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Short communication

Enhanced 3D hierarchical double porous Co_3O_4/graphene architecture for superior rechargeable lithium ion battery

Fu Sun[a,b], Kai Huang[a,b,*], Xiang Qi[a,b], Tian Gao[a,b], Yuping Liu[a,b], Xianghua Zou[a,b], Jianxin Zhong[a,b,*]

[a] *Hunan Key Laboratory for Micro-Nano Energy Materials and Devices, Xiangtan University, Hunan 411105, PR China*
[b] *Laboratory for Quantum Engineering and Micro-Nano Energy Technology, Faculty of Materials and Optoelectronic Physics, Xiangtan University, Hunan 411105, PR China*

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Abstract

We have successfully fabricated the enhanced 3D hierarchical double porous Co_3O_4/graphene architecture by employing a simple, facile and inexpensive microwave-assisted method. The ultimately formed hierarchical porous configuration can provide more rapid electrolyte diffusion to the active materials due to macro- and micro-porosity. The Co_3O_4 nanoparticles (NPs), which are homogeneously distributed on graphene sheets, showed high reversible capacities as well as significantly enhanced cycling performance and high rate capabilities when evaluated as anode for lithium ion battery. The superior performance could be attributed to the unique enhanced 3D hierarchical double porous architecture. Our results opened a new doorway to prepare novel anode architecture for high performance lithium ion batteries.

Keywords: Lithium ion battery; Hierarchical porous structure; Cobalt oxide nanoparticles; Reduced graphene

1. Introduction

Co_3O_4 is of great importance in many applications; specifically, it has recently attracted intensive research efforts in lithium ion batteries since the seminal work by Tarascon and coworkers [1]. Regarding to this end, it is highly expected to meet the requirements of future energy storage systems due to its high theoretical capacity (890 mAh g^{-1}), more than two times larger than that of graphite (372 mAh g^{-1}) [2,3]. However, its large volume expansion/contraction, the low intrinsic electronic conductivity and severe particle aggregation associated with the Li^+ insertion and extraction process generally result in electrode pulverization and electrical disconnection contact, leading to the ultimate capacity decay and poor cycling stability [2]. To circumvent these intractable drawbacks, versatile strategies have been developed, including the monotonous materials of Co_3O_4, such as nanotubes [3], nanowires [4], nanoparticles [5], nanorods [6], octahedral cages [7] as well as other carbon-based [8,9], and metal-based [10] composites of Co_3O_4. Lately, the utilization of graphene in fabricating anode active materials for lithium ion battery is becoming more and more appealing due to its high two-dimensional electrical conductivity, superior mechanical flexibility, high chemical and thermal stability as well as large surface area [11]. Composites of graphene-based anode materials prepared either by mortar [12] or by simple solution mixture [14,15] showed superior performance in lithium ion batteries. The combination of active materials and ancillary materials to form functional systems is highly believed to be a valid approach to achieve the substantial improvement. Nevertheless, due to the fact that the usefully active surface area of practical graphene-based material depends strongly on the exterior surfaces readily accessible to electrolyte, the formation of a bulk electrode generally detracts the highly expected enhancement [4,16,17]. These previous endeavors highlight the need of alternative synthetic approaches that employ innovative architecture and facile techniques for preparing next generation lithium ion battery [13].

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*Corresponding authors. +86 73158292195.
E-mail addresses: huangk@xtu.edu.cn (K. Huang), jxzhong@xtu.edu.cn (J. Zhong).

