinsertion processes. Compared to the pristine LFP, the porous  
18 graphene aerogel-wrapped LiFePO<sub>4</sub> submicron-rod composite (LFP@GA) presents  
19 excellent specific capacity, rate performance and cyclability, enabling a potential  
20 material for use in Li-ion batteries.

## 21 **2. Experimental**

## 1 2.1. Preparation

2 A modified Hummers method was used to prepare the graphene oxide (GO) [38].  
3 The 3D graphene aerogel-wrapped LiFePO<sub>4</sub> submicron-rod composite (LFP@GA)  
4 was prepared through a solvothermal method followed with rapid freeze-drying. First,  
5 FeSO<sub>4</sub>·7H<sub>2</sub>O (Aladdin Chemistry Co.Ltd, AR, 99.0%), NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (Aladdin  
6 Chemistry Co.Ltd, AR, 99.0%) and LiOH (Aladdin Chemistry Co.Ltd, AR, 98.0%)  
7 were dissolved in distilled water with the molar ratio of 1:1:2 to form a homogeneous  
8 solution. Subsequently, isopropanol (Aladdin Chemistry Co.Ltd, AR, 99.9%) and  
9 nitrilotriacetic acid (NTA, Aladdin Chemistry Co.Ltd, AR, 99.0%) were added and  
10 then adjusting the pH to 9 by adding concentrated ammonia solution drop by drop.  
11 Afterwards, the obtained mixture was transferred into the autoclave and kept at 200 °C  
12 for 20 h. The final products were washed to get rid of the remaining ions and dried to  
13 obtain the LFP submicron-rods. To prepare the LFP@GA, the as-obtained LiFePO<sub>4</sub>  
14 submicron-rods were re-dispersed into the as-prepared 3.0 mg·mL<sup>-1</sup> of GO suspension  
15 under intense stirring, followed by freeze-drying and heating at 500 °C for 5 h in a  
16 reducing atmosphere (10 vol% H<sub>2</sub> in Ar) to generate the 3D porous GA-wrapped  
17 LiFePO<sub>4</sub> submicron-rod composite (LFP@GA). During the heat treatment, the  
18 hydrogen is used to avoid the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> in LiFePO<sub>4</sub>.

## 19 2.2. Structural characterization

20 X-ray diffraction (XRD) was performed on Xpert Pro MPD diffractometer with  
21 Cu K<sub>α</sub> radiation ( $\lambda = 0.15418$  nm). The Raman data were recorded on an IVNIA  
22 spectroscopy with an argon ion laser operating at 514 nm at room temperature. The

1 morphology of samples was investigated with scanning electron microscopy (SEM,  
2 PHILIPS XL30TMP) and transmission electron microscope (TEM, JEM-2000 UHR  
3 SETM/EDS). N<sub>2</sub> adsorption-desorption tests were conducted on Autosorb-1-MP/LP.  
4 The amount of carbon was obtained by the thermal gravimetric analysis (TGA) on  
5 STA449/6/G (NETZSCH-Gerätebau GmbH) with a temperature rate of 10 °C min<sup>-1</sup>  
6 from 30 to 1000 °C in air.

### 7 2.3. Electrochemical measurements

8 For preparing the electrode, the as-synthesized LFP@GA sample was mixed  
9 with Super P acetylene black and polyvinylidene fluoride (PVDF) (80:12:8 in weight)  
10 in N-methyl-2-pyrrolidone (NMP) to generate a homogeneous slurry. The obtained  
11 slurry was uniformly **cast** on the aluminum foil and dried overnight under vacuum at  
12 100 °C. The loading of obtained working electrodes (Ø=1.4 mm) is controlled at 1-2  
13 mg cm<sup>-2</sup>, and according to the weight ratio of active material (80%), the mass loading  
14 of active material is around 0.8-1.6 mg cm<sup>-2</sup>. The CR2032 type coin cells were  
15 fabricated in the Ar-filled glove box using Li metal as the anode, the microporous  
16 polypropylene film (Celgard 2400) as the separator, and 1 M LiPF<sub>6</sub> in EC-DMC (1 : 1  
17 in volume) as the liquid electrolyte. **For preparation of the pristine LFP electrode, the**  
18 **weight ratio of the pristine LFP, Super P and PVDF was controlled to be 63:29:8, to**  
19 **ensure the same amount of conductive additives as the LFP@GA electrode.**

