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Graphical abstract: Co(OH)$_2$ arrays/GNSs composites are constructed by preferentially oriented growth and exhibit a high-performance used as anode materials for lithium-ion batteries.
Free-Standing Cobalt Hydroxide Nanoplatelet Array Formed by Growth of Preferential-Orientation on Graphene Nanosheets as Anode Material for Lithium-Ion Batteries

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Cobalt hydroxide arrays/graphene nanosheets (Co(OH)2 array/GNSs) composites are formed by growth of preferential-orientation versus basal planes of GNSs. Notably, the Co(OH)2 nanoplates, possessing special hexagonal morphology with the length of about 130 nm and average thickness of about 20 nm, stand vertically rather than lie flat on the surface of graphene sheets. More interestingly, the (001) crystal plane of Co(OH)2 is vertical to graphene basal plane and forms strong covalent bond interaction (Co-C bond) with graphene layer, which should be driving force for the preferential growth of nanoarrays on graphene. Co(OH)2 array/GNSs composites exhibit not only high specific capacity, but also outstanding high-rate performance when used as anode material for lithium-ion batteries. At the current density of 50 mAg−1, the reversible capacity is 976 mAhg−1 and remains at 1103 mAhg−1 after 50 cycles without any fading. At 500 and 1000 mAg−1, the reversible capacities can reach 696 and 496 mAhg−1, which are 71 and 51 % of that at 50 mAg−1, respectively. Excellent electrochemical performance should be attributed to the array structure of Co(OH)2 as well as synergistic effect between Co(OH)2 and graphene. Therefore, Co(OH)2 array/GNSs composites are expected to have potential applications in LIBs.

1. Introduction

Cobalt hydroxide, owning unique layered structure as well as excellent electrochemical properties, exhibits great promising application potential in the field of energy storage 1-11. Traditionally, cobalt hydroxide has long been studied as a key active materials to improve the performance of alkaline storage batteries 1,2. In recent years, Co(OH)2, as a class of intriguing electrode materials for supercapacitors, exhibits high activity of Faradic reactions, and high energy and power density 3-5, which has been receiving numerous attention. Very recent reports 6-12 indicate that Co(OH)2 also possesses promisingly high specific capacities when used as anode material in lithium-ion batteries (LIBs). However, the relevant work in the anode area is limited, which may be attributed to an anxiety about “hydrogen” from the hydroxides just as described by the reference 9. In addition, it can be seen obviously that electrochemical performance of Co(OH)2 from these limited reports needs to be improved urgently for their practical application in further.

Design of novel Co(OH)2 nanostructures or composites in favour of Li-ion diffusions and storage is, therefore, in great need. Due to its outstanding properties, graphene has been regarded as a promising matrix for growing other functional materials as well as for enhancing and/or extending their performance 13. Many efforts have also been devoted to explore synthesis of novel graphene-based Co(OH)2 architectures for energy storage 9, 11, 14-16. However, most of Co(OH)2/graphene composites are used as electrode materials for supercapacitors 14-16. These strategies, aiming toward design of high-performance supercapacitors based on fast surface Faradic reactions, may be not suitable to be employed in advanced anode materials for LIBs storing/releasing energy by repeated solid-state diffusion of Li-ion. In these pioneering work for supercapacitors, it would like to design Co(OH)2 to a two-dimensional structure with the length of several micrometer and the nanoscale thickness offering a high surface area and favourable contacting interface with electrolyte, which may be easy to collapse or even peel from current collector during the repeated intercalation/deintercalation of Li-ion. Up to now, there are only two reports on Co(OH)2/graphene composite anode materials for LIBs. 9, 11 The electrochemical performance of the composites has been enhanced largely compared with that of pure Co(OH)2, but there is still a long way to go for their application in future. Therefore, it is still a challenge work for the construction of Co(OH)2/graphene for high-performance anode materials.

