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Carbon-Encapsulated Co_3O_4 Nanoparticles as Anode Materials with Super Lithium Storage Performance

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A high-performance anode material for lithium storage was successfully synthesized by glucose as carbon source and cobalt nitrate as Co_3O_4 precursor with the assistance of sodium chloride surface as a template to reduce the carbon sheet thickness. Ultrafine Co_3O_4 nanoparticles were homogeneously embedded in ultrathin porous graphitic carbon in this material. The carbon sheets, which have large specific surface area, high electronic conductivity, and outstanding mechanical flexibility, are very effective to keep the stability of Co_3O_4 nanoparticles which has a large capacity. As a consequence, a very high reversible capacity of up to 1413 mA h g^{-1} at a current density of 0.1 A g^{-1} after 100 cycles, a high rate capability (845, 560, 461 and 345 mA h g^{-1} at 5, 10, 15 and 20C, respectively, $1\text{C} = 1 \text{ A g}^{-1}$), and a superior cycling performance at an ultrahigh rate (760 mA h g^{-1} at 5C after 1000 cycles) are achieved by this lithium-ion-battery anode material.

Lithium-ion batteries (LIBs), as a kind of electrochemical energy conversion and storage device, have been intensively explored during the past decades for the fact that they have been widely applied as power sources for portable electronic devices^{1,2}. Carbon-based materials are commonly used as an anode for LIBs³. But low theoretical capacity (372 mA h g^{-1}) is the major concern, which puts sand on the wheel of its application in hybrid electric vehicles and electric vehicles where a power source with high energy density and high power density is needed^{1,4}. Thus state-of-the-art LIBs can be explored only when eximious alternative electrode materials with high capacity, high conductivity, super rate capability and long cycle life are found.

Transition metal oxides (M_xO_y ; $\text{M} = \text{Co}, \text{Fe}, \text{Ni}, \text{Cu}, \text{Mn}, \text{etc.}$)^{5–13} are considered as feasible anode alternatives because of their high specific capacities induced by conversion reaction mechanism, which was first proposed and elucidated by Poizot *et al.*¹⁴. However, bulk transition metal oxides are still far from application as LIB anode materials because they suffer from problems associated with the relatively poor electrical conductivity and the large volume change that occurs during the Li^+ insertion and extraction¹⁵. Poor conductivity always leading to low power density and large volume change will induce pulverization¹⁶, which result in an insufficient lithium storage performance and a rapid capacity decay¹⁷. Thus, fabrication of high-performance transition metal oxide electrode materials with large reversible capacities and good cycling stabilities remains a great challenge.

Currently a popular strategy toward alleviating these problems is nanostructuring. Compared to their bulk counterparts, nanosized electrode materials own many merits. Firstly, nanosized materials are generally too tiny to be pulverized^{18,19}. Meanwhile the void between the nanosized electrode materials can provide spaces to buffer the mechanical stress induced by the volume change¹⁷. Consequently, nanostructured electrode materials usually have a higher reversible capacity as well as a longer cycle life than

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Figure 1. Schematic illustration of the *in situ* sol-gel technique to fabricate $\text{Co}_3\text{O}_4\text{@C@PGC}$ nanosheets by using the surface of NaCl particles as the template.

their bulk counterparts. Secondly, nanostructured electrode materials hold a very high surface-to-volume ration, which provide plenty of reaction sites and shorter diffusion paths²⁰. Thus, these electrodes present a high rate capacity and a high power density. Substantial efforts have been made on nanostructuring and huge progress has been made on it^{4,21,22}. Meanwhile, these works also obviously show that nanostructuring can't solely solve all the problems thoroughly that transition metal oxides have suffered as LIBs anode materials. Nanoparticles (NPs) tend to aggregation after tens of cycling. This problem has been partially alleviated by separating them by graphene^{6,23,24} which is a new two-dimensional carbon material owning superior electrical conductivity, high surface-to-volume ration, ultrathin thickness, structural flexibility, and chemical stability²⁵. But such physical adsorption is not very strong enough. After dozens of circulations, they can also be desorbed from the surface. The nanovoids included in the nanostructured electrode materials can't strongly support the structural stability and integrity. The initial morphology generally loses after dozen of cycles because of pulverization. If these nanovoids can be filled in by some solid materials which not only give a support to the nanostructured materials and buffer the inner stress but also improve the electric conductivity, then the LIBs anode materials are integrated as a unite. The properties of LIBs anode must be meliorated a lot.

