Embedding Co$_3$O$_4$ nanoparticles into graphene nanoscrolls as anode for lithium ion batteries with superior capacity and outstanding cycling stability

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**ABSTRACT**

Co$_3$O$_4$ is a promising high-performance anode for lithium ion batteries (LIBs), but suffers from unsatisfied cyclability originating due to low electrical conductivity and large volume expansion during charge and discharge process. Herein, we successfully constructed the Co$_3$O$_4$ nanoparticles embedded into graphene nanoscrolls (GNSs) as advanced anode for high-performance LIBs with large capacity and exceptional cyclability. The one-dimensional (1D) Co$_3$O$_4$/GNSs were synthesized via liquid nitrogen cold quenching of large-size graphene oxide nanosheets and sodium citrate (SC) modified Co$_3$O$_4$ nanoparticles, followed by freeze drying and annealing at 400 °C for 2 h in nitrogen atmosphere. Benefiting from the interconnected porous network constructed by 1D Co$_3$O$_4$/GNSs for fast electron transfer and rapid ion diffusion, and wrinkled graphene shell for significantly alleviating the huge volume expansion of Co$_3$O$_4$ during lithiation and delithiation. The resultant Co$_3$O$_4$/GNSs exhibited ultrahigh reversible capacity of 1200 mAh g$^{-1}$ at 0.1 C, outperforming most reported Co$_3$O$_4$ anodes. Moreover, they showed high rate capability of 600 mAh g$^{-1}$ at 5 C, and outstanding cycling stability with a high capacity retention of 90% after 500 cycles. Therefore, this developed strategy could be extended as an universal and scalable approach for integrating various metal oxide materials into GNSs for energy storage and conversion applications.

1. Introduction

Lithium ion batteries (LIBs) are the predominant power source for portable electronics and electric vehicles [1–4]. However, commercial graphite as anode exhibits a low capacity of 372 mAh g$^{-1}$, and limited energy density of 100–180 Wh kg$^{-1}$ for LIBs [5–7], severely preventing certain applications that require high energy density of 200–500 Wh kg$^{-1}$. To this end, one choice is to develop high-capacity metal oxide anodes, such as Co$_3$O$_4$ (a theoretical capacity of 890 mAh g$^{-1}$). So far, various Co$_3$O$_4$ nanostructures, such as nanosphere [8,9], nanosheet [10], and hollow structure have been developed [11]. Unfortunately, Co$_3$O$_4$ suffers from poor electrical conductivity, huge volume change during repeating cycling, leading to electrode structural fractures and unstable solid electrolyte interphase (SEI) formation. As a result, low capacity and fast performance decay are usually attained. Therefore, developing Co$_3$O$_4$ based anodes with high capacity and stable cyclability is urgently needed.

To overcome the above obstacles, an efficient approach is to construct the hybrids of Co$_3$O$_4$ and nanocarbons, such as Co$_3$O$_4$/graphene, Co$_3$O$_4$/carbon nanotube. In such hybrids, the presence of nanocarbons, e.g., graphene, carbon nanotube, could greatly improve the electrical conductivity of Co$_3$O$_4$, and alleviate the volume expansion, resulting in the enhancement of lithium storage [12–20]. However, high-performance Co$_3$O$_4$ anodes with long cycling life (> 500 cycles) and high capacities (> 1000 mAh g$^{-1}$) were rarely reported, probably due to the self-aggregation of Co$_3$O$_4$ nanostructures and unstable SEI formation caused by direct contact between Co$_3$O$_4$ and electrolyte. A good mode is to engineer the separated Co$_3$O$_4$ nanostructures well encapsulated by atomically-thin graphene, as demonstrated by Yang’s work, in which Co$_3$O$_4$ nanoparticles were well encapsulated by graphene via electrostatic interaction [21]. However, the aggregation of Co$_3$O$_4$ nanoparticles to some extent was still not fully avoided, consequently maintaining 94% retention of the initial capacity after 130 cycles. Nevertheless, rational construction of high-performance Co$_3$O$_4$ nanostructures wrapped by one-dimensional (1D) graphene nanoscrolls (GNSs) has not yet been reported.