20 The charge/discharge curves were recorded from 2.5 to 4.0 V (vs. Li<sup>+</sup>/Li) with  
21 the Neware BTS-5V5mA system. Cyclic voltammetry (CV) and electrochemical  
22 impedance spectroscopy (EIS) measurements were performed with the

1 electrochemical workstation (CHI 660D) after 5 charge-discharge cycles at 0.1 C. The  
2 CV measurements were conducted at 0.1 and 1 mV s<sup>-1</sup> from 2.5 to 4.2 V (vs. Li<sup>+</sup>/Li),  
3 and the EIS measurements were conducted between 100 kHz to 100 mHz (the applied  
4 bias voltage is 10 mV). All the measurements were performed at room temperature.

### 5 **3. Results and discussion**

6 The overall synthesis strategy for constructing the 3D porous GA-wrapped  
7 LiFePO<sub>4</sub> submicron-rods (LFP@GA) is shown in Fig. 1. The raw materials were first  
8 dissolved in distilled water to obtain a homogeneous mixture (Fig. 1a) and the  
9 LiFePO<sub>4</sub> submicron-rods were obtained after the solvothermal reaction. During the  
10 solvothermal process, the nitrilotriacetic acid (NTA) and isopropanol, as complexing  
11 agent and solvent respectively, play an important role in the growth of the rod-like  
12 LiFePO<sub>4</sub>. NTA can provide four coordination bonds for metal ions and possess the  
13 strong complexing ability to form the stable chelate compound. In addition, the  
14 electronic structure and properties of different crystal planes of LiFePO<sub>4</sub> are different  
15 due to the various Fe and P contributions at the crystal surface [39]. A larger  
16 proportion of Fe atoms on the crystal surface leads to a stronger metallic property and  
17 then a stronger Fe-NTA coordination bond, which may cause the inhibition and slow  
18 growth of the crystal surface due to the more reduced energy. During the anisotropic  
19 growth process of LiFePO<sub>4</sub>, the crystal grows along the direction with relatively  
20 larger surface energy, while the crystal surface with relatively smaller energy grows  
21 slowly [39]. At the same time, a chain structure may be formed due to the hydrogen



1 bond between NTAs (or isopropanol), which is adsorbed on a specific crystal surface  
2 of LiFePO<sub>4</sub> and acts as a soft template to guide the eventual formation of the rod-like  
3 LiFePO<sub>4</sub>. This phenomenon is similar to the "ethylene glycol and oleic acid effect"  
4 reported by Rangappa et al [40]. The as-obtained LiFePO<sub>4</sub> submicron-rods were  
5 re-dispersed into the pre-synthesized GO suspension (Fig. 1b), and the 3D porous  
6 graphene aerogel wrapped LiFePO<sub>4</sub> submicron-rods composite (LFP@GA) was  
7 formed after a rapid freeze-drying process and subsequent heat treatment (Fig. 1c).  
8 The GO was partially reduced to graphene during the heat treatment. As shown in Fig.  
9 1c and d, the reduced graphene sheets are tightly wrapping the monodispersed  
10 LiFePO<sub>4</sub> submicron-rods and further intertwining to form a three-dimensional porous  
11 conductive network, which can not only effectively enhance the overall electronic  
12 conductivity and promote the electronic and Li<sup>+</sup> transport of the LFP@GA composite,  
13 but also effectively buffer the structural change during the continuous cycling.

14 The obtained samples were examined by XRD to identify the phase structures  
15 and typical XRD patterns are shown in Fig. 2a. All the peaks for LFP and LFP@GA  
16 are well indexed to the orthorhombic LiFePO<sub>4</sub> (JCPDS NO. 01-083-2092) without  
17 any impurity, implying the high purity and crystallinity [41]. Compared to that of the  
18 pristine LFP, the (011) peak at 23-24° is almost disappeared in the XRD pattern of the  
19 LFP@GA composite, and the intensity ratio of the (412) and (610) peaks changes as  
20 well. These slight variation might be ascribed to the presence of graphene nanosheets  
21 wrapped on the surface of LFP submicron-rods, which may change the gathering of  
22 the LFP crystals and alter the X-ray diffractions of some specific planes.