Cobaltous oxide (Co_3O_4) has received much attention in LIBs on the basis that it has a high theoretical capacity of 890 mA h g^{-1} , more than twofold of the currently commercial graphite^{26,27}. In order to overcome the shortage of bulk Co_3O_4 electrode, different kind of nanostructured Co_3O_4 combining various forms of carbon were designed as LIBs anode materials, which really improved their electrochemical performance^{3,16,25,26,28–36}. In this paper, the synthesized Co_3O_4 NPs with an average grain diameter of 20.4 nm were successfully encapsulated by a layer of thin carbon shell, forming $\text{Co}_3\text{O}_4\text{@C}$ core-shell structures which were homogeneously embedded in porous graphitic carbon (designed as $\text{Co}_3\text{O}_4\text{@C@PGC}$) nanosheets. The electrochemical properties of such materials were tested as a LIBs anode. It presented very high reversible capacity and excellent rate performance and cycling stability. It might be possible to extend this technique to other kind of nanostructured metal oxide for important applications in high-performance LIBs, supercapacitors, adsorbents, catalysts and sensors in many scientific disciplines.

Results and Discussion

The overall synthetic procedure of the $\text{Co}_3\text{O}_4\text{@C@PGC}$ nanosheets is schematically illustrated in Fig. 1. Two strategies were involved in this procedure. Firstly, the water-soluble NaCl particle surface was utilized as the template for the nanosheets because NaCl has a face-centered cubic (fcc, Fm3m (225), $a = 0.5642 \text{ nm}$) crystal structure, and its growth rate can be controlled by varying the concentration and temperature^{37–39}. Secondly, glucose and cobalt nitrate were chosen as the carbon precursor and the metal precursor, respectively, due to their low cost. In the synthesis, the NaCl, $\text{C}_6\text{H}_{12}\text{O}_6$ and $\text{Co}(\text{NO}_3)_2$ were first dissolved in distilled water to get a homogeneous solution. After gradually heated to 80°C , the solution color changed from pink to blue, the sample viscosity increased greatly, and then the polymerization of the glucose began, which resulted in the generation of a very thin frame homogeneously coated on the NaCl particle surface. After that, the composite powders were calcinated at 750°C under N_2 . During this process, the $\text{Co}(\text{NO}_3)_2$ should be decomposed into cobalt oxide⁴⁰. The oxide was subsequently reduced by $\text{C}_6\text{H}_{12}\text{O}_6$ into Co NPs with the protection of inactive gas^{29,35}. The fresh generated carbon layer usually encapsulated the Co NPs firstly, and then piled up in the form of porous graphitic carbon. As a result,

Figure 2. The typical XRD patterns of the $\text{Co}@\text{C}@\text{PGC}$ nanosheets and $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets.

the coating layer on the surface of the NaCl particles was converted to carbon-encapsulated Co NPs embedded in porous graphitic carbon (designed as $\text{Co}@\text{C}@\text{PGC}$) nanosheets. In the second step, the Co NPs were further *in situ* oxidized into Co_3O_4 NPs as the $\text{Co}@\text{C}@\text{PGC}$ nanosheets were calcinated in air. Finally, the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets were obtained on the surface of the NaCl particles as shown by the images of Fig. S1.

The XRD patterns of $\text{Co}@\text{C}@\text{PGC}$ and $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets were both shown in Fig. 2. A peak appears at $2\theta = 26.5^\circ$ in both XRD patterns, which corresponds to the diffraction peak of (002) crystallographic plane of graphite (JCPDS 65-6212). That means the carbonization of $\text{C}_6\text{H}_{12}\text{O}_6$ takes place at step one, and the annealing in air at step two has little damage on the carbon. Except of graphite, all peaks in the XRD pattern of $\text{Co}@\text{C}@\text{PGC}$ belong to Co (JCPDS 15-0806), which implies that the cobalt has been completely reduced from its oxide. Only Co_3O_4 phase is shown in the XRD pattern after calcinations in air except of graphite. It suggests that the calcination in step two is very effective to accomplish the conversion from the precursor ($\text{Co}@\text{C}@\text{PGC}$ nanosheets) to the targeted sample ($\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets). The average sizes of NPs were both calculated based on the full width at half maximum intensity of (311) for Co_3O_4 and (111) for Co using Scherrer's formula. The estimated average particle size of Co_3O_4 is very close to Co, which is about 20.4 nm. In addition, NaCl phase isn't found in both XRD patterns. So NaCl particles were completely removed in the water-washing process.