It is also an interesting topic to combine both layered materials, graphene and Co(OH)2, into well-designed nanostructures. From the perspective of spatial geometry, growth orientation of layers of Co(OH)2 versus basal plane of GNSs can be divided mainly into two ones. One orientation is that Co(OH)2 layers can be parallel to graphene layers. The other one is that Co(OH)2 layers...
can be vertical to graphene layers, as shown by Scheme 1. Controlling growth orientations should lead to the construction of various novel nanostructures. Parallel growth of Co(OH)₂ layers on graphene will form sheet-on-sheet graphene/Co(OH)₂ composites, while, more interesting, vertical growth should construct into Co(OH)₂ nanosheet/plate arrays on graphene. In previous reports, it is suggested that one- or two-dimensional nanotransition metal oxide active materials can be assembled into nanoarrays on substrates to improve their electrochemical performance by enhancing kinetics of Li-diffusion, facilitating the electron conductivity by substrate, and efficiently buffering the volume changes by the nanospace between the arrays. In this regard, it is favourable to enhancing the electrochemical performance of Co(OH)₂ by preparation of Co(OH)₂ nanosheet/plate arrays on graphene. At present, there still has been a plenty of synthesis studies on Co(OH)₂/graphene composites, most of Co(OH)₂ nanocrystals are only simply dispersed on the graphene and there are very few reports on the preparation of Co(OH)₂ arrays on graphene nanosheets. Moreover, there is no report on the design of the nanostructures of Co(OH)₂ array based on growth of preferential orientation of hydroxide layers on graphene, especially preferentially vertical orientation of hydroxide layers versus graphene basal plane. There is also no investigation on the key factors affecting the orientation of Co(OH)₂ on graphene.

In this work, we construct hexagonal cobalt hydroxide arrays on graphene nanosheets substrate (Co(OH)₂/GNSs) with vertical orientation of hydroxide layers relative to graphene basal plane by a facile method. The processes involved in the formation of Co(OH)₂ array/GNSs are schematically demonstrated in Scheme 1. First, the mixture, where Co(NO₃)₂ is dispersed homogeneously on GNSs with less functional groups, is obtained. Then, the Co(NO₃)₂ adsorbed on the graphene nanosheets (GNSs) is reacted in situ with KOH solution to form Co(OH)₂ arrays with small size of plate. And it was found that the (001) crystal plane of Co(OH)₂ is vertical to graphene basal plane and strong interfacial interaction exists between GNSs and Co(OH)₂. The key factors affecting on the preferentially orientated growth are also explored. And the nanoarray with interesting structures exhibits superior Li-battery performance when it is used as anode materials for LIBs.

\[\text{Scheme 1. Schematic illustration of preferentially orientated growth of Co(OH)₂}}\]

2. Experimental Section

**Preparation of Graphene Nanosheets:** The graphene nanosheets (GNSs) were fabricated from natural graphite by the Staudenmaier’s method according to our previous work. For comparison, the GNSs were oxidized by HNO₃ (16 mol/L) at 80 °C for 6 h. And plenty of functional groups were formed at the surface of GNSs. The original and HNO₃-oxidizing GNSs were used to prepare graphene/ cobalt hydroxide nanosheets in the subsequent experimental procedure.

**Fabrication of Co(OH)₂/graphene composites and pure Co(OH)₂:** A facile approach was employed to synthesize hexagonal cobalt hydroxide/graphene composites (Co(OH)₂ array/GNSs) at room temperature. Typically, the GNSs (20 mg) and Co(NO₃)₂·6H₂O (126.4 mg) were well dispersed in ethanol with the help of ultrasonicator KQ-700DE at 700 W. After removing ethanol at 80 °C under vigorous stirring, the Co(NO₃)₂/GNSs composites were obtained. The composites were added to KOH aqueous solution (30 wt%) slowly. After stirring for 10 min, the mixture was transferred into 50 ml funnel, then filtered and washed with deionized water until the pH value was 7. After drying, Co(OH)₂ array/GNSs composite was obtained. For comparison, pure Co(OH)₂ without GNSs and Co(OH)₂/graphene composites with HNO₃-oxidizing GNSs were also prepared using the same procedure described above.

**Characterization:** The morphologies and structures of the obtained products were investigated by scanning electron microscope (SEM, ZEISS SUPRA 55), transmission electron microscope (TEM, Hitachi H-800) and high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010).

**Characterization:**

- **X-ray diffraction (XRD) measurements** were performed with a Rigaku D/Max-2500B/PCX system using Cu Ka radiation (λ= 1.5406 Å) over the range of 5–90° (2θ) at room temperature. The Raman spectra were recorded from 1000 to 2000 cm⁻¹ at room temperature using a HR 800 Raman spectrometer (produced by HORIBA Jobin Yvon company) with an excitation line of 532 nm and using an Olympus microscope and a 50×microscopy objective to focus the laser beam onto a spot of 1 µm².

- **Thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements** were conducted on a NETZSCH STA449C simultaneous thermal instrument. The samples were heated from room temperature to 1000 °C at 5 °C/min under flowing air.