1 Nevertheless, there is no clear observation of graphene for LFP@GA, indicating that  
2 graphene does not affect the crystal structure of LFP, probably due to the overlap of  
3 (111) diffraction peak of LFP [21].

4 Raman spectroscopy was further recorded to verify the phase structure and  
5 reduction of GO in the LFP@GA composite. As shown in Fig. 2b, LFP displays the  
6 band at about  $950\text{ cm}^{-1}$ , which can be attributed to the symmetric  $\text{PO}_4^{3-}$  stretching  
7 vibration [42]. Meanwhile, GO exhibits the obvious vibrational peaks at around 1360  
8 and  $1590\text{ cm}^{-1}$ , respectively ascribed to the D-band which represents the  
9 disorders/defects in the graphite structure and G-band which indicates the presence of  
10 graphite carbon) [41]. Compared to LFP and GO, the LFP@GA composite shows  
11 peaks of both of LFP and GO, indicating the successful introduction of GO in the  
12 LFP@GA composite. However, the intensity ratio of the D-band and G-band in the  
13 LFP@GA composite changes significantly compared to GO. In general, the intensity  
14 ratio of D-band and G-band ( $I_D/I_G$ ) is used to reflect the degree of surface disorder of  
15 carbon materials. The  $I_D/I_G$  value of LFP@GA was calculated to be 1.15, higher than  
16 that of GO (0.86), indicating the increase of disorder of GA in the LFP@GA  
17 composite. This point might be resulted from the removal of the oxygen-containing  
18 groups on the surface of GO, verifying the reduction of GO during the heat treatment  
19 process [43].

20 The morphology of the samples is implied in Fig. 3. Fig. 3a and b exhibit that the  
21 most of LFP crystallizes into uniformly distributed submicron-rods of 200-400 nm in  
22 diameter and 0.6-1.5  $\mu\text{m}$  in length. The addition of nitrilotriacetic acid (NTA) and

1 isopropanol is essential for the formation of the LFP submicron-rods, as the interface  
2 state of the solution system could be changed and the added NTA and isopropanol  
3 may be absorbed on some of the formed LFP crystal surfaces, resulting in the  
4 orientation growth into a rod-shape structure. The obtained  $\text{LiFePO}_4$  submicron-rods  
5 with intermediate size can shorten the  $\text{Li}^+$  diffusion distance in the radial direction,  
6 and relieve the **agglomeration** of the particles and alleviate the stress of material  
7 resulted from the Li-ion insertion and deinsertion, thus increasing the structure and  
8 cycling stability. Fig. 3c and d display typical SEM images of LFP@GA. The  
9 three-dimensional porous network structure composed of intertwined graphene sheets  
10 are clearly observed, which is conducive to the infiltration of electrolytes and the  
11 rapid diffusion of Li-ion [21]. The rapid freezing in liquid nitrogen and following  
12 freeze-drying is the key to form the 3D porous composite. When exposing to  
13 extremely low temperatures (liquid nitrogen), the components of system tend to  
14 shrink and come closer together, leading to the close contact between graphene and  
15  $\text{LiFePO}_4$  and also effectively preventing the re-stacking of graphene sheets and  
16 agglomeration of the  $\text{LiFePO}_4$  submicron-rods. Though the graphene sheets are of  
17 two-dimensional, they are flexible and easily bent to uniformly cover and wrap the  
18 one-dimensional rod-shaped  $\text{LiFePO}_4$  materials during the rapid freezing and  
19 freeze-drying process. As shown in Fig. 3d, most of the rod-shaped  $\text{LiFePO}_4$  materials  
20 are uniformly wrapped with the flexible and crosslinked graphene sheets (GA). After  
21 introducing the graphene aerogel, the retained  $\text{LiFePO}_4$  submicron-rods are closely  
22 enwrapped by graphene sheets, assuring a large contact area between  $\text{LiFePO}_4$  and