The morphology of $\text{Co}@\text{C}@\text{PGC}$ and $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets was shown in the SEM image of Fig. 3a,b, respectively. As shown in Fig. 3a, a lot of nanosheets with a thickness of about 20 nm and an area of $1\text{--}10\ \mu\text{m}^2$ interconnected with each other to build up a porous architecture. This architecture can be reserved even after calcinations in air, which is evidenced by the SEM image shown in Fig. 3b. The inset in Fig. 3b clearly shows that the thickness of the nanosheets is around 20 nm. The morphology of $\text{Co}_3\text{O}_4/\text{C}$ composites without adding NaCl was also observed by SEM, shown in Fig. S2. The flakes are very thicker and larger than $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets. Their thickness is more than 500 nm. They just pile up on each other, leaving very little space between them. The thin sheets observed in $\text{Co}@\text{C}@\text{PGC}$ and $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ disappear thoroughly in $\text{Co}_3\text{O}_4/\text{C}$ composites. It suggests that NaCl particles have played a crucial role in building up such porous architecture of nanosheets. A TEM image and HRTEM image of $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets are shown in Fig. 3c,d, respectively. The graphite carbon nanosheets seem to be transparent to the electron beam and show a very low contrast in the image, which again suggests that the nanosheet is very thin, around tens of nanometers. The black rings located on the sheet of Fig. 3c indicate a foam-like structure of the graphite. Co_3O_4 NPs, with diameters ranging from 5 to 40 nm, are well-dispersed in the PGC nanosheet. The selected area electron diffraction pattern in the inset of Fig. 3c further verifies the encapsulated core being Co_3O_4 NPs. In fact, the Co_3O_4 NPs were firmly anchored by the porous graphite nanosheets. As shown in Fig. 3d,a Co_3O_4 crystal is perfectly encapsulated by thin and well-graphitized onion-like carbon shells. The HRTEM interference fringes of the Co_3O_4 crystal can be clearly discerned. They have a spacing of 0.24 nm, as denoted in Fig. 3d, which is equal to the spacing of (311) plane of Co_3O_4 . The spacing of the interference fringe of the shell is 0.34 nm, which is also equal to the spacing of (002) plane of graphite. And the thickness of graphite shell is about 9 nm. The morphology of $\text{Co}@\text{C}@\text{PGC}$ nanosheets is also characterized by TEM and HRTEM (Fig. S3a,b). Carefully comparing the results, it is found that there is little difference on the morphology of the graphite carbon sheets and the crystal sizes. It again makes sure that the calcinations didn't hurt the graphite carbon sheets and none coalescence happened among Co NPs. The Co NPs just were oxidized at its place and converted to Co_3O_4 NPs.

Figure 3. (a) SEM image of Co@C@PGC nanosheets; (b) SEM image of Co₃O₄@C@PGC nanosheets and the inset is SEM image of high magnification; (c) TEM and (d) HRTEM image of Co₃O₄@C@PGC nanosheets.

The Raman spectrum shown in Fig. 4a further confirms the existence of graphitic structure in Co₃O₄@C@PGC nanosheets. Both G band and D band obviously appeared the spectrum at 1603 cm⁻¹ and 1346 cm⁻¹, respectively. The G band is the result of a radial C=C stretching mode of sp²-bonded carbon in the basal plane of the crystalline graphite. Thus it is considered as the intrinsic Raman signal for graphite. The D band is associated with disorder, allowing zone edge modes of the graphite structure to become active due to the lack of long-range order in amorphous and quasi-crystalline forms of carbon materials^{41,42}. Thus, the integral intensity ratio of G peak to D peak (I_G/I_D) is usually used to evaluate the degree of crystallization of carbon materials⁴³. The value of I_G/I_D for the Co₃O₄@C@PGC nanosheets is ~1.3, indicating that the obtained nanosheets own well-crystallized graphitic structures⁴⁴. This will be beneficial for electronic conduction of Co₃O₄ NPs. The carbon content is determined by TGA and the result is shown in Fig. 4b. As the sample is heated to 750 °C in air, the carbon will be completely burnt out. So, the weight loss in TGA result is equal to the carbon content. The carbon content of the Co₃O₄@C@PGC nanosheets is 29.1 wt% which is comparable to the Co₃O₄/C composites (30.0 wt%, Fig. S4).

