In situ prepared reduced graphene oxide/CoO nanowires mutually-supporting porous structure with enhanced lithium storage performance

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\textbf{A B S T R A C T}

An efficient method is demonstrated to synthesize reduced graphene oxide/CoO nanowires (rGO/CoO) mutually-supporting porous structure, which is in situ prepared by annealing self-assembled graphene oxide (GO)/Co(OH)\textsubscript{2}–0.11H\textsubscript{2}O nanowires composite in N\textsubscript{2} atmosphere. The CoO nanowires are uniformly and tightly anchored on the rGO sheet surface, preventing the aggregation of the CoO nanowires and the restacking of rGO sheets. As an anode material for lithium ion batteries (LIBs), rGO/CoO electrode displays excellent electrochemical performance including a high reversible capacity of 994 mAh g\textsuperscript{-1} even after 100 cycles with 96.3% capacity retention of the initial discharge capacity, super rate capability (718, 577, 504, 388 and 262 mAh g\textsuperscript{-1} at 0.8, 3.2, 5.7 and 10C, respectively, 1C = 1 A g\textsuperscript{-1}) and extremely excellent cycling performance at high rates (621 mAh g\textsuperscript{-1} at 1C after 620 cycles; 520 mAh g\textsuperscript{-1} at 3C even after 750 cycles).

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1. Introduction

Since the reversible conversion mechanism on lithium storage was discovered [1], transition metal oxides, such as FeO\textsubscript{x} [2,3], CoO\textsubscript{x} [4–6], and NiO [7,8], have been promising alternative anode materials, instead of commercial graphite, for Lithium ion batteries (LIBs) electrode because of the high theoretical specific capacity (> 600 mAh g\textsuperscript{-1}). The conventional reduction/oxidation processes take place following the below chemical equation [9]:

\[ \text{M}_x\text{O}_y + 2\text{Li} \rightarrow x\text{M} + y\text{Li}_2\text{O} \]

M represents a kind of transition metals. It is interesting that Li\textsubscript{2}O, formed in the reduction process, shows electrochemical activity in the reverse process, because the fresh surfaces of the pristine metal nanoparticles generated in the reduction process have very strong ability on catalization [10]. Nowadays, there has been numerous evidence that nanoscaled metal oxides structure can provide improved electrochemical performances compared to their bulk counterparts, for they always have shorter path length for Li-ion transport and higher surface area for electrolyte/electrode contact [7]. However, they still suffer lots of shortages which block the usage of them as anode materials for LIBs. The poor electrical conductivity prevents them having good rate capacity performance. They tend to agglomerate during lithiation/delithiation, which always induce an inferior cycling stability [11]. At the same time, some parts of the active materials may exfoliate from electrode or current collectors because of pulverization, which is also harmful to the reversible capacity. To circumvent these shortages, mixing the nanostructured metal oxides with conductive and stretchable materials, such as carbonaceous materials, is an efficient method [12,13].

Graphene, as a monolayer of carbon atoms arranged in a honeycombed network of six-membered rings, has triggered a gold rush since its discovery. Its good mechanical properties, high theoretical surface area of 2630 m\textsupersq g\textsuperscript{-1}, good electronic conductivity suggest it would have a bright prospect in LIBs. What is more, it has high theoretical lithium storage of 744 mAh g\textsuperscript{-1} [14,15]. Thus, graphene can support another advanced anode materials...
meanwhile it also can act as a pathway for the flow of electrons from the active material to current collector [16–18]. Up to now, many nanoparticles (NPs) MxOy/graphene composites have been investigated as LIB anode materials, such as SnO2/graphene [19], Mn3O4/graphene [20], CuO/graphene [21], and Fe2O3/graphene [22]. They usually exhibit much better electrochemical performance than their bare counterparts. However, the NPs are still prone to aggregate during cycling because of non-intimate/tight contact between the NPs and graphene sheets (GS) layers [23,24]. On the other hand, the overlapping of GS during electrode preparation and electrochemical test is also a critical problem, which may result in inadequate adhesion of graphene. Therefore, in order to adequately utilize the unique properties of individual GS and fully harness the synergistic effect between GS and MxOy, the main challenges in the synthesis of graphene/MxOy composites lie in how to effectively enhance the contact between GS and MxOy and inhibit too much overlapping and agglomeration of GS.