In this work, we demonstrate the rational construction of the Co$_3$O$_4$ nanoparticles embedded into 1D GNSs (denoted as Co$_3$O$_4$/GNSs) as high-performance anode for rechargeable LIBs with superior capacity and exceptional cycling stability. The 1D Co$_3$O$_4$/GNSs were synthesized...
via liquid nitrogen Co$_3$O$_4$ nanoparticles wrapped by 1D GNSs via liquid nitrogen cold quenching of large-size graphene oxide (GO, 15–30 μm) nanosheets and sodium citrate (SC) modified Co$_3$O$_4$ nanoparticles, and subsequent freeze drying and thermal reduction. Benefiting from the interconnected porous networks of 1D Co$_3$O$_4$/GNSs for fast electron transfer and rapid ion diffusion, and wrinkled encapsulation graphene shell for efficiently alleviating the huge volume changes of Co$_3$O$_4$ during lithiation and delithiation [22], the as-fabricated Co$_3$O$_4$/GNSs as LIB anode presented excellent lithium storage performance of ultrahigh reversible capacity of 1200 mAh g$^{-1}$ at 0.1 C, stable cycling performance with a capacity retention of 90% after 500 times, and outstanding rate capacity of 600 mAh g$^{-1}$ at 5C, outperforming most reported Co$_3$O$_4$ anodes.

2. Experimental

2.1. Preparation of graphene and Co$_3$O$_4$

Large-size GO nanosheets were prepared from natural graphite by a modified Hummers method, as reported in our previous work [23].

Co$_3$O$_4$ nanoparticles were synthesized using a modified solvothermal reaction [24–26]. Typically, C$_4$H$_6$CoO$_4·$4H$_2$O (0.5 g) was dissolved in ethanol (25 mL). Then NH$_4$H$_2$O (2.5 mL) was added to the solution and stirred for 30 min. The solution was transferred to a Teflon-lined stainless steel autoclave, sealed, and heated at 150 °C for 12 h. Afterwards, the autoclave was cooled to room temperature. Finally, the product was collected by centrifugation and washed several times with distilled water and ethanol.

2.2. Preparation of Co$_3$O$_4$/GNSs

Firstly, a certain amount of SC (1.0 mg mL$^{-1}$) was added to modify Co$_3$O$_4$ aqueous dispersion (1.0 mg mL$^{-1}$) under mechanical stirring and sonication. Then, the dispersion of SC-modified Co$_3$O$_4$ was slowly added into the GO suspension with aid of sonication for 20 min. The resultant suspension was transferred to a centrifuge tube (10 mL), and heated up to 80 °C. Then, the tubes were putted in liquid nitrogen to prepare the hybrid of Co$_3$O$_4$/GO nanoscrolls. After that, the completely frozen solid was vacuum freeze dried, and then annealed at 400 °C for 2 h in nitrogen atmosphere, giving rise to the hybrid, denoted as Co$_3$O$_4$/GNSs-400. For comparison, we also used the similar procedures to prepare the products annealed at 600 °C and 800 °C, which were denoted as Co$_3$O$_4$/GNSs-600 and Co$_3$O$_4$/GNSs-800, respectively.

2.3. Materials characterization

The morphology and structure of Co$_3$O$_4$/GNSs-400, Co$_3$O$_4$/GNSs-600 and Co$_3$O$_4$/GNSs-800 hybrids were characterized by scanning electron microscopy (SEM, Sirion 200FEI, Netherlands), transmission electron microscopy (TEM, Tecnai F20, 200 kV), X-ray diffraction (XRD, Cu Kα radiation, Panalytical X PertPro) and X-ray photoelectron spectroscopy (XPS, VG ESCA2000) measurements. Raman analysis was conducted using a Renishaw InVia Raman microscope equipped with 785 nm laser and WiRe software. Thermogravimetric analysis (TGA) was performed in air at 10 °C min$^{-1}$ from room temperature to 1000 °C on a Perkin-Elmer instrument.