Figure 4c,d show the N₂ adsorption/desorption isotherms and pore size distributions of the Co₃O₄@C@PGC nanosheets, respectively. The plot shown in Fig. 4c is a typical type IV N₂ adsorption–desorption isotherm⁴⁵ with a distinct hysteresis loop in the relative pressure range of 0.45–0.97, indicating a mesoporous structure and a narrow mesopore size distribution. In addition, the steep slope above 0.97 and the slow slope below 0.45 indicate the existence of macropores and micropores in the nanosheets. The pore size distribution was plotted in Fig. 4d. The pore size distribution ranges from 1.7 to 300 nm and has two preponderances at 2.5–2.8 nm and 18–22 nm. The average pore diameter is about 9.2 nm based on Barrett–Joyner–Halenda (BJH) adsorption. The BET specific surface area is measured to be ~246 m² g⁻¹. These results particularly characterize the porous structure of the graphite carbon sheets. Obviously, such small crystal size of Co₃O₄, which is comparable to the pore size, is incapable to contribute more pore and surface area. The porous structures of Co₃O₄@C@PGC nanosheets are vital for the electrochemical performance because they provide easy diffusion for electrolyte and facile accessibility of the active sites. They are also effective to accommodate huge volume change during lithium ion insertion/extraction and maintain the integrity, increase the electronic conductivity, and promote the formation of uniform SEI films and improve the stability of them^{46,47}, which endows the LIBs excellent cycle stability.

The initial three cycles of the representative cyclic voltammogram (CV) performed on a coin half-cell at room temperature between 0.01 and 3.0 V at a sweep rate of 0.1 mV s⁻¹ is presented in Fig. 5a. In accord with previous results, the first cycle shows lots of differences from the subsequent ones on CV curves, especially on the discharge branch^{21,48,49}. In the first discharge process, the obvious cathodic peak was located at around 0.97 V, which was attributed to the electrochemical reduction of Co₃O₄ to metallic

Figure 4. (a) Raman spectrum of the Co₃O₄@C@PGC nanosheets; (b) The TGA profile of the Co₃O₄@C@PGC nanosheets; (c) The N₂ adsorption/desorption isotherms and (d) the pore size distribution of the Co₃O₄@C@PGC nanosheets.

cobalt accompanying the formation of Li₂O and the solid electrolyte interphase (SEI) film^{26,28}. In the anodic process, broad peaks located at around 2.15 V can be ascribed to the reversible oxidation reaction from cobalt to Co₃O₄²³. The total electrochemical reaction mechanism of Co₃O₄ anode can be described by the following electrochemical conversion reaction⁵⁰:

The main reduction peak is shifted to ~1.15 V, and the peak intensity drops significantly from the second cycle, indicating the occurrence of some irreversible reactions associated with formation of the SEI film in the first cycle¹³. On the other hand, the oxidation peak at ~2.2 V in the anodic sweep exhibits little change during the three cycles, suggesting that the SEI formed on the PGC nanosheets surfaces in the first cycle is very stable.

Typical galvanostatic charge/discharge curves of the Co₃O₄@C@PGC nanosheets electrodes at a current density of 0.1 A g⁻¹ between 0.01 and 3.00 V are shown in Fig. 5b. The initial charge and discharge capacities are approximately 1187 and 1859 mA h g⁻¹, respectively, resulting in an initial Coulombic efficiency of ~64%. The initial irreversible capacity loss of the Co₃O₄@C@PGC nanosheets could be associated with the inevitable formation of SEI and decomposition of electrolyte^{51,52} and in good agreement with the above CV results. The discharge voltage plateau at ~1.1 V in the first cycle shift to ~1.2 V since the second cycle, just corresponding to the shift of reduce peak in CV curves from 0.97 V to 1.15 V. The areas under the charge and discharge curves are comparable, indicating a very low energy loss during charge/discharge. Starting from the 10th cycle, both charge and discharge curves are overlapping the previous one up to the 100th cycle, which indicates that the Co₃O₄@C@PGC nanosheets exhibit excellent cycle stability^{24,53}.