In this paper, uniform and well-crystalline Co(CO3)0.5(OH)·0.11H2O nanowires, served as CoO precursor, were firstly fabricated via a glycol-assisted hydrothermal method. Then the positively charged nanowires were negatively charged graphene oxide (GO) sheets because of electrostatic interaction. As the composites were sintered in nitrogen atmosphere, the Co precursor and GO sheets were thermally in situ decomposed to CoO nanowires and rGO. Eventually, a unique self-assembled rGO/CoO nanowires mutually-supporting porous structure was successfully prepared. The in situ direct generation of rGO/CoO composites by one-step thermal treatment ensures a strong interaction and better structural stability. The electrochemical test results indicate the as-prepared rGO/CoO composite owns high specific capacity, good cycling stability and excellent rate capability.

2. Experimental Section

2.1. Preparation of the precursor Co(CO3)0.5(OH)·0.11H2O nanowires

In this work, we have devised a chemical route to synthesize Co(CO3)0.5(OH)·0.11H2O nanowires. In a typical synthesis, 245 mg of CoCl2·6H2O (Tianjin Guangfu Technology Development co., LTD. AR) and 150 mg of urea (CH4N2O, Sinopharm Chemical Reagent Co., LTD. AR) were dissolved in a mixture of 15 ml ethylene glycol (C2H4O2, Sinopharm Chemical Reagent Co., LTD. AR) and 15 ml de-ionized water (18.2 MΩ, produced by using a Millipore Direct-Q System and was used throughout the experiments). After the CoCl2·6H2O and urea totally dissolved under stirring, the solution was transferred to a 50 ml Teflon lined stainless steel autoclave for a hydrothermal reaction at 120 °C for 4 h. After natural cooling, CoO precursor powders were collected after centrifuging, washing with plentiful de-ionized water and freeze-drying.

2.2. Preparation of rGO/CoO composite

Graphite oxide was synthesized by an improved Hummers method (see Supporting Information). A homogeneous GO suspension (0.2 g L−1, pH ≈ 3.6) was obtained by dispersing the resultant mixture in de-ionized water under ultrasonication for 2 h. Meanwhile, a homogeneous CoO precursor dispersion (1 g L−1, pH ≈ 8.0) was obtained by dispersing the resultant mixture in de-ionized water under ultrasonication for 0.5 h. Then, plenty of GO aqueous solution was slowly dropped into CoO precursor dispersion under mild magnetic stirring with pH = 4, forming large amounts of aggregation. The precipitate was collected through centrifuging (5000 rpm for 5 min), and those redundant GO can be removed at the same time. Finally, the GO/CoO(CO3)0.5(OH)·0.11H2O composite powders were obtained by freeze-drying and further annealed in flowing N2 at 500 °C for 2 h to prepare rGO/CoO powders. For comparison, pure CoO was also synthesized by annealing CoO precursor powders in the same conditions.

2.3. Characterization

The prepared samples were investigated by X-ray diffractometer (XRD, Rigaku D/max 2500 pc, Cu Ka radiation: λ = 1.5406 Å), X-ray photoelectron spectroscopy (XPS, ESCALAB Mk II spectrometer using unmonochromatized Al Ka radiation), Raman spectrum (Lab RAM HR Raman spectrometer using laser excitation at 514.5 nm from argon ion laser source). Morphologies and structures were characterized with a scanning electron microscopy (FESEM, JEOL JSM–7600 F field emission) operated at an acceleration voltage of 8.0 kV, and transmission electron microscopy (TEM, JEOL 2100F, 200 kV). The Micromeritics ASAP 2020 analyzer was used to determine Brunauer-Emmett-Teller (BET) surface areas and Barrett–Joyner–Halenda (BJH) porosities. Thermogravimetric analysis (TGA, SDT 2960) was measured up to 760 °C at a heating rate of 5 °C min−1 in air. Zeta potential was measured by dynamic light scattering (Malvern Nano-ZS, UK). Fourier transform infrared spectroscopy (FTIR, NEXUS, 670) was carried out with a DTGS detector by making pellets with KBr powders.