2.4. Electrochemical measurements

For LIB measurements, the working electrode was obtained by mixing active material (Co$_3$O$_4$/GNSs-400, Co$_3$O$_4$/GNSs-600, Co$_3$O$_4$/GNSs-800, and pure Co$_3$O$_4$), acetylene black and polyvinylidene fluoride at a weight ratio of 80:10:10 with N-methyl-2-pyrrolidone as solvent, followed by coating the slurry onto a copper foil and dried under vacuum at 80 °C for 12 h. The electrolyte was 1 M LiPF$_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 V/V). Lithium foil (Aldrich) was taken as count and reference electrodes, and Celgard 2300 was served as the separator. The cells were assembled in glove box filled with high-purity argon. The galvanostatic charge-discharge (GCD) experiments were tested by LAND CT2001A batteries testing system in a voltage range of 0.01–3.0 V. Cyclic voltammogram (CV) measurement was carried out at a scan rate of 0.1 mV s$^{-1}$ using an electrochemical working station (CHI660D, Chenhua Co, Shanghai). Electrochemical impedance spectroscopy (EIS) experiments were carried out using a PARSTAT 4000 electrochemical workstation in the frequency range of 0.01–10$^5$ Hz.

3. Results and discussion

The fabrication process for Co$_3$O$_4$/GNSs is illustrated in Fig. 1a. Firstly, a green agent SC was chosen to modify Co$_3$O$_4$ nanoparticles, grafted with enriched carboxyl and hydroxy groups, thus producing the strong interaction with oxygen-containing groups on GO nanosheets via hydrogen-bond formation, and the intimate coupling of SC-modified Co$_3$O$_4$ nanoparticles and GO together [27,28]. The intimate and strong coupling between SC on Co$_3$O$_4$ and oxygen-containing groups on GO guaranteed the efficient encapsulation of Co$_3$O$_4$ into GNSs. Subsequently, liquid-nitrogen cold quenching of the above solution would help the transformation of Co$_3$O$_4$-functionalized GO nanosheets into GO nanoscrolls (GONSs) embedded with Co$_3$O$_4$ (Co$_3$O$_4$/GONSs). After freeze drying and thermal treatment at 400 °C for 2 h of Co$_3$O$_4$/GONSs, the Co$_3$O$_4$/GNSs (denoted as Co$_3$O$_4$/GNSs-400) were obtained. The structure of the as-obtained Co$_3$O$_4$/GNSs-400 was first characterized by XRD pattern, Raman spectrum, XPS, and TGA/DTG measurements, as shown in Fig. 2. The diffraction peaks appearing in the range of 24–28° were ascribed to the restacking of graphene sheets in Co$_3$O$_4$/GNSs-400. Except this, all other diffraction peaks of Co$_3$O$_4$/GNSs annealed at 400 °C were well indexed to the pure phase of Co$_3$O$_4$ (JCPDS NO.42–1467, Fig. 2a). It is noted that, with increased annealing temperature from 600° to 800°C, the phase transformation from Co$_3$O$_4$...
to CoO (JCPDS No.43–1004) occurred (Fig. S1). Raman spectra further confirmed the structural integration of Co3O4 and GNSs (Fig. 2b, Fig. S2). The typical D and G bands appeared at 1360 cm\(^{-1}\) and 1580 cm\(^{-1}\) were assigned to the GNSs [29,30], and the ratio of I\(_D\)/I\(_G\) for GNSs slightly decreased with increased annealing temperature (Fig. S2). The several characteristic signals between 190 and 700 were detected derived from Co\(_3\)O\(_4\) in Co\(_3\)O\(_4\)/GNSs-400 [31,32]. XPS measurement (Fig. 2c) demonstrated the existence of carbon, oxygen and cobalt in Co\(_3\)O\(_4\)/GNSs-400, and high-resolution Co2p spectrum showed two peaks at 780 eV and 795 eV, corresponding to the Co 2p3/2 and Co 2p1/2 of Co3O4, respectively (inset of Fig. 2c). The unique existence of high-content O=C-O and C–O bonds (oxygen content = 26.2%) in Co\(_3\)O\(_4\)/GNSs-400 disclosed the strong interfacial bonding between Co3O4 nanoparticles and graphene at 400 °C (Fig. 2d, Fig. S3). However, with elevated temperature to 600 and 800 °C, the contents of both O=C-O and C–O bonds (oxygen content = 15.1% and 6.2%) greatly declined, suggesting high temperature (≥ 600 °C) could weaken or even damage the connection of Co3O4 particles and GNSs linked by the oxygen bridges (Co-O-C). Then, the electrochemical performance would be possibly decreased.