The cycle performances of the Co₃O₄@C@PGC nanosheets, Co₃O₄/C composite and Co₃O₄ NPs were investigated at a current density of 0.1 A g⁻¹. The results were shown in Fig. 5c. The Co₃O₄@C@PGC nanosheets electrode has the best cyclic retention and the highest reversible capacity. After 100 cycles, the reversible capacity is as high as 1413 mA h g⁻¹. The capacity is even higher than the theoretical capacity of Co₃O₄, which is common in many reported literatures^{19,26,28,29,54–57}. Such high specific capacity should be related to the following points: firstly, the tiny Co₃O₄ NPs have large specific surface area where more active sites for lithium ions are located¹⁹. Secondly, the reversible decomposition of the electrolyte and extra lithium ion adsorption/desorption on the SEI during cycling may lead to the high experimental lithium storage capacity as well^{27,58}. Thirdly, the pure PGC nanosheets have a reversible capacity of 580 mA h g⁻¹ (Fig. S5), so there would be synergetic effects between graphitic carbon and Co₃O₄ NPs^{26,55}.

Figure 5. (a) Representative CV curves of an electrode based on the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets obtained at a voltage range of 0.0 to 3.0 V (vs Li^+/Li) and potential scan rate of 0.1 mV s^{-1} . (b) Voltage profiles of the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets electrode at a current density of 0.1 C. (c) Charge/discharge capacities of the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets, $\text{Co}_3\text{O}_4/\text{C}$ composite and Co_3O_4 NPs at a current density of 0.1 C. (d) Rate capabilities and cycle performance of $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets and $\text{Co}_3\text{O}_4/\text{C}$ composite electrodes cycled at different rates from 0.1 to 20 C. (e) Cycle performance and Coulombic efficiency for the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets electrode at a higher current density of 5 C. (1 C = 1 A g^{-1}).

In contrast, the reversible capacity of the $\text{Co}_3\text{O}_4/\text{C}$ composite is much lower, which is only $\sim 763 \text{ mA h g}^{-1}$ at the end of the 100 cycles. But it also has an excellent cycling stability. Although, the bulk carbon in $\text{Co}_3\text{O}_4/\text{C}$ composite prevents the Co_3O_4 NPs from playing their best in the lithium storage capacity, it still takes an important role in holding the integrity of the structure. The Co_3O_4 NPs show the fastest capacity fading and the lowest reversible capacity which is below 549 mA h g^{-1} after 40 cycles. In the case of bare Co_3O_4 NPs, SEI trends towards rupture to accommodate the volume change induced by Li^+ expansion/contraction. The Co NPs forming in discharging processes also have catalyzing effect on SEI and are harmful to the integrity of the film. Thus the electrode material surface will cyclically expose itself to the electrolyte and more and more SEI films consecutively form on it, which leads to continual consuming of electrolyte and the fast capacity fading^{3,59}. However, a very thin carbon shell covers the electrode material in $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets, which induces a strong synergistic effect between porous graphitic carbon nanosheets and carbon-encapsulated Co_3O_4 NPs²⁶. During the charge/discharge process, the carbon shell is very beneficial to stabilize SEI film and avoid rupturing. Meanwhile, it is also effective to prevent the Co_3O_4 NPs from agglomerating. The porous sheet structure of carbon which links the shelled Co_3O_4 NPs provides enough space to accommodate the huge volume changes. In addition, the high specific surface area of $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets ensures a high contact area between the electrode and electrolyte. So Li^+ has plentiful diffusion accesses from electrolyte into electrode interior,

Figure 6. Nyquist plots of the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets, $\text{Co}_3\text{O}_4/\text{C}$ composite and Co_3O_4 NPs after 10 cycles at a current density of 0.1 C over the frequency range from 100 kHz to 0.01 Hz.

which will intensively enhance the transport rate of Li^+ . All these factors are vital for the electrode to retain the excellent cycling stability and high reversible storage capability¹¹.