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Recently, a self-assembled graphene hydrogel prepared by the one-step hydrothermal method was reported by Shi and coworkers [14]. This graphene hydrogel is characterized by a well-defined three-dimensional (3D) porous network, which offers an opportunity to optimize the ionic diffusion in graphene-based electrodes as it allows most of the graphene sheets to be exposed to electrolyte and at the same time provides open channels for unobstructed transportation of electrolyte. In addition, the 3D configuration can also provide a shorter diffusion path length for lithium ions and a higher electrode surface area [15]. Moreover, in contrast to the in-plane surface in traditional electrodes, the out-of-plane dimension in a 3D configuration may enable the battery to have a small area footprint [16]. Encouraged by the aforementioned architecture cachet provided by the 3D configuration, herein, we report a strategy to fabricate the novel enhanced 3D hierarchical double porous Co_3O_4/graphene architecture as anode for lithium ion battery. The enhanced 3D Co_3O_4/graphene architecture, which is assembled in the macroporous nickel foam (NF) and assisted by microwave irradiation, possesses hierarchical porous channels that facilitates the transportation of ions and electrolyte and high conductivity of electron, both of which are essential factors for high-performance lithium ion battery [17]. In the last, the simple and facile synthesis in association with the absence of need of polymer binder opens a new avenue as a readily applicable means of addressing the practical application challenges associated with the next generation of rechargeable lithium ions batteries.

2. Experimental

2.1. Material synthesis

GO was synthesized by oxidizing graphite with a procedure following the modified Hummers' method [19]. The dried GO and purchased Co_3O_4 nanoparticles were carefully scaled and then were dispersed into de-ionized (DI) water to form a uniform solution. A commercial NF was dipped with the as-prepared mixture and then dried in the air naturally. The “dipping and drying” process was repeated several times to load the NF with sufficient mixture. Bear in mind that the ratio of Co_3O_4 and graphene can be determined by the solution mixture. In the last, the composite was reduced by the microwave (MM721NG1-PW) after 10 min. The total mass loading is determined before the “dipping and drying” process and after the final reduction process. In this presentation, we have fabricated two samples: the 60% (in weight) Co_3O_4 and 80% (in weight) Co_3O_4 -based samples. The total mass of the two samples are 4.2 mg and 5.6 mg respectively.

2.2. Structural characterization and electrochemical test

The morphologies and composition of the samples were characterized using scanning electron microscopy (SEM, JEOL, JSM-6360) and the Raman instrument (JAS.C.O R-500). To the electrochemical testing, standard CR2032 coin cells were assembled in an Ar-filled glove box (Mikrouna). All the discharge/charge capacity tests of the fabricated electrodes is determined by galvanostatic cycling the half cells over certain potential range between 0.01 V and 3 V in a battery tester. (NEWARE BTS-5 V 5 mA, Neware Technology Co., Ltd., China). All measurements were performed at room temperature.

3. Results and discussions

We have employed the microwave method to fabricate the enhanced 3D hierarchical porous Co_3O_4/graphene architecture composite as it can offer great advantages such as faster synthesis and higher energy efficiency compared with conventional methods [18]. Beforehand, graphene oxide (GO) was prepared from graphite powders according to a modified Hummers' method [19]. Co_3O_4 nanoparticles are purchased from Alfra Company. Firstly, a piece of commercially available NF was cleaned by water and acetone several times. Then appropriate amount of GO and Co_3O_4 nanoparticles are dispersed in a beaker to form uniformly distributed solution. Thirdly, the NF was subsequently loaded with Co_3O_4/GO mixture using a facile “dipping and drying” process. Finally, after appropriate cycles of “dipping and drying”, the composite was treated in a microwave oven (MM721NG1-PW) to efficiently reduce GO whilst form the enhanced 3D hierarchical double porous Co_3O_4/graphene architecture [20]. The fabrication process is schematically illustrated in Fig. 1a, b and c.