- **X-ray photoelectron energy spectrum (XPS) analysis** was carried on using monochromatic AlK (1486.6 eV) X-ray sources with 30 eV pass energy in 0.5 eV step over area of 650 mm². The all curve fittings were carried out by using Gaussian-Lorentzian (20%) peak shape after a Shirley background correlation.

**Electrochemical measurements:** The electrochemical experiments of the samples were carried out using 2032-type coin cells. The working electrodes were prepared by mixing active material, acetylene black, and poly (vinylidifluoride) (PVDF) at a weight ratio of 8:1:1 and pasting the mixture onto foam nickel. And counter electrode was lithium sheet. Electrolyte was 1M...
LiPF₆ solution in ethylene carbonate/dimethyl carbonate EC-DMC (1:1 v/v). The coin cells were assembled in argon-filled glove box with both moisture and oxygen content below 1 ppm.

Galvanostatic charge–discharge cycling tests were carried out on LAND CT2001A multi-channel battery testing system at various current densities in the voltage range from 0.01 to 3 V at room temperature.

The cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were carried out on a ZAHNER ENNIUM electrochemical working station. For the cyclic voltammetric measurements, the sweep rate was 0.1 mV s⁻¹ and potential range was from 0.01 V to 3 V. For the EIS measurements, the frequency range was from 0.01 Hz to 100 kHz and the amplitude was 5 mV.

3. Results and Discussion

Figure 1. SEM images of (a) GNSs and (b) Co(OH)₂ array/GNSs, (c, d) magnifying SEM images in selected area of red and blue boxes of image (b), (e) HRTEM image of a composite-nanosheet of Co(OH)₂ array/GNSs, and (f) HRTEM and (g) clear lattice fringe images of a Co(OH)₂ nanosheet standing on the GNSs in the selected area of yellow box of image (e).

Figure 1 exhibits the morphology and structure of original GNSs and as-prepared Co(OH)₂ array/GNSs composite nanoplates. Two-dimensional GNSs with wave-like structure are almost transparent under the electron beam (Fig. 1a). Fig. 1b shows a typical SEM image of Co(OH)₂ array/GNSs composite nanoplates. The Co(OH)₂ nanoplates possess average width of about 130 nm and average thickness of about 20 nm (Fig. 1c).

From the tilted nanoplates as shown in the red circles of Fig. 1d, it can be seen that Co(OH)₂ owns very interesting hexagonal structures. Notably, most of these hexagonal nanoplates stand vertically rather than lie flat on the surface of graphene sheets. In addition, the weight content of Co(OH)₂ in the composite of Co(OH)₂ array/GNSs is approximately 70 wt% calculated from the weight loss in TG measurement (ESI, Fig. S1). Here, it needs to be emphasized that the length of Co(OH)₂ nanosheet/wire is around several micrometers or even beyond 10 μm in previous reports. In contrast, the length of Co(OH)₂ nanoplate in this work is much shorter, which will benefit the diffusion of Li-ion and also shorten the length of electronic transfer from active materials to conductive substrate.

HRTEM image of Co(OH)₂ array/GNSs composite nanoplates (Fig. 1e) confirms in further the Co(OH)₂ nanoplates are vertical to basal plane of GNSs. Therefore, it is very easy to investigate the nanoplate from the side. Interestingly, the side-view HRTEM images (Fig. 1e-g) confirm the well-crystalline lamellar structure of the nanoplate with an interplanar spacing of 4.6 Å, which is in accordance with the (001) crystal plane of Co(OH)₂, indicating that the (001) plane composed of a Co layer sandwiched by two OH layers is vertical to graphene basal plane, as shown by Scheme 1d. There is few report on the preparation of Co(OH)₂ arrays on graphene nanosheets, but the case, layer-vertical-to-layer just like shown here, is never observed directly.

Figure 2. XRD patterns of (a) Co(OH)₂ and (b) Co(OH)₂ array/GNSs.

For comparison, Co(OH)₂ without GNSs is also prepared. Fig. 2a shows the XRD pattern of pure Co(OH)₂, in which all of the diffraction peaks are very sharp and indexed well with pure Co(OH)₂. However, no impurity phases are found, indicating high crystalline degree and high phase purity of Co(OH)₂. Compared with Co(OH)₂, Co(OH)₂ array/GNSs shows a broad C(002) diffraction peak at 25° (Fig. 2b), corresponding to the relative short-range order in stacked graphene sheets.