The electrode made by $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets also has the best rate capability, as shown in Fig. 5d. After three cycles at 0.1 C, the electrodes were firstly tested at 1 C ($1\text{ C} = 1\text{ A g}^{-1}$). It is obvious that the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ electrode still needs ten more cycles to activate all active materials for its reversible capacity increases with cycle number until the 11th cycle^{50,56}. Meanwhile, the $\text{Co}_3\text{O}_4/\text{C}$ composite electrode shows a stable capacity as tested at 1 C. The reversible capacity of the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets electrode reaches a very high value of 1105 mA h g^{-1} at the eleventh cycle^{23,60}, while the $\text{Co}_3\text{O}_4/\text{C}$ composite electrode maintains a reversible capacity of 502 mA h g^{-1} during these cycles. At each tested specific current density including 2, 5, 10, and 15 C, the average reversible capacity of the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ electrode (1030, 845, 560 and 461 mA h g^{-1}) is much higher than $\text{Co}_3\text{O}_4/\text{C}$ composite electrode (430, 323, 240, 185 mA h g^{-1}). Even at 20 C, the average reversible capacity (345 mA h g^{-1}) is still very close to the theoretical capacity of graphite. When the current rate finally returns to the initial value of 1 C after 61 cycles, the electrode can recover its initial capacity of 1030 mA h g^{-1} with a little bit loss. And it is still sustainable up to the 70th cycle. The high reversible capacity and excellent rate performance indicate that the electrode has a high energy density and power density. So the electrode occupies the up-right corner of Ragone plot, as shown in Fig. S6⁶¹. In order to further confirm the durability of this nanosheet anode to work at a higher rate, the cyclability of the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets electrode has been further investigated upon 1000 cycles at 5 C and the result is shown in Fig. 5e. In the initial 20 cycles, the specific capacity gradually increases up to 820 mA h g^{-1} , corresponding to a process of activating the active substance, which is common in the literature^{50,56}. It is striking to note that the specific capacity can remain as high as 760 mA h g^{-1} even after 1000 cycles.

In order to uncover the mechanism which endow the electrode with superior electrochemical performance, electrochemical impedance spectroscopy (EIS), a promising tool for investigating diffusion issues, was conducted at frequencies from 100 kHz to 0.01 Hz on the electrode of $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets, $\text{Co}_3\text{O}_4/\text{C}$ composite, and Co_3O_4 NPs after 10 cycles at a current density of 0.1 C, respectively. The corresponding Nyquist plots are shown in Fig. 6, which is vital to clarify the electrode kinetics. The three impedance spectra have similar features: a medium-to-high-frequency depressed semicircle and a low-frequency linear tail. The semicircle at high frequency is an indication of SEI resistance (R_{SEI}) and contact resistance (R_f), the semicircle across the medium-frequency region represents the charge-transfer impedance (R_{ct}) on the electrode/electrolyte interface, and the low-frequency linear tail corresponds to the Warburg impedance (Z_w) associated with the diffusion of lithium ions in the bulk electrode (R_e)^{7,36,44,62,63}. The $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets electrode has the smallest semicircle diameter. So it possesses the lowest contact and charge-transfer impedances. That is to say, Li^+ and electron are able to transport fastest during the electrochemical insertion/extraction reaction in the electrode, which makes it reasonable that the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets electrode shows the best rate performance.

As compared with the results in literature^{3,29–33,57,64–70}, the $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ electrode possesses a much larger reversible capacity at any rate, as shown in Fig. 7. This should be related to the unique structure it has. The synthesis techniques and structure characters were summarized in Table S1. The excellent electrochemical performance of $\text{Co}_3\text{O}_4@\text{C}@\text{PGC}$ nanosheets anode can be illustrated by the mechanism suggested in Fig. 8 and Fig. S7. The size of the Co_3O_4 NPs in the paper is small enough. It is very close to the minimal size below which pulverization can't happen^{18,19}. Meanwhile the Co_3O_4 cores are firmly covered by well-graphitized onion-like carbon shells. Either the pulverization wouldn't happen in this

Figure 7. Comparison of capacity at different rates for $\text{Co}_3\text{O}_4/\text{C}/\text{PGC}$ nanosheets electrode with those of Co_3O_4 nanostructure and $\text{Co}_3\text{O}_4/\text{C}$ composite anodes reported.