In this report, we have fabricated two samples: 60% Co_3O_4 (in weight) composite and 80% Co_3O_4 (in weight) composite. After we have fabricated the composite, we have taken some photographs, as shown in Fig. 1d,e and f. Raman spectra analysis was firstly employed to confirm the composition of the enhanced 3D hierarchical porous Co_3O_4/graphene architecture composite. From Fig. 1h, we can clearly discern characteristic peaks at about 190 cm^{-1}, which is in good agreement with the typical raman mode of Ni [21], and peaks at about 475, 515 and 681 cm^{-1}, which can be assigned to Co_3O_4 [22], the D-band (disordered-induced phonon mode,), and the G-band (graphite band) of the reduced graphene [23] The constituent was also confirmed by the energy dispersive spectroscopy (EDS) microanalysis. As shown in Fig. 1i, strong signals from Ni, Co, O and C can be abundantly detected.

To further confirm we have successfully fabricated the enhanced 3D hierarchical porous Co_3O_4/graphene architecture, the scanning electron microscopy (SEM) is employed. Firstly, as shown in Fig. 2a, the NF has a three dimensional macroporous structure with pore sizes in the range of 50–150 μm. Also, we can discern that the Ni filigrees are interconnected with virtually free of junctions, insuring continuous coating of Co_3O_4/graphene mixture suspension. After cycles of “dipping and drying” process and microwave irradiation reduction, we can see that the NF was loaded with sufficient Co_3O_4/graphene mixture, as shown in Fig. 2b. To further confirm that the NF has been fully packed with Co_3O_4/graphene mixture, the cross SEM picture has been taken, as shown in Fig. 2c and d. When the composite is further zoomed in, from Fig. 2e, we can