2.4. Electrochemical Measurements

Electrochemical measurements were carried out by using 2025 coin-type cells. Metallic lithium sheets were used as both counter and reference electrode. The working electrode is prepared by mixing active materials, acetylene black and polyvinylidene-fluoride (PVDF) in a weight ratio of 7:2:1 with N-methyl-2-pyrrolidinone (NMP) as solvent and pasting the mixture onto the copper foil, followed by vacuum drying at 110 °C for about 12 h. The electrolyte is a mixture of 1 M LiPF6 in ethylene carbonate (EC)/

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Fig. 1. Schematic illustration of the procedures for preparation of rGO/CoO nanowires mutually-supporting porous structure.
dimethyl carbonate (DMC) with the weight ratio of 1:1. The cells were assembled in an argon-filled glove box with the moisture and oxygen contents were less than 0.1 ppm. Electrochemical tests were performed using a multi-channel battery testing system (LAND CT2001A) between 0.01 and 3 V at room temperature. Cyclic voltammogram (CV) and electrochemical impedance spectral (EIS) were tested with an IVIUMSTAT electrochemical workstation. To calculate the special capacity, we only used the mass of active materials, excluding conductive agent and binder.

3. Results and Discussion

The preparing procedure of rGO/CoO nanowires mutually-supporting porous structure is illustrated in Fig. 1. In short, the positively charged disperse CoO precursor is firstly attached to the negatively charged disperse GO sheets by mutual electrostatic interaction in aqueous solutions without using any active agent [4,25,26]. Then CoO nanowires are in situ generated on the surface of rGO by thermal treatment in a nitrogen atmosphere (Co (CO₃)₀.₅(OH)₀.₁₁H₂O decomposes to CoO following: Co (CO₃)₀.₅(OH)₀.₁₁H₂O − CoO + 0.₅CO₂ + 0.₆₁H₂O), meanwhile the GO sheets are reduced partly by losing oxygen-containing surface groups at the same procedure. After that, the rGO/CoO mutually-supporting hierarchical porous structure is prepared. This method should heavily improve the interaction/adhesion force between nanowires and rGO sheets.

Graphite oxide was synthesized by an improved Hummers method [25]. The method is very effective to produce abundant monolayer graphene with high quality, which is prove by the XRD diffraction results, the FTIR spectra and the SEM image of graphite oxide shown in Fig. S1 and the AFM mapping and depth profile results shown in Fig. S2. A hydrothermal process is used to synthesize CoO precursors, Co(CO₃)₀.₅(OH)₀.₁₁H₂O nanowires, wherein ethylene glycol is employed as a structure directing agent. The formation reactions can be described by the following steps:

\[
\text{CO(NH₂)}₂ + 3\text{H₂O} \rightarrow 2\text{NH₄}⁺ + 2\text{OH}⁻ + \text{CO₂} \quad (1)
\]

\[
2\text{OH}⁻ + \text{CO₂} \rightarrow \text{H₂O} + \text{CO₃}²⁻ \quad (2)
\]
Co\textsuperscript{2+} + 0.5\text{CO}_3\textsuperscript{2-} + \text{OH}^- + 0.11\text{H}_2\text{O} \rightarrow \text{Co(CO}_3\text{)}_{0.5}\text{(OH)}\cdot 0.11\text{H}_2\text{O} \quad (3)

In the process, urea primarily acts as a source to generate hydroxyl and carbonate anions, as showed in Equation 1 and Equation 2, while the Co\textsuperscript{2+} in Equation 3 required are from cobalt salt. The resultant transparent aqueous solution after mixing suggests all the CoO precursor nanowires are homogeneously attached on the surface of the GO sheets and the absorbent charges on both particles, which are essential for colloidal, are annihilated (Fig. S3 and S4).

Fig. 2 provides the typical X-ray diffraction (XRD) patterns of the obtained products. The as-prepared CoO precursor (curve a) can be reasonably indexed and assigned to Cobalt Carbonate Hydroxide Hydrate, Co\text{(CO}_3\text{)}_{0.5}\text{(OH)}\cdot 0.11\text{H}_2\text{O} (JCPDS 48–0083) \[27,28\]. For pure CoO (curve b) and rGO/CoO composite (curve c), all diffraction peaks at 2-theta values of 36.5°, 42.4°, 61.5°, 73.7°, 77.5° can be indexed to diffractions of \{111\}, \{200\}, \{220\}, \{311\}, and \{222\} faces of standard cubic CoO (JCPDS 43–1004), indicating the complete transformation of the Co\text{(CO}_3\text{)}_{0.5}\text{(OH)}\cdot 0.11\text{H}_2\text{O} into the CoO phase. No conventional stacking peak of graphene is detected at 2\theta = 25° − 27°, suggesting that CoO nanowires effectively prevent rGO from severe restacking \[29\].