1 graphene and good connection among the monodisperse  $\text{LiFePO}_4$  rods to enhance the  
2 overall electron conductivity of the material. Meanwhile, the unique porous structure  
3 can not only effectively shorten the  $\text{Li}^+$  and electron transport distance, provide plenty  
4 of space for storing the electrolyte, but also act as  $\text{Li}^+$  diffusion channels and  
5 accommodate the stress of material. These advantages mentioned above are  
6 conducive to enhance the electrochemical activity and rate performance of the  
7  $\text{LiFePO}_4$  materials. The microstructure of LFP@GA is further investigated by TEM in  
8 Fig. 4. It is clear that the  $\text{LiFePO}_4$  submicron-rods are enwrapped tightly by graphene  
9 sheets. The observed lattice fringe with a width of  $3.48 \text{ \AA}$  shown in Fig. 4b consists  
10 with the (111) plane of  $\text{LiFePO}_4$ , demonstrating that the LFP submicron-rods is of  
11 highly crystallinity [13,44].

12 In order to measure the amount of carbon for LFP@GA composite, the thermal  
13 gravimetric analysis (TGA) measurements were performed on both samples, as  
14 illustrated in Fig. 5a. The original  $\text{LiFePO}_4$  is oxidized to  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Fe}_2\text{O}_3$   
15 between  $320$  and  $550 \text{ }^\circ\text{C}$ , resulting in an increase in mass. For LFP@GA composite,  
16 the carbon component is oxidized to carbon dioxide and released at about  $450 \text{ }^\circ\text{C}$ ,  
17 leading to a weight loss [45]. From around  $500 \text{ }^\circ\text{C}$ , the two samples keep stable. The  
18 mass fractions of  $\text{LiFePO}_4$  micro-rod and GA for the composite are respectively  
19 calculated to be around  $78.4 \text{ wt } \%$  and  $21.6 \text{ wt } \%$ .

20  $\text{N}_2$  adsorption/desorption analysis was performed to analyze the internal porous  
21 characteristics of LFP and LFP@GA. As illustrated in Fig. 5b, the isotherms for LFP  
22 correspond to the type III curve, implying a microporous structure. By comparison,

1 LFP@GA displays a obvious hysteresis loop, which is a typical characteristic type IV  
2 isotherm for mesoporous materials [46]. In addition, the corresponding  
3 Brunauer-Emmett-Teller surface area and BJH desorption cumulative pore volume for  
4 LFP@GA are respectively  $30.786 \text{ m}^2 \text{ g}^{-1}$  and  $0.101 \text{ cm}^3 \text{ g}^{-1}$ , greatly larger than those  
5 of LFP ( $4.554 \text{ m}^2 \text{ g}^{-1}$  and  $0.019 \text{ cm}^3 \text{ g}^{-1}$ ), probably attributed to the unique porous  
6 framework composed of interlaced graphene sheets and  $\text{LiFePO}_4$  submicron-rods.  
7 These results imply that LFP@GA material possesses a high contact area with the  
8 electrolyte, which can offer abundant reaction sites for  $\text{Li}^+$  insertion and more paths  
9 for  $\text{Li}^+$  diffusion, resulting in the enhancement of the **rate capability and activation for**  
10 **all active materials [47].**

11 The structural characterizations analyzed above indicate that the  $\text{LiFePO}_4$   
12 submicron-rods and the 3D graphene aerogel composite (LFP@GA) have been  
13 successfully prepared by the nitrilotriacetic acid assisted solvothermal process and the  
14 subsequent freeze-drying self-assembly. The added nitrilotriacetic acid (NTA) and  
15 isopropanol may play an essential role in controlling the rod-like structure of LFP  
16 during the solvothermal process, due to the changed interface state of reaction media  
17 and the partially cover of the formed LFP crystal surface. Subsequently, the graphene  
18 sheets are self-assembled into 3D porous conductive network by the rapid  
19 freeze-drying process and heat treatment, meanwhile, the randomly dispersed  
20 one-dimensional LFP submicron-rods are tightly wrapped into the graphene aerogel  
21 architecture. Such a combination of  $\text{LiFePO}_4$  submicron-rods and porous GA

1 framework is expected to effectively enhance the transport of electron and  $\text{Li}^+$  during  
2 the electrochemical reaction process of LFP.