Similarly, both
Co(OH)$_2$ nanosheets represent the typical character of a hexagonal phase P-3m1(164), that is brucite-like $\beta$-Co(OH)$_2$ phase. Additionally, SEM image (Fig. 3a) shows that pure Co(OH)$_2$ also presents hexagonal plate-like structure, and length and thickness of pure Co(OH)$_2$ are similar with those of nanosheets in Co(OH)$_2$ array/GNSs. The difference is that all of pure Co(OH)$_2$ nanosheet lay flat on the membrane of copper mesh in the vision of TEM measurement, and no standing nanoplate is observed, which is similar to that in previous reports. It can be deduced that GNSs play an important role in the preferentially oriented growth of Co(OH)$_2$ in the hybrids.

It is interesting to consider what controls the preferentially oriented growth of Co(OH)$_2$ nanosheets on the GNSs. In previous reports, graphene oxide (GO) with plenty of oxygen-containing functional groups was usually used as matrix to prepare the graphene-based cobalt hydroxide composites. In these composites used GO as matrix, Co(OH)$_2$:GNSs nanosheets/plates generally lay flat on GNSs. Dai et al. suggested that oxidation degree of graphene could affect the morphology of metal hydroxide nanocrystals. Compared this work with previous reports, it can be deduced that orientation of Co(OH)$_2$ versus GNSs should also be related to the functional groups. To confirm the influence of surface nature on growth of Co(OH)$_2$ nanoplate in further, GNSs after oxidization by HNO$_3$ (GNSs-HNO$_3$), was also used to prepare graphene-based Co(OH)$_2$ composites (Co(OH)$_2$:GNSs-HNO$_3$). Surprisingly, it can be found that all of hexagonal Co(OH)$_2$ lay flat on rather than stand on the GNSs (ESI, Fig. S2 and S3). Our results imply obviously that surface nature of GNSs will control the preferentially orientation growth of Co(OH)$_2$ nanosheets on the GNSs due to that surface nature affect the interfacial reaction and interaction between metal hydroxide and graphene.

To clarify the interfacial nature between GNS and standing Co(OH)$_2$ nanosheets, Raman measurements were carried out (Figure 4). It indicates the existence of obvious interfacial interaction between GNSs and Co(OH)$_2$. The intensity ratio of D band to G band ($I_D/I_G$) is used to reflect the degree of graphite layers. The value of $I_D/I_G$ (ESI, Table S1) for GNSs is ca. 0.96, while that of composite increases to ca. 1.04, indicating that the Co(OH)$_2$ on GNSs leads to the increased degree of graphene layers which should be attributed to the destruction of continuity of $\pi$ network of graphene by the interfacial interaction between Co(OH)$_2$ and GNSs.

More valuable information for interfacial nature can be obtained by X-ray photoelectron spectroscopy (XPS) measurement just as shown by our previous work. Overall XPS spectra in Fig 5(a) show that GNSs are composed of both C and O elements, while Co(OH)$_2$:GNSs composites are composed of C, O and Co elements. The C1s spectra of GNSs can be decomposed into the dominant peak at 284.6 eV to C=C-C, and other three peaks of oxygen-containing functional groups at 286.1 eV to C-O, 287.3 eV to C=O, and 289.5 eV to O-C=O, respectively. Besides four peaks of C=C-C and oxygen-containing peaks, a new peak in C1s spectrum of Co(OH)$_2$:GNSs is presented at 283.1 eV, which should be attributed to Co-C bond according to previous reports. Correspondingly, a peak at 778.6 eV, ascribed to Co-C bond, can also be observed in the spectrum of Co(OH)$_2$:GNSs-HNO$_3$. Figure 5(d), the O1s spectra were fitted to two peaks. The peak at 533.2 eV refers to C=O bond, and the other peak in the spectrum of GNSs at 531.2 eV should be attributed to C=O:O=C. Compared with that in GNSs, the intensity of peak at 531.2 eV in the composites increases largely. Generally, the peak of O1s in Co(OH)$_2$ is present at ca. 531.2 eV. However, in addition, O1s peak in the C-O-Metal bond is located at ca. 531-533 eV in previous reports. It can be deduced that orientation of Co(OH)$_2$ versus GNSs should also be related to the functional groups. To confirm the influence of surface nature on growth of Co(OH)$_2$ nanoplate in further, GNSs after oxidization by HNO$_3$ (GNSs-HNO$_3$), was also used to prepare graphene-based Co(OH)$_2$ composites (Co(OH)$_2$:GNSs-HNO$_3$). Surprisingly, it can be found that all of hexagonal Co(OH)$_2$ lay flat on rather than stand on the GNSs (ESI, Fig. S2 and S3). Our results imply obviously that surface nature of GNSs will control the preferentially orientation growth of Co(OH)$_2$ nanosheets on the GNSs due to that surface nature affect the interfacial reaction and interaction between metal hydroxide and graphene.