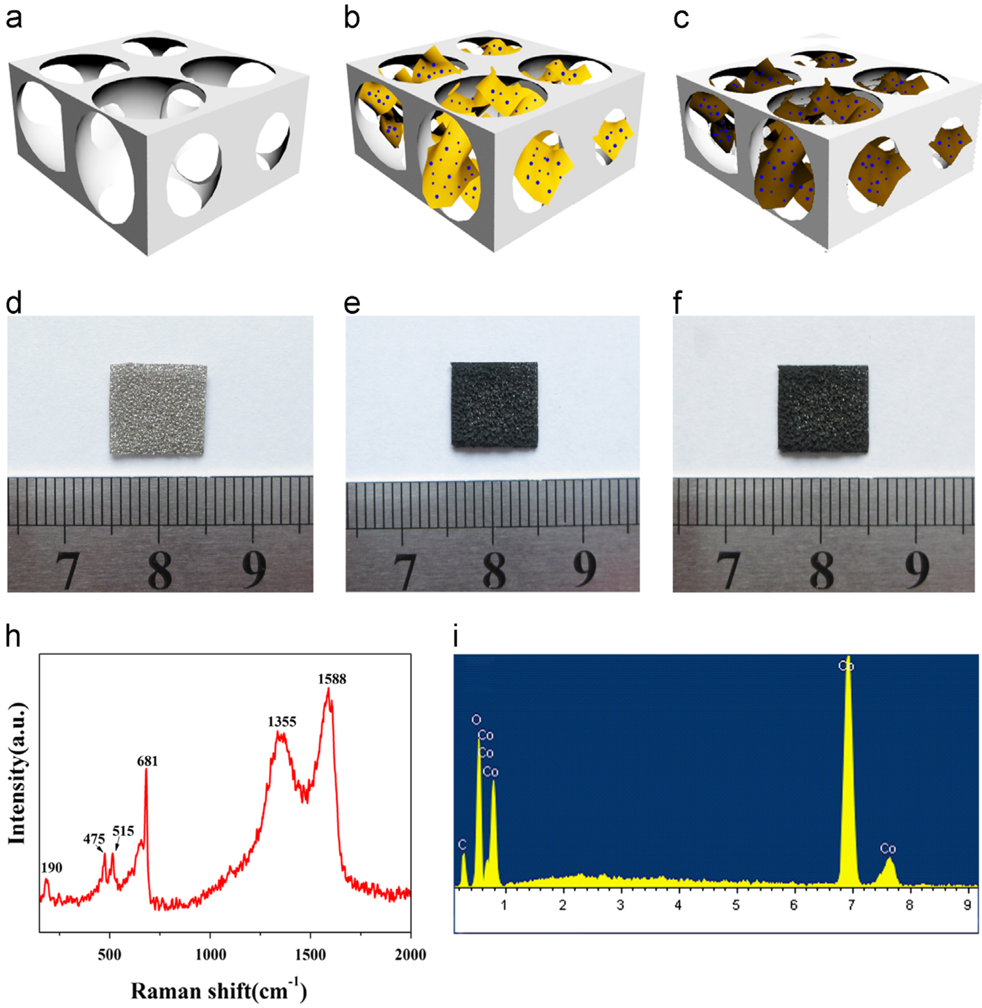

Fig. 1. (a), (b) and (c) Illustration of the enhanced 3D hierarchical porous Co_3O_4/graphene architecture composite: (a) pure nickle foam, (b) Co_3O_4/graphene oxide mixture dipped nickle foam, (c) reduced Co_3O_4/graphene nickle foam, (d) pure nickle foam, (e) Co_3O_4/graphene oxide mixture dipped nickle foam, (f) reduced Co_3O_4/graphene nickle foam; (h) Raman spectra and (i) the energy dispersive spectroscopy (EDS) of the enhanced 3D hierarchical porous Co_3O_4/graphene architecture composite(80% Co_3O_4);

clearly see that the smooth NF skeletons were uniformly covered with a layer of mixture and the cross-linked hierarchical porous structure. Actually, the conformal coating can be ascribed to the mechanical flexibility of graphene oxide and strong van der Waals interactions between the NF and GO [24]. One important thing to be pointed out is that, from Fig. 2d and e, we can clearly discern that various of microporosity, formed either by physically cross-linked 3D graphene, junction slot between graphene sheets and NF or by intertwining among graphene sheets, developed on top of the macro-porous NF, forming the enhanced 3D hierarchical double porous Co_3O_4/graphene architecture [25]. In addition, after conformal coating onto the skeleton of NF and the reduction, it still maintained a macro-porous nature where its intricate assembly of pores remained and no layer was detached away from the NF skeleton and the configuration was perfectly preserved. In the last, from a closer examination, as shown in Fig. 2f, one can obviously discern that the Co_3O_4 NPs are uniformly distributed on graphene sheets. It is also noteworthy that a significant portion of Co_3O_4 NPs are encapsulated within graphene layers, as marked in Fig. 2f. Such a geometric confinement of metal oxide within graphene has reported to improve their interface contact and to suppress the agglomeration of NPs, thereby remarkably promoting the electrochemical activity [26]. Another feature of microwave synthesis has to be pointed out is that it can provide formation of covalent bonds between metallic NPs and carbon [29] and form a strongly stable entity. This is essential because in order to maintain good reversibility of the Li ions into electrode materials, their pristine structure needs to be maintained during insertion/de-insertion cycles. From the abovementioned, it can be safely said that we have successfully fabricated the enhanced 3D hierarchical double porous Co_3O_4/graphene architecture through a simple and facile procedure and that we can therefore expect a superior high performance.

Subsequently, our attention was devoted to the functional investigation of the obtained enhanced 3D hierarchical double porous Co_3O_4/graphene architecture composite as electrode in Lithium ion battery, with the voltage window from 0.01 V to 3 V. Beforehand, the theoretical capacity (*C*) of our composite