3 Fig. 6a shows the initial charge/discharge curves for LFP and LFP@GA at 0.1 C.  
4 An obvious discharge voltage plateau at about 3.4 V appears in both samples,  
5 corresponding to the insertion of  $\text{Li}^+$  in  $\text{FePO}_4$  [11]. LFP@GA displays a capacity of  
6  $162.7 \text{ mAh g}^{-1}$ , higher than LFP ( $\sim 155.7 \text{ mAh g}^{-1}$ ). The capacity enhancement is due  
7 to introducing 3D porous graphene aerogel conductive network, which significantly  
8 increases the Li insertion active sites, the availability of active material and the  
9 electrode/electrolyte interfacial area. Moreover, the charge/discharge potential plateau  
10 of the LFP@GA sample is more flat than that of LFP (inset in Fig. 6a), and the  
11 polarization of charge/discharge plateaus for LFP@GA is lower (56 mV) in  
12 comparison to that of LFP (91 mV), demonstrating more accelerated  $\text{Li}^+$  diffusion  
13 into the porous graphene aerogel framework of LFP@GA electrode. The  
14 charge/discharge characteristics of LFP@GA at various rates are shown in Fig. 6b.  
15 Discharge specific capacities of 162.7、161.8、154.2、145.4、134.1、119.9 and 90.9  
16  $\text{mAh g}^{-1}$  at 0.1, 0.2, 0.5, 1, 2, 5 and 10 C are respectively obtained. The rate  
17 capabilities of both samples were further explored (Fig. 6c). As current rate is  
18 increased, the capacity for LFP reduces significantly, while LFP@GA keeps more  
19 stable, especially at high rates ( $>2 \text{ C}$ ). At 5 C, LFP@GA reveals a capacity of 119.9  
20  $\text{mAh g}^{-1}$ , significantly larger than LFP ( $40.6 \text{ mAh g}^{-1}$ ). Meanwhile, the capacity for  
21 LFP@GA at 5 C ( $119.9 \text{ mAh g}^{-1}$ ) is larger than some of the previously-reported  
22  $\text{LiFePO}_4$ -graphene composite materials, such as the graphene oxide encapsulated

1 micro/nano  $\text{LiFePO}_4$  particles ( $\sim 110 \text{ mAh g}^{-1}$  at 5 C) [48], graphene  
2 nanoribbon-wrapped  $\text{LiFePO}_4$  particles ( $\sim 117 \text{ mAh g}^{-1}$  at 5 C) [49], and core-shell  
3 structural carbon coated  $\text{LiFePO}_4$  submicron rod ( $\sim 104 \text{ mAh g}^{-1}$  at 5 C) [50]. The  
4 good rate capability for LFP@GA is ascribed to the well-crystallized LFP  
5 submicron-rods as well as the **multiple** pathways for both  $\text{Li}^+$  and electron constructed  
6 by GA. The cycling performance of the LFP@GA composite was tested at different  
7 rates for around 100 cycles, as shown in the inset of Fig. 6d. The results indicate that  
8 in comparison to the capacity retention of 92.5% at 1 C, the capacity retention is  
9 higher at 0.2 C (96.6%) and lower at 10 C (91.7%), which might be attributed to the  
10 gradual deterioration of kinetics for the cell as the discharge rate increases [51]. The  
11 long term cycle performance of LFP and LFP@GA were further tested and compared  
12 at 1 C, as shown in Fig. 6d. For the pristine  $\text{LiFePO}_4$  submicron-rods, the  $\text{Li}^+$   
13 lithiation/delithiation procedure may cause the stress, which results in the partial  
14 structure destruction of the electrode material. During the continuous cycling, the  
15  $\text{LiFePO}_4$  submicron-rods may break into small particles, leading to the formation of  
16 loose aggregates and the fast decay in discharge capacity within 200 cycles during  
17 cycling (Fig. 6d). **The LFP@GA electrode displays a capacity retention of 88.5% after**  
18 **200 cycles, superior to that of LFP (76.2%).** The reduced graphene sheets are tightly  
19 wrapping the monodispersed  $\text{LiFePO}_4$  submicron-rods and further intertwining each  
20 other to form a 3D porous conductive network, which can not only serve as the elastic  
21 porous framework to alleviate the structural change due to the good mechanical  
22 flexibility, but also maintain the electronic connection and effectively improve the

1 structure and cycling stability during the continuous charge/discharge processes (Fig.  
2 6d). After further 1000 cycles, the LFP@GA electrode still displays an excellent  
3 capacity retention (86.5%). The results demonstrate that the 3D porous framework  
4 can effectively alleviate the volume change and increase the structure stability during  
5 the continuous  $\text{Li}^+$  intercalation and de-intercalation processes [52].