The TGA/DTG curves (Fig. 2e) were conducted in air to prove the thermal stability of GNSs in Co\(_3\)O\(_4\)/GNSs-400 before 400 °C, and the first weight loss of 7.6 wt% is mainly from the evaporation of the absorption water and the decomposition of residual oxygen-containing groups of GNSs. Further, the second weight loss up to 600 °C of Co\(_3\)O\(_4\)/GNSs-400 is 23.9 wt%, which is assigned to the decomposition of GNSs, as confirmed by DTG profile with a fast decomposition peak at 485 °C (Fig. 2f). In this case, the interfacial interaction would be destroyed due to the decomposition of GNSs and SC-derived carbon at higher temperature of > 485 °C (Fig. S3). The third decomposition temperature appearing around 790 °C is owing to the carbothermic reduction reaction from Co3O4 to CoO by carbon species, which is good agreement with XRD patterns (Fig. 1a and Fig. S1).

The morphology of Co\(_3\)O\(_4\)/GNSs-400 was examined by SEM and TEM images. As shown in Fig. 3, SEM image of Co\(_3\)O\(_4\)/GNSs-400 showed the interwoven porous network of 1D wrinkle nanoscrolls, with diameter of 200–500 nm and length of ten of micrometers. It can be seen that the Co\(_3\)O\(_4\) nanoparticles were well encapsulated with graphene without any exposed region, and uniformly dispersed in the interior channels of GNSs (Fig. 3a, b). This rational construction of nanoscroll structure is beneficial to the presence of SC. To verify the fact of the intimate interface between Co\(_3\)O\(_4\) nanoparticles and GNSs, Co\(_3\)O\(_4\)/GNSs-400 were dispersed in ethanol by sonication for 20 min to open the scrolled structure. As expected, TEM and high-resolution TEM (HRTEM) images provided solid evidences for the formation of
encapsulation structure and strong interfacial interactions between Co$_3$O$_4$ and GNSs (Fig. 3c and d), in which Co$_3$O$_4$ nanoparticles were stably anchored on graphene, and a thin-layer carbon was tightly formed on the surface of nanoparticles derived from the decomposition of SC. It is indicated that SC plays two important roles in the formation of Co$_3$O$_4$/GNSs-400. First, SC can ensure the intimate interaction between Co$_3$O$_4$ and GO and guarantee the efficient encapsulation of isolated Co$_3$O$_4$ nanoparticles inside the channels of GNSs during cold quenching process. Second, the existence of SC-derived few-layer carbon could significantly enhance the interfacial contact of Co$_3$O$_4$ and GNSs, and promote the structural integrity. As a result, such construction of Co$_3$O$_4$ nanoparticles embedded into 1D GNS-based porous network can endow fast electron transfer of Co$_3$O$_4$ along the wrinkled encapsulation graphene shell of GNSs [33] and rapid ion diffusion in the GNS-based network, and sufficiently alleviate the volume changes of Co$_3$O$_4$ during charge and discharge process. Therefore, Co$_3$O$_4$/GNSs hold great potential as anode for LIBs [34].