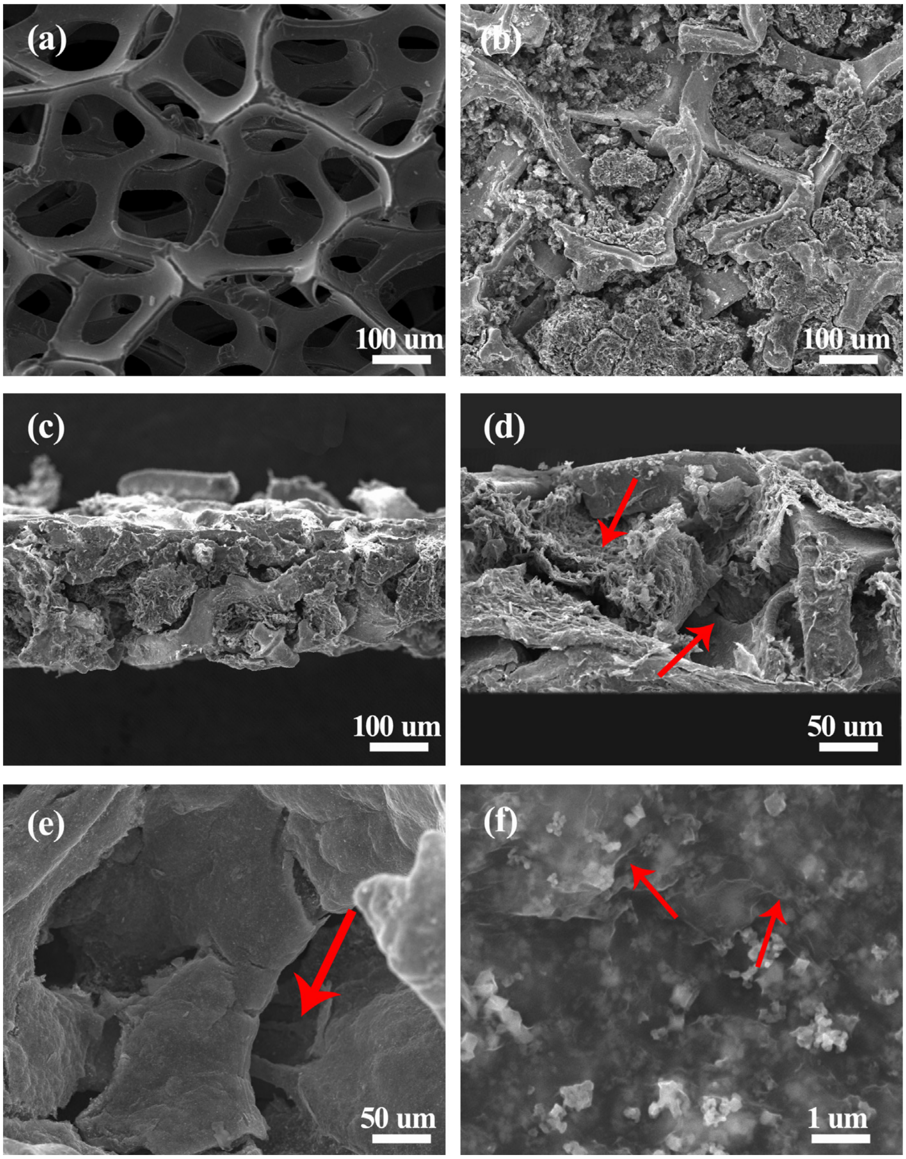

Fig. 2. SEM photographs of the as-prepared enhanced 3D hierarchical double porous Co_3O_4/graphene architecture composite (80% Co_3O_4): (a) pure nickle foam; (b) reduced Co_3O_4/graphene nickle foam; (c) and (d) cross-view of reduced Co_3O_4/graphene nickle foam composite; (e) the zoomed-in reduced Co_3O_4/graphene nickle foam; and (f) the Co_3O_4/graphene mixture.