Figure 8. Schematic illustration of $\text{Co}_3\text{O}_4/\text{C}/\text{PGC}$ nanosheets with fast Li^+ diffusion, effective electron transport, and excellent stress relaxation during Li^+ extraction/insertion.

experiment, or, even if it happened, the particle would be split into finite particles which still connect with the carbon shell, just as illustrated by Fig. S7. Thus it doesn't cause any loss in lithium storage. Because the NPs are firmly anchored by the carbon shell, it can't migrate and coalescent with adjacent particles. Thus aggregation of NPs is eliminated in this material. Co nanocrystals would be generated by Co_3O_4 NPs because of the reversible conversion reaction¹⁹. They are very harmful to SEI films, because the fresh Co surface has strong catalytic power on the decomposition of SEI films. But in this experiment, the Co crystals are completely separated by carbon shell. The SEI film should be more stable than the literature. Carbon materials always have good mechanical flexibility, which endow the shells with the ability to expand and contract with Co_3O_4 NPs during lithium ion insertion/extraction process. Finally, the volume change is accommodated by the abundant macropore and mesopore in the PGC nanosheets. So the structure of the material is so robust which guarantee the stability of the reversible capacity during cycle charge/discharge. The Co_3O_4 NPs were integrated into PGC nanosheets. Thus, a continuous network is constructed by the conductive carbon, which ensures the electron transport freely. The porous structure of the nanosheets provides a huge interfacial area with electrolyte. The electrode has abundant accesses for Li^+ to interior active materials. The thin film structure of $\text{Co}_3\text{O}_4/\text{C}/\text{PGC}$ nanosheets shortens the diffusion path of Li^+ . So the electrode can work very well at a very high specific current density. At last, the thin film structure is also very favorable for the adsorption of lithium ions on both sides, edges, and other defects of these nanosheets^{59,62}. In addition, there may be a strong synergistic effect between PGC nanosheets and Co_3O_4 NPs²⁶. That may explain the reason why the specific capacity of the $\text{Co}_3\text{O}_4/\text{C}/\text{PGC}$ electrode is higher than the theoretical specific capacity of Co_3O_4 .

In summary, porous graphitic carbon nanosheets encapsulating small and uniform Co_3O_4 NPs with an average grain diameter of about 20.4 nm were successfully fabricated. In this strategy, $\text{Co}_3\text{O}_4/\text{C}/\text{PGC}$ nanosheets were compounded using glucose as the carbon source, cobalt nitrate as the Co_3O_4 precursor,

and a surface of sodium chloride as the template. In this unique architecture, the PGC nanosheets with high elasticity can effectively preserve the structural and interfacial stabilization of Co_3O_4 NPs as well as accommodate the mechanical stress resulting from the severe volume change of Co_3O_4 NPs during lithium ion insertion/extraction, while the interconnected porous graphitic carbon networks with large surface area, superior electrical conductivity, high mechanical flexibility and stability lead to remarkably enhanced structural and electrical integrity as well as excellent kinetics for ion and electron transport of the overall electrode. As a result, such a nanostructured electrode exhibits an extremely durable high-rate capability: a capacity of 1030 mA h g^{-1} is achieved at 2 C , 560 mA h g^{-1} at 10 C , and 345 mA h g^{-1} at 20 C . Cycling at 5 C after 1000 cycles leads to a recovered capacity of 760 mA h g^{-1} , still almost 2 times more than the capacity of graphite. The obtained good performance opens up new opportunities in the development of high performance next-generation LIB used for alternative energy and electric transportation.