The electrochemical performance of Co$_3$O$_4$/GNSs-400 as anode materials for LIBs were further evaluated, as shown in Fig. 4. Fig. 4a shows the initial three cycles of the representative CV curves for Co$_3$O$_4$/GNSs-400 tested in the voltage range of 3.0 and 0.01 V (vs Li$^+$/Li) at a scan rate of 0.1 mV s$^{-1}$. It was observed that in the first cycle, the strong cathodic peak appearing at 0.5 V was associated with the reduction of Co$_3$O$_4$ to metallic Co and the irreversible formation of SEI film, while this peak was shifted to 0.95 V caused by polarization during subsequent cycles [35,36]. And the anodic peak located at
2.15 V was ascribed to the gradual oxidation of Co to Co$_2$O$_4$. Moreover, CV curves were almost overlapped in the second and third cycles, presenting high reversibility of the redox reactions. The high reversibility is also confirmed by GCD curves of Co$_3$O$_4$/GNSs-400 tested at 0.1 C (Fig. 4b). Notably, this hybrid electrode delivered an initial discharge capacity of 1650 mAh g$^{-1}$ and reversible charge capacity of 1180 mAh g$^{-1}$. The reversible capacity of Co$_3$O$_4$/GNSs-400 was still remained 1200 mAh g$^{-1}$ even after 100 cycles with high capacity retention of 90%, outperforming most reported Co$_3$O$_4$ based anodes (Table. S1). The superior capacity can be attributed to the following factors: (i) Co$_3$O$_4$ nanoparticles embedded into 1D GNSs could provide more active sites from the wrinkled GNSs and separated Co$_3$O$_4$ nanoparticles for the insertion of Li ions during cycling, enabling the full utilization of active materials. (ii) Nanosized Co$_3$O$_4$ could present extra reversible capacity over their theoretical value, which was attributed to a capacitive interface storage including electric double layer capacitance and pseudocapacitance in polymeric gel-like films [37,38]. Furthermore, Co$_3$O$_4$/GNSs-400 represented outstanding rate capability (Fig. 4c, d). For instance, at varying current densities of 0.1, 0.2, 0.5, 1 and 2 C, Co$_3$O$_4$/GNSs-400 electrode exhibited the specific capacities of 1270, 1100, 1000, 895, and 710 mAh g$^{-1}$, respectively. Even testing at an ultrafast rate of 5 C, a large specific capacity of 600 mAh g$^{-1}$ was maintained. Impressively, when current density was switched to 0.1 C, a stable capacity of 1266 mAh g$^{-1}$ was restored, suggestive of outstanding rate capability. To further confirm long-life cyclability, Co$_3$O$_4$/GNSs-400 was investigated at 1 C for 500 cycles. Notably, the specific capacity can remain as high as 800 mAh g$^{-1}$ after 500 cycles with a high capacity retention of 90%, indicative of rational construction of Co$_3$O$_4$/GNSs-400 with excellent cycling performance (Fig. 4e). Thereby, it is concluded that 1D GNS-structurally-encapsulated Co$_3$O$_4$ nanoparticles, with a strong interfacial interaction, can sufficiently improve the structural integrity and lithium storage performance.