6 Fig. 7a shows the CVs for LFP and LFP@GA electrodes at a low scanning rate  
7 of  $0.1 \text{ mV s}^{-1}$ . Both samples exhibit a single potential interval between cathodic and  
8 anodic peaks, suggesting the occurrence of a single electron transfer reaction  
9 mechanism, which corresponds respectively to the  $\text{Li}^+$  insertion/deinsertion processes  
10 within the LFP crystal lattice [53,54]. The redox peak profile of LFP@GA is more  
11 sharper and symmetric than that of LFP, meanwhile, the potential interval between the  
12 anodic and cathodic peaks for LFP@GA is around 163 mV, smaller than 186 mV for  
13 LFP, indicating the improved electrode kinetics owing to the modified  $\text{Li}^+$  diffusion  
14 and electron conductivity offered by 3D porous graphene aerogel network. Fig. 7b  
15 displays the selected CV curves for LFP@GA electrode in the continuous 20 cycles at  
16  $1 \text{ mV s}^{-1}$ . The shape and intensity of peaks are almost unchanged, demonstrating the  
17 good stability and reversibility for  $\text{Li}^+$  insertion/deinsertion in the 3D porous  
18 GA-wrapped LFP rod composite electrode.

19 The reaction kinetics process of the LFP and LFP@GA electrodes was further  
20 analyzed by the EIS (Fig. 7c). The EIS curves can be reasonably fitted and analyzed  
21 by an equivalent circuit (the inset in Fig. 7c). The semi-circle in the high-to-medium  
22 frequency region represents the charge-transfer resistance ( $R_{ct}$ ) through the



1 electrode/electrolyte interface. The slope line in low-frequency region denotes the  
2 Warburg impedance ( $Z_w$ ) involved with the diffusion of  $\text{Li}^+$  within the electrode [55].  
3 As shown in the Fig. 7c, the  $R_{ct}$  value for LFP@GA ( $\sim 100 \Omega$ ) is significantly reduced  
4 compared to LFP ( $\sim 120 \Omega$ ), suggesting the greatly increased charge transfer kinetics  
5 for  $\text{Li}^+$  insertion/deinsertion by improving the electronic conductivity of LFP with the  
6 conductive graphene covering and the connectivity of the discrete rods with the  
7 three-dimensional porous network. The  $\text{Li}^+$  diffusion coefficient ( $D_{\text{Li}}$ ) can be  
8 calculated through the slope lines in Warburg region according to the following  
9 formula [20,56]:

$$10 \quad D_{\text{Li}} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (1)$$

11 Where  $A$  represents the surface area of electrode,  $n$  denotes the transferred electron  
12 number for each molecule within the electro-chemical reaction,  $F$  expresses the  
13 Faraday constant,  $C$  represents  $\text{Li}^+$  concentration ( $7.69 \times 10^{-3} \text{ mol cm}^{-3}$ ), and  $\sigma$  denotes  
14 the Warburg factor related with  $Z_{re}$  ( $Z_{re} \propto \sigma \omega^{-1/2}$ ). After linearly fitting the plot  
15 between  $Z_{re}$  and  $\omega^{-1/2}$ ,  $\sigma$  is estimated (Fig. 7d) and subsequently  $D_{\text{Li}}$  is calculated from  
16 equation 1. The  $D_{\text{Li}}$  values for LFP and LFP@GA are respectively calculated to be  
17  $9.11 \times 10^{-14}$  and  $1.75 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ . The improved  $D_{\text{Li}}$  of LFP@GA is due to the  
18 enlarged electrolyte/electrode contact area resulting from the constructed graphene  
19 aerogel porous network.