Raman spectroscopy is an effective means for the characterization of carbonaceous materials with different existential forms \[30,31\]. To verify the existence of rGO, Raman spectrum was recorded (Fig. 3a). Generally, the D-band is attributed to disorder and defects in the hexagonal graphitic layers, while the G-band is attributed to the vibration of sp\textsuperscript{2} carbon atoms in a 2D hexagonal lattice \[32\]. The relative intensity ratio of ID/IG is therefore an indication of the graphene quality \[33\]. The calculated value of 0.94 agrees well with that of rGO \[34\], indicating GO was partly reduced. To gain insight into the chemical composition, TGA was performed on the rGO/CoO (Fig. S5). The sharp weight change from to Co\textsubscript{3}O\textsubscript{4} (Fig. S6) and complete combustion of rGO. On the basis of the final weight of Co\textsubscript{3}O\textsubscript{4}, the original content of CoO is calculated to be \~{\text{92 wt\%}}.

The more detailed elemental composition and chemical state of the as-prepared rGO/CoO are further characterized by XPS measurements. The different peaks of Co (Co 2{s}, Co LMM{2}, Co 2p{1,2}, Co 2p{3,2}, Co LMM, Co 3{s}, Co 3{p}) and O (O 1{s}, O KLL) in the survey XPS spectrum for rGO/CoO composite (Fig. 3b) are attributed to CoO \[35\]. Meanwhile, the strong peak of C 1{s} is expected from rGO. From the XPS spectrum of the Co 2{p} core level (Fig. 3c), the peak at 780.0 eV for 2p{3,2} corresponds to the shakeup satellite peak at 786.2 eV for 2p{3,2}, and the peak at 795.6 eV for 2p{1,2} is attributed to the shakeup satellite peak at 802.0 eV for 2p{1,2}, indicating the characteristic of Co\textsuperscript{2+} \[35\]. The high-resolution C 1{s} spectrum is shown in Fig. S7. The strong C 1{s} peak (284.4 eV) corresponds to graphitic carbon (sp\textsuperscript{2} domain) in rGO \[23\], whereas the other peaks arising from the residual oxygenated carbons (carbon in C − O at 285.0 eV; carbonyl carbon, C=O, 285.9 eV; carboxylate carbon, O−C=O, 288.4 eV) after the de-oxygenation process accompanying the reduction of GO \[35,36\]. Fig. 3D shows the spectrum of O 1{s}, which could be divided into three independent peaks. The peak at 528.9 eV is ascribed to oxygen in CoO, and the peak at 532.6 eV is assigned to C − O − C and/or C − OH groups (epoxy and/or hydroxyl). Specially, the peak at 531.2 eV corresponds to C − O groups or Co − O − C linkages \[23,35,37\]. To the best of our knowledge, the strong chemical contact between the MxOy and graphene via the oxygen bonding (M=O−C) would be beneficial to interfacial charge transfer and reduce the loss of active materials, which can improve electrochemical performance of the composites \[21,23,38\].

The morphology of the CoO precursor and its evolution after annealing were detected by SEM and the images are shown in Fig. 4a and b. The pristine precursor is nanowire with a diameter of 15−25 nm and length of several micrometers. The wire surface is smooth and flat. After annealing, the wire changed to a dot-line, a

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**Fig. 4.** FESEM images of (a) CoO precursor nanowires; (b) CoO after annealing; (c) GO/CoO precursor by electrostatic interaction; (d) rGO/CoO after annealing.