To highlight the importance of engineering the strong interface between Co$_3$O$_4$ and GNSs, we also compared the electrochemical performance of Co$_3$O$_4$/GNSs-400, Co$_3$O$_4$/GNSs-600, CoO/GNSs-800, Co$_3$O$_4$/graphene via simple mixture of Co$_3$O$_4$ and graphene, and pure Co$_3$O$_4$, as measured at a current density of 0.1 C. It is worth noting that, with increasing annealing temperature, the channels of wrapped GNSs become more irregular, the aggregation of Co$_3$O$_4$ nanoparticles in Co$_3$O$_4$/GNSs-600 and CoO/GNSs-800 increased non-uniformly, and became a little larger in comparison with Co$_3$O$_4$/GNSs-400. It was also observed that the amounts of active site wrinkles of GNSs in Co$_3$O$_4$/GNSs-600 and CoO/GNSs-800 were less than that of Co$_3$O$_4$/GNSs-400 (Fig. S4), in addition to the phase change(Fig. 2a, Fig. S1), and weakened connection of nanoparticles and GNSs (Fig. 2d, Fig. S3). As a result, the first reversible capacity of Co$_3$O$_4$/GNSs-400 (1200 mAh g$^{-1}$, Fig. 5a) was much higher than those of Co$_3$O$_4$/GNSs-600 (900 mAh g$^{-1}$) and CoO/GNSs-800 (550 mAh g$^{-1}$) at 0.1 C. Also, Co$_3$O$_4$/GNSs-400 exhibited higher reversible capacity of 1180 mAh g$^{-1}$ after 100 cycles, which is superior to Co$_3$O$_4$/GNSs-600 (800 mAh g$^{-1}$), CoO/GNSs-800 (520 mAh g$^{-1}$), Co$_3$O$_4$/graphene (568 mAh g$^{-1}$), and pure Co$_3$O$_4$ (490 mAh g$^{-1}$). The EIS result disclosed the disparity of reaction dynamics in Co$_3$O$_4$/GNSs-400, Co$_3$O$_4$/GNSs-600, and CoO/GNSs-800, as shown in Fig. 5b. Clearly, the Co$_3$O$_4$/GNSs-400 electrode exhibited the lower charge transfer resistance (26.5 Ω) than those of Co$_3$O$_4$/GNSs-600 (31.5 Ω) and CoO/GNSs-800 (33.2 Ω), manifesting the fast charge transfer behavior of Co$_3$O$_4$/GNSs-400. This result further demonstrated that the optimal annealing temperature for engineering strong interface of Co$_3$O$_4$ and GNSs can effectively improve their electrochemical performance of LIBs [39].

The outstanding electrochemical performances of Co$_3$O$_4$/GNSs are ascribed to the rational construction of Co$_3$O$_4$ nanoparticles embedded into 1D GNSs with a strong interfacial interaction. First, the unique 1D hollow structure of GNSs could not only offer efficient nanospaces for accommodating Co$_3$O$_4$ nanoparticles and enhance the structural integrity, but also promote speeding transport of electrons and migration of Li ions at electrode/electrolyte interface. Second, the enriched wrinkles of GNSs, separated Co$_3$O$_4$ nanoparticles pertain to a capacitive interface storage from polymeric gel-like films, and empty channels along 1D GNSs could provide more active sites and hollow nanospaces for storing extra reversible Li during cycling, enabling the enhancement of specific capacity [40–45]. Third, the Co$_3$O$_4$ nanoparticles covalently encapsulated by 1D GNSs can sufficiently improve the structural stability during charge and discharge process, and the wrinkled GNSs can severe as an elastic flexible support that can efficiently encapsulated the separated Co$_3$O$_4$ nanoparticles with a strong interfacial coupling, and significantly alleviate the volume expansion of Co$_3$O$_4$ during lithiation and delithiation. As a consequence, Co$_3$O$_4$/GNSs exhibited superior reversible capacity and exceptional cycling stability.

4. Conclusion

The successful synthesis of embedding the SC-modified Co$_3$O$_4$ nanoparticles into GNSs was developed via liquid nitrogen cold quenching, freeze drying and annealing treatment, which can be applied to prepare high-performance anode for LIBs with superior capacity, outstanding rate capability and exceptional cycling stability. The resulting Co$_3$O$_4$/GNSs show the developed 1D electrically conduct the pathways for fast electron transfer, a strong interfacial coupling of Co$_3$O$_4$ and GNSs, and wrinkled encapsulation shell for alleviating the volume change of Co$_3$O$_4$ during lithiation and delithiation. As LIB anode, they exhibited excellent lithium storage performance, such as
ultrahigh reversible capacity of 1200 mAh g\textsuperscript{-1} at 0.1 C, outstanding cycling stability with a capacity retention of 90\% after 500 cycles, and high rate capacity of 600 mAh g\textsuperscript{-1} at 5 C, outperforming most reported Co\textsubscript{2}O\textsubscript{4} based materials. Therefore, it is believed that this developed strategy can be extended as a universal and flexible approach for integrating various functional materials, e.g., metal oxides, with GNSs for various energy storage and conversion applications.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.pnsc.2018.02.005.

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