is calculated as follows: $C_{\text{theoretical}} = C_{Co_3O_4} \times$ mass percentage of $Co_3O_4 + C_{\text{graphite}} \times$ mass percentage of graphite$=890 \times 60$ (80)%$+372 \times 40$ (20)%$=682$ (786) mAh g^{-1}. The first potential versus capacity trace shows the well-known signature of conversions of Co_3O_4, that is, a long voltage plateau at about 1 V followed by a sloping curve down to the cutoff, as shown in Fig. 3a and b. The first discharge specific capacity of enhanced 3D hierarchical porous Co_3O_4/graphene architecture composite is about 700 (900) mAh g^{-1}, which is larger than the theoretical prediction value. This phenomenon is attributed to the formation of a solid electrolyte interphase (SEI). Since the second cycle, thanks to this unique hierarchical structure, not only is the coulombic efficiency enhanced, but also the electrode is found to show excellent capacity retention, as shown in Fig. 3c, despite there is a large polarization which is ineluctable for transition metal oxide. As for the capacity loss in the 2nd cycle, there are mainly three reasons, that is, the loss of two Li per Co_3O_4 formula due to the $Co_3O_4 \rightarrow CoO$ composition transformation after the first redox action [4], the particularity of a heterogeneous interfacial storage mechanism of transition metal oxide [27] and the reactions of Li with O, H-containing groups resided on the incompletely reduced graphene [28]. However, an unanticipated substantially superior capacity retention about 500 (600) mA hg^{-1} is found even after 50 cycles, as shown in Fig. 3c. No obvious capacity decline or tendency of capacity decay can be obviously found. This is much better compared with the previously reported electrochemical behavior of mixed Co_3O_4/G anodes where a clearly and continuous capacity decay can be observed [29]. Considering that the rate capability is also very important for practical applications, charge–discharge curves at different current densities were also measured. Reversibility of storage

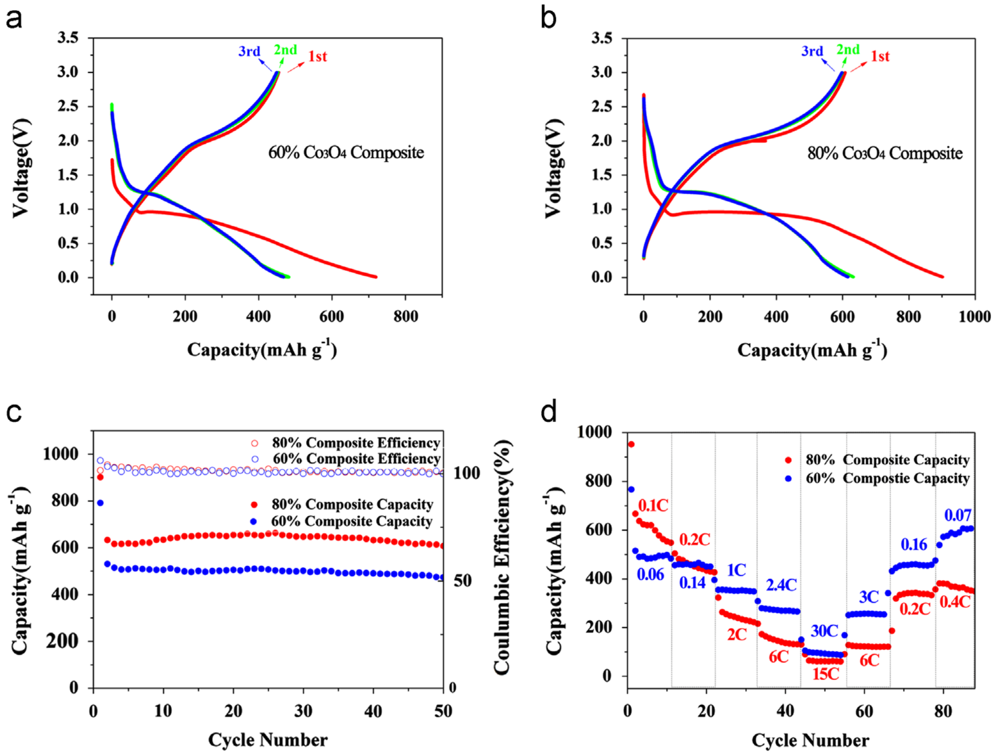

Fig. 3. Electrochemical characterization of 60% Co_3O_4 composite and 80% Co_3O_4 composite: (a) first three voltage-capacity profiles of the as-prepared 60% Co_3O_4 composite composite cycled at 0.2 C; (b) first two voltage-capacity profiles of the 80% Co_3O_4 composite cycled at 0.2C; (c) capacity-cycle profile of the of the as-prepared composite anode; (d) specific capacity of the as-prepared composite between 3 and 0.01 V at current densities of 0.06 (0.1), 0.04 (0.2), 1 (2), 2.4 (6), 30 (15), 3 (6), 0.16 (0.2) and 0.07 (0.4) C.