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about 230 to 431°C is primarily attributed to the oxidation of CoO.
sequence of NPs with a diameter of about 10–20 nm. The effect of rGO on the morphology evolution of the wires was also investigated by SEM. The images are shown in Fig. 4c and d which can be compared to Fig. 4a and b. The adding of GO doesn’t affect the morphology of the wire, as shown in Fig. 4c. Co (CO3)0.5(OH)·0.11H2O nanowires are uniformly adsorbed on GO sheets, and both of them supported each other. Thus a 3D loose network system with lots of voids is formed by them. As shown in Fig. 4d, the annealing has very less effect on the morphology of the system. The wire is still long and smooth and the sheet is still large and flat. It doesn’t show a similar view like the image in Fig. 4b. A similar phenomenon was also observed by TEM. After annealing, the wire changed to a sequence of NPs of about 10–20 nm as shown in Fig. 5a. And the wire retained its morphology by the help of rGO after annealing as proved by the image of Fig. 5b. In fact, the line still consisted of similar size nanocrystals as proved by the image of Fig. 5c. It seems like a line because these nanocrystals link with each other firmly. The grain boundary between vicinal crystals can be clearly detected by the HRTEM image shown in Fig. 5d. The morphology characterization by SEM and TEM revealed that the CoO wires were firmly anchored on the rGO surface. So the integrity of the wires was retained even after annealing. Meanwhile the existence of the wires between rGO sheets is also effective to inhibit the restacking of rGO sheets. The production of our method is indeed scalable, as indicated by the panoramic SEM images shown in Fig. S8.

The N2 adsorption-desorption isotherms are showed in Fig. S9, and the insets are their corresponding BJH pore-size distributions. The isotherms of the CoO powers can be classified as type IV [27], and the corresponding BET specific surface area is 13.9 m² g⁻¹ (Fig. S9a). No peaks were observed in the inset of Fig. S9a which suggests the pore-size distribution is dispersive. However, the BET specific surface area of the rGO/CoO is 66.4 m² g⁻¹ (Fig. S9b), almost five times that of pure CoO, and a pore size centered at 3.7 nm (inset of Fig. S9b). The thermal decomposition of Co(CO3)0.5(OH)·0.11H2O is always accompanied with the release of H2O and CO2, which induces the discontinuous CoO nanowire. So the mesopores may distribute in the interstices between CoO NPs. The higher surface area of the rGO/CoO may be attributable to the presence of rGO, aparting from CoO phase. The porosity and high specific surface area will enhance the electrolyte/active material contact area, shorten the Li-ion diffusion length, and relieve the strain induced by the volume change during the electrochemical reaction, which would benefit the electrochemical performance [39].

Coin cells with metallic lithium anodes are packaged to investigate the lithium storage performance of the CoO and rGO/CoO composite. Fig. 6a and b show CV profiles of the electrodes at a scan rate of 0.1 mV s⁻¹ over a voltage range of 0.01–3.00 V. In the first cycle of pure CoO, two well-defined cathodic peaks are observed, a sharp one at around 1.03 and a tiny one 0.62 V. The tiny one may be due to the irreversible formation of a solid electrolyte interphase (SEI) [40,41], which disappeared in the following scans. The sharp one shift to ~1.3 V in subsequent cycles and tends to be stable, which correspond to the electrochemical reduction of CoO to Co metal NPs accompanying lithiation. A similar peak and trend was also observed in rGO/CoO electrode CV curves. But the sharp peak of rGO/CoO electrode appeared at much lower potential of about 0.49 V than pure CoO electrode, which may be due to the introduction of graphene. After all, the reduction potential of graphene relative to Li is generally very low at about 0.02 V [42]. In the anodic scans, both electrodes show a peak at ~2.1 V which corresponds to the oxidation of Co metal NPs accompanying delithiation [43]. In subsequence scans, the peaks slightly shift to the positive side. It is interesting to find that the peak area obviously increased in the sequence scans of rGO/CoO electrode, which suggest the increase of charging capacity. For the rGO/CoO electrode, the electrochemical reaction process of lithium with CoO and carbon could be described as follows [14,44]:

\[
\text{CoO} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Co} + \text{Li}_2\text{O}
\]
Fig. 6. CV curves of the electrodes at a scan speed of 0.1 mV s\(^{-1}\) in the voltage window of 0.01–3 V: (a) CoO (b) rGO/CoO; discharge–charge curves of the electrodes at a current density of 0.1 A g\(^{-1}\) for the first three cycles: (c) CoO (d) rGO/CoO.