Methods

Synthesis of $\text{Co}_3\text{O}_4@\text{C@PGC}$ nanosheets. All the chemicals were of analytical grade and were used without further purification. Firstly, 1.8 g of glucose (Sinopharm Chemical Reagent Co., LTD. AR), 0.582 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., LTD. AR) and 15 g of NaCl (Tianjin Guangfu Technology Development Co., LTD. AR) were dissolved in 50 ml of deionized water under magnetic stirring until a transparent blue solution was obtained. Then, the solution was transferred into a drying oven and dried at 80°C for 24 h . The dry block of crystal was ground to fine powder in an agatemortar. The composite powder was heated in a tubular vacuum furnace at 750°C for 2 h under flowing N_2 . Finally, it was annealed again at 300°C for 4 h under air. Once cooled to room temperature, the as-synthesized black powder was washed by deionized water several times to remove NaCl , and then $\text{Co}_3\text{O}_4@\text{C@PGC}$ nanosheets were obtained. For comparison, $\text{Co}_3\text{O}_4/\text{C}$ composites were also synthesized by carbonizing the mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and glucose without adding NaCl at the same conditions. Meanwhile, Co_3O_4 NPs were also synthesized by sintering $\text{Co}_3\text{O}_4@\text{C@PGC}$ nanosheets at 600°C for 2 h in air. And PGC nanosheets were obtained by immersing $\text{Co}_3\text{O}_4@\text{C@PGC}$ nanosheets in plenty of nitric acid for 4 h at 70°C with magnetic stirring to remove the Co_3O_4 NPs.

Materials Characterization. XRD measurements were taken on X-ray diffractometer (XRD, Rigaku D/max) with $\text{Cu K}\alpha$ radiation at a wavelength of $1.5406 \text{ \AA}$ to determine the phase composition and crystallinity. Field emission scanning electron microscope (FESEM) images were acquired on a JEOL JSM-6700F micro-scope operated at 5 kV . The transmission electron microscope (TEM), high-resolution TEM (HR-TEM) images were recorded on a JEOL JEM-2100F high-resolution transmission electron microscope at 200 kV . Thermogravimetry analysis (TGA) was performed with a Perkin-Elmer (TA Instruments) instrument up to 750°C at a heating rate of $10^\circ\text{C min}^{-1}$ in air. The Raman spectrum was recorded on the Lab RAM HR Raman spectrometer using laser excitation at 514.5 nm from an argon ion laser source to validate the $\text{Co}_3\text{O}_4@\text{C@PGC}$ nanosheets. Brunauer-Emmett-Teller (BET) surface areas and porosities of the products were determined by nitrogen adsorption and desorption using a Micromeritics ASAP 2020 analyzer.

Electrochemical Measurements. Electrochemical measurements were conducted on a coin-type test cell (CR2025) with metallic lithium sheet as both counter and reference electrode. The working electrode is fabricated by mixing active material ($\text{Co}_3\text{O}_4@\text{C@PGC}$ nanosheets, $\text{Co}_3\text{O}_4/\text{C}$ composites, Co_3O_4 NPs and PGC nanosheets), conductive material (acetylene black, Hong-xin Chemical Works) and binder polyvinylidene fluoride (PVDF, DuPont Company, 99.9%) in a weight ratio of 8:1:1 with N-methyl-2-pyrrolidone (NMP, Aladdin Reagent, AR) as solvent. The mixture was fully stirred for several hours in a weighing bottle into slurry. Then, it was uniformly pasted on Cu foil substrates. After vacuum drying at 120°C for 12 h , the electrode disks ($d = 12 \text{ mm}$) were punched and weighed. The working electrode has approximately $0.5\text{--}1.0 \text{ mg}$ of active material. The diameter of counter electrode (16 mm) is larger than working electrode. The electrolyte is 1 M LiPF_6 in a mixture of ethylene carbonate and diethyl carbonate (1:1 by weight) and a Celgard 2400 polypropylene membrane was used as the separator. The cells were assembled in an argon-filled glove box in which both the moisture and oxygen contents were controlled to be less than 0.1 ppm . Cyclic voltammetry (CV) was performed on an IVIUMSTAT electrochemical workstation at 0.1 mV s^{-1} in the range of $0.01\text{--}3.0 \text{ V}$. Galvanostatic charge-discharge cycling tests were performed using an LAND CT2001A battery testing system in the voltage range between 0.01 V and 3 V . Electrochemical impedance spectroscopy (EIS) experiments were carried out using an IVIUMSTAT electrochemical workstation in the frequency range of $0.01\text{--}100 \text{ kHz}$ at room temperature. All of the specific capacities in this work were estimated by using the weight of the active materials.

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Author Contributions

X.L. and G.W. conceived and designed the experiments. X.L. performed the experiment. S.W., Z.J., J.L. and Q.J. provided helps in the experiments. X.L. and G.W. wrote the paper and all authors discussed the experiments and final manuscript.

Additional Information

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