capacity of both samples was observed when the rate was first stepwise increased from 0.06 C (0.1 C) to 30 C (15 C) and then switched back to 0.07 C (0.4 C), as shown in Fig. 3d.

The highly reversible capacity, excellent cyclic performance and high Coulombic efficiency with good rate capability evidenced the occurrence of the superior electrochemical performance in the enhanced 3D hierarchical double porous Co_3O_4/graphene architecture composite as alternative candidate for anode material of high performance Lithium ion batteries (LIBs). We strongly believe that the superior Li battery performance can be explained as follows: firstly, the enhanced 3D hierarchical double porous Co_3O_4/graphene architecture provides more rapid electrolyte diffusion to the active materials due to macro- and micro-porosity. The structural inter-connectivities, mechanically percolated networks not only possess a higher electrical conductivity and maintain better structural stability, but also are favorable for a quick infiltration of electrolyte, assuring more effective access of electrolyte to active materials. This feature is particularly helpful for high power applications when the battery is charged or discharged at high current. In addition, the porosity in the enhanced 3D hierarchical double porous Co_3O_4/graphene architecture can accommodate the large volume change during lithium insertion and extraction, which is beneficial for maintaining the integrity of the electrode. Secondly, the mixture of graphene and Co_3O_4 NPs self-assembled on the NF plays an essential role. On the one hand, the graphene sheets in the enhanced 3D hierarchical double porous Co_3O_4/graphene architecture not only provide an elastic buffer space to cushion the volume expansion/contraction of Co_3O_4 NPs during Li insertion/extraction process but also efficiently prevent the aggregation of Co_3O_4 NPs upon continuous cycling. Thus, the large capacity, good coulombic efficiency, high rate capability and cycling stability can be obtained. This is also the case when considering that the fracture or destruction of the electrode structure will result in the ultimate capacity decay and poor performance. On the other hand, the Co_3O_4 NPs, which are homogeneously distributed on graphene sheets, can not only further shorten the Li^+ ion diffusion length, but also are believed to prevent the agglomeration of graphene sheets. On the basis of the above analyses, it is concluded that the synergetic effect between the enhanced 3D hierarchical double porous configuration and Co_3O_4 NPs/graphene is responsible for the excellent electrochemical performance of the overall anode. As a result, it can be highly expected that this unique enhanced 3D hierarchical double porous Co_3O_4/graphene architecture, combining the advantages of Co_3O_4 nanoparticles and graphene sheets as well as its cost-effective, simple and facile fabrication method, opens up an efficient new route to investigate the transition metal oxide/carbon electrodes for next-generation rechargeable lithium ions batteries.

4. Conclusions

In summary, we report a simple, facile and inexpensive method to fabricate graphene-based enhanced 3D hierarchical porous Co_3O_4/graphene architecture. By employing microwave irradiation as the reduction method, physically cross-linked microporous 3D graphene network is formed on top of the macroporous NF, leading to the enhanced 3D hierarchical double porous Co_3O_4/graphene architecture. In the meantime, the Co_3O_4 NPs are uniformly anchored on the as-obtained architecture. Owning to this unique configuration, the composite exhibits a large reversible capacity, excellent cyclic performance, high Coulombic efficiency and good rate capability, highlighting the advantages of anchoring of NPs on enhanced 3D hierarchical double porous architecture for energy storage applications in high performance LIBs.

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