Fig. 7. (a) Charge/discharge capacities of the CoO and rGO/CoO electrode at a current density of 0.1C; (b) Rate capabilities and cycle performance of the CoO and rGO/CoO electrode cycled at different current rates from 0.1 to 10C; (c) Cycle performance and Coulombic efficiency for rGO/CoO electrode at higher current density of 1C (for the first 10 cycles at 0.1C, 1C = 1 A g\(^{-1}\)).
3C + Li^+ + e^- → LiC_3

Fig. 6c and d show the discharge/charge curves of both electrodes at a current density of 0.1 A g⁻¹ for the first three cycles. The curves of CoO electrode are well consistent with the CV curves. For the first discharge curve, the slope changing at about 0.96 V corresponds to the tiny reduction peak at 1.03 V and the voltage plateaus at 0.77 V corresponds to the sharp reduction peak at 0.62 V. The discharge and charge capacities are 876 mA h g⁻¹ and 608 mA h g⁻¹ in the 1st cycle, respectively, indicating a Coulombic efficiency of 69.4%. It can deliver a reversible discharge capacity of 638 mA h g⁻¹ in the 2nd cycle and this reversible capacity is retained in the 3rd cycle. The discharge/charge curves of the rGO/CoO electrode are also consistent with the aforementioned CV curves. The discharge and charge capacities are 1031 mA h g⁻¹ and 746 mA h g⁻¹ in the 1st cycle, respectively, with an initial Coulombic efficiency of 72.4%. The excite charge capacity is shown by the charge curves, which increase from 746 mA h g⁻¹ for the 1st cycle to 816 mA h g⁻¹ for the 3rd cycle.

The cycle performance of the rGO/CoO electrode was tested at a current density of 0.1 A g⁻¹, and it was compared with the pure CoO electrode (Fig. 7a). The capacity of the rGO/CoO is superior to the CoO at the initial cycle. The reversible capacities are gradually increasing in the first dozens of cycles, which may be attributed to the formation of a polymeric surface film attached to the active material [14]. It gets a maximum value of 1027 mA h g⁻¹ at the 36th cycle, which is about 99.5% of the initial discharge capacity, and it can still maintain 994 mA h g⁻¹ even after 100 cycles. The value is even higher than the theoretical value of rGO/CoO composite (C_theoretical = C_{CoO} × mass percentage of CoO + C_{graphene} × mass percentage of graphene = 716 × 92% + 744 × 8% = 718.2 mA h g⁻¹). Such high specific capacity of rGO/CoO should be attributed to the following points: firstly, the rGO sheets have numerous significant disorder and defects, which can also contribute to the lithium storage capacity, except for the inherent capacity (formation of intercalation compounds Li_xC) [14,45]. Secondly, the reversible decomposition of the electrolyte with the formation of SEI and extra lithium-ion adsorption/desorption on the SEI during cycling may also lead to the high experimental lithium storage capacity [10,46]. For the pure CoO electrode, the initial capacity only is maintained for 18 cycles. After that, it declines sharply from 708 to 506 mA h g⁻¹.

The rGO/CoO electrode also exhibits excellent rate performance. As shown in Fig. 7b, the rate performance was compared with the CoO electrode. The electrode delivers average reversible capacities of 960, 846, 790, 718, 646, 577, 504, 388 and 262 mA h g⁻¹ for 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 5.0, 7.0 and 10 C, respectively. It means 28% capacity is retained even after the current density enlarged 100 times from 0.1C to 10C. As the current rate returns to 0.1C, the initial capacity is reserved. The curve even persist the increasing trend during 72-82 cycles and 102-108 cycles, just same like the trend in first 11 cycles. Finally, the capacity rises above 1046 mA h g⁻¹ at the 112th cycle, which is very close to the initial discharge capacity (1068 mA h g⁻¹). However, as the current density increase from 0.1 to 5C, the specific capacity of the CoO electrode decreases sharply to only 7.8% of its initial capacity. As the current density increases even higher up to 10C, the specific capacity is close to zero. When the current density returns to 0.1C, the electrode can’t regain its initial capacity yet. Only 60% capacity is recovered. In fact, the cycle performance of the rGO/CoO electrode is much better than 100 cycles. As shown in Fig. 7c, the electrode can maintain a reversible capacity of 790 mA h g⁻¹ at 1st current rate of 1C to the 130th cycle. Then it suffers a sharp fading to 530 mA h g⁻¹ from the 130th cycle to the 180th cycle. After that, the capacity levels off above 610 mA h g⁻¹ until the 620th cycle with a Coulombic efficiency of around 98.3–100.4%. At a higher current density of 3C (Fig. S10), the trend is similar to 1C, but the specific capacity still can maintain 520 mA h g⁻¹ even after 750 cycles. The reasons for the obvious capacity decreases at high rates maybe as follows [11,47,48]: (1) the continuous reduction of active materials due to the insetting of metal Co in Li₂O matrix partially, especially it occurs at high rates; (2) the brush-fire aggregation of the active materials to larger clusters cannot be completely avoided; (3) the structure strain of the active materials can’t be totally eliminated during cycling even though the voids and rGO sheets could accommodate the volume change of the active species. The rate performance and cycle life of rGO/CoO are comparable to or even better than the reported results in Table S1. All these results confirm the merits of the rGO/CoO electrode.