20 As analyzed and discussed above, the remarkable electrochemical performance  
21 of LFP@GA may be ascribed to the synergy effects of LFP submicron-rods and GA

1 with highly porous conducting network. The conducting graphene framework not  
2 only increase the full coverage and intrinsic connection between the graphene sheets  
3 and LFP submicron-rods, but also offer a large number of paths for facilitating the  
4 rapid transport of electron and Li ion. Moreover, the combination of rod-shaped LFP  
5 and porous 3D structure can effectively relieve the stress resulted from the structural  
6 change during the insertion/deinsertion of  $\text{Li}^+$ . Therefore, the LFP@GA composite  
7 displays significantly enhanced specific capacity, rate performance and cyclability  
8 compared to LFP.

#### 9 **4. Conclusions**

10 In conclusion, the 3D porous graphene aerogel-wrapped  $\text{LiFePO}_4$  submicron-rod  
11 composite has been prepared successfully through a solvothermal method followed  
12 with rapid freeze-drying. The unique porous composite structure is composed of  
13  $\text{LiFePO}_4$  submicron-rods and interwoven graphene sheets with plenty of open pores.  
14 The conductive graphene sheets in the composite are tightly wrapping the  
15 monodispersed  $\text{LiFePO}_4$  submicron-rods and further intertwining to form a  
16 three-dimensional porous conductive network, to effectively enhance the overall  
17 electronic conductivity and promote the electronic transfer of the LFP@GA  
18 composite. Meanwhile, the one-dimensional submicron rod-shaped  $\text{LiFePO}_4$  and  
19 three-dimensional porous graphene aerogel network can effectively shorten the  $\text{Li}^+$   
20 diffusion path and alleviate the stress of material caused by the Li-ion  
21 insertion/deinsertion. The combination of the highly conductive, interwoven and

1 mechanically strong 3D graphene aerogel and the enwrapped LiFePO<sub>4</sub>  
2 submicron-rods brings excellent capacity performance, rate capability and cycle  
3 stability compared to LFP, demonstrating that the 3D porous graphene aerogel  
4 wrapped composite offers a potential pathway for widespread application in Li-ion  
5 batteries. Further optimizations of the micro-rod size, graphene content and doping,  
6 porosity, etc., would lead to even better electrochemical performance for the present  
7 porous GA-wrapped LiFePO<sub>4</sub> submicron-rods composite.

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1 **Figure captions:**

2 **Fig. 1.** Schematic illustration for preparing LFP@GA through a solvothermal and  
3 following freeze-drying method. (a) The  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and LiOH are  
4 dissolved in distilled water to obtain a homogeneous mixture; (b) The as-obtained  
5  $\text{LiFePO}_4$  rods after the solvothermal reaction are mixed with the GO suspension; (c)  
6 The  $\text{LiFePO}_4$  rods are well-enwrapped into the 3D porous graphene aerogel after the  
7 rapid freeze-drying and heat treatment process; (d) An magnified area from (c),  
8 displaying the corresponding ion diffusion and electron transport mechanisms.

9 **Fig. 2.** (a) XRD patterns for LFP and LFP@GA. (b) Raman spectra of LFP, GO and  
10 LFP@GA.

11 **Fig. 3.** SEM images for LFP (a, b) and LFP@GA (c, d).

12 **Fig. 4.** (a) TEM image and (b) high-resolution TEM image corresponding to the  
13 marked area of (a) for LFP@GA.

14 **Fig. 5.** Thermogravimetric curves (a) and  $\text{N}_2$  adsorption/desorption isotherms (b) for  
15 LFP and LFP@GA.

16 **Fig. 6.** (a) Charge/discharge curves for LFP and LFP@GA at 0.1 C. (b)  
17 Charge/discharge curves for LFP@GA at various rates. (c) Charge/discharge  
18 capacities at various rates for LFP and LFP@GA. (d) Cycling performance  
19 comparisons between the LFP and LFP@GA electrodes at 1 C. The inset in (d) is the  
20 cycling performance comparisons of LFP@GA at different rates for around 100  
21 cycles.

- 1 **Fig. 7.** (a) CVs for LFP and LFP@GA ( $0.1 \text{ mV s}^{-1}$ ). (b) Selected CVs for LFP@GA
- 2 electrode in the successive 20 cycles ( $1 \text{ mV s}^{-1}$ ). (c) The equivalent circuit and EIS
- 3 curves for LFP and LFP@GA. (d) Slopes of  $Z_{re}$  vs  $\omega^{-1/2}$  line.