In order to clarify the difference of the electrochemical performances, EIS measurements are also carried out at frequencies from 100 kHz to 0.01 Hz on both electrodes before test and after 100 cycles at 0.1C to uncover the electrode kinetics evolution and its relationship to electrochemical performance (Fig. 8). The Nyquist plots could be well fit by using a commonly adopted equivalent circuit (the inset of Fig. 8) [49–51]. In the equivalent circuit, R is the electrolyte resistance; Rct is the contact and charge-transfer resistance; Zwl is the Warburg impedance related to the diffusion of Li ions into the bulk electrodes, and CPE is the constant phase-angle element, involving double layer capacitance. The kinetic parameters summarized in Table S2 in the Supporting Information. Whether the EIS was tested initially or after 100 cycles, the charge-transfer resistance (Rct) for the rGO/CoO composite is much smaller than the CoO electrode. This indicates that the rGO/CoO composite electrode possess lower charge-transfer impedances, which can lead to rapid electron transport during lithiation/delithiation process and thus result in significant improvement on the rate performance. The tail for the rGO/CoO electrode at low frequency has higher slope than the CoO electrode, which indicates that the rGO/CoO electrode possesses lower lithium diffusion impedance [52]. The impedances both increased after 100 cycles, which may be attributed to the formation of SEI film [53–55]. But such increase in impedance does not lead the decline of capacity. As shown in Fig. 7, the capacity of each electrode also increased during the initial cycles. This phenomenon is also observed in other literatures [53–55]. Maybe, it means impedance has little effect on capacity during cycling at low current density.

The excellent electrochemical performance of the rGO/CoO anode should be ascribed to the unique structure it has [56–58]. In this experiment, the attachment was completed before the
annealing which induce the conversion of CoO precursor nanowires to CoO and GO sheets to rGO. The procedure is obviously effective to enhance the adhesion force between CoO nanowire and rGO. The CoO nanowires in fact are tightly anchored on the rGO sheets, so the integrity of the nanowires is kept as shown in Fig. 4d and Fig. 5b. Thus, the rGO/CoO electrode can possess an outstanding electronic conductivity to rGO benefiting from the good adhesion. And rGO sheets are able to act as an expressway for charge transfer. So the conductivity of the electrode is improved. Secondly, CoO nanowires are firmly anchored on rGO sheets surface. So the CoO NPs which constitute the nanowire have little chance to shed and aggregate. Meanwhile, the rGO which is separated by the CoO nanowires also have little chance to restack. Thus, the voids between the network of the CoO wires and rGO can be reserved. The voids and the interstices in the wires formed during gas releasing are essential for high performance for they supply uniform interspaces to accommodate the large volume change electrodes suffer during lithiation/delithiation. So the cycle performance of the electrode can be improved. Finally, the voids and interstices, together with rGO sheets, can also supply a large interface and pathway for Li+ reaction and diffusion. The nanowires, NPs indeed, with small diameter heavily shorten the hard pathway for Li+ diffusion inside active materials. Li+ diffusion rate in the cell assembled by the rGO/CoO electrode is improved, which induce the excellent rate performance.

4. Conclusions
In summary, we have developed a novel and effective route for the synthesis of mutually-supporting porous rGO/CoO nanowire composite electrode for LIBs. The as-prepared rGO/CoO wire composite shows a significantly improved specific capacity, cycle performance and excellent rate capability compared to a pure CoO wire counterpart, which is primarily due to the advantageous combination of rGO and CoO nanowires. We think the in situ generation of rGO/CoO nanowire composite through calcining CoO precursor attached on GO sheets is vital to have such stable structure. The nanowires are firmly anchored on the rGO sheets surface, which prevent the aggregation of the nanowires and the restacking of rGO sheets and endow the electrode good conductivity and perfect electrochemical performance. Furthermore, this method may also be extended to build various other promising rGO/MxOy structures for important applications such as sensors, catalysts, adsorbents, and supercapacitors.

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Appendix A. Supplementary data
Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.12.190.

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