The Co(OH)$_2$:GNSs-HNO$_3$ composites exhibit absolutely different interfacial nature by comparing their XPS spectra with those of the Co(OH)$_2$:GNSs (ESI, Fig. S4). In the C1s spectrum of Co(OH)$_2$:GNSs-HNO$_3$ (ESI, Fig. S4b), no peak of Co-C bonds at 283.1 eV is presented except four peaks of C=C-C and oxygen-containing peaks. Likewise, the peak at 778.6 eV, corresponding to Co-C bonding, is also not observed. In the Co(OH)$_2$:GNSs-HNO$_3$ (ESI, Fig. S4c), compared with O1s spectrum of Co(OH)$_2$:GNSs (ESI, Fig. S4d), it can be found, besides C-O peak at 533.2 eV and the peak at 531.2 eV from C=O and Co(OH)$_2$, that a new peak at 531.9 eV is presented in the O1s spectrum of Co(OH)$_2$:GNSs-HNO$_3$, which...
should be attributed to C-O-Co binding according to previous reports.24-28

Based on the XPS results above, interfacial interaction of Co-C covalent bond exists in the Co(OH)2 array/GNSs, while C-O-C bonding connection is the Co(OH)2/GNSs-HNO3. The C-O-Co binding formation should be attributed to the reaction between basic hydroxyl planes of the brucite plates and plenty of –COOH acidic groups in GO, according to very recent reports.15, 29

Considering that the layer-structure of Co(OH)2 is a Co layer sandwiched by two OH layers, Co(OH)2 nanosheets/plates are, therefore, more apt to grow flatly along the basic plane of GNSs in the previous work based on GO as matrix14-16 as well as GNSs oxidized by HNO3 in this work (ESI, Fig. S2 and S3). In contrast, Co-C binding formation in Co(OH)2 array/GNSs indicates that GNSs can connect preferentially with end face of Co(OH)2 nanosheets. Banhart et al. have revealed that metal atoms can be bonded with graphene, especially with the defect.30 Simultaneously, if considering the sandwiched Co layer structure of Co(OH)2, it is easy to understand that Co-C bond can be formed by bonding between bare Co atoms at the end face of Co(OH)2 and defects of GNSs. Model of interaction can be schematically demonstrated in Scheme 1e. Co(OH)2 nanosheets/plates are, therefore, more apt to grow vertically on the basic plane of GNSs. Here, the interfacial interaction of Co-C bond between GNSs and Co(OH)2 as well as nanoarray-like construction will be helpful to the improvement of electrochemical performance of Co(OH)2 as anode materials for LIBs.

Figure 6. (a) Cyclic voltammograms of the Co(OH)2 array/GNSs at scan rate of 0.1 mV s−1, (b) the initial discharge-charge curve of Co(OH)2 and Co(OH)2 array/GNSs at 50 mAg−1, (c) the rate-performance of Co(OH)2 and Co(OH)2 array/GNSs at various current densities, and (b) the cyclic performance of Co(OH)2 array/GNSs at various current densities.

The electrochemical activity of Co(OH)2 array/GNSs as anode materials is measured by cyclic voltammograms (CV) at room temperature (Fig. 6a). In the first cycle, a large cathodic current peak appears centred at ca. 1.0 V and followed by two weak anodic peaks centred at ca. 1.14 and 1.64 V, respectively, and a strong one at ca. 2.06 V. The cathodic peak at ca. 1.0 V should be attributed to the reduction to Co3+ of Co(OH)2 to Co2+ as well as the formation of solid electrolyte (SEI) films, while the three anodic peaks are ascribed to the multistep reactions of oxidation of Co2+ to Co3+ according to previous reports.9,22 Compared with the 1st cycle, a new cathodic peak appears at 1.28V and a new anodic peak appears at 1.33 V. At the same time, anodic peak at 1.14 and 1.64 V disappears in the second cycle. And the both anodic and cathodic peaks of third cycle are consistent with those of second cycle, indicating that stable reversible electrochemical reaction has been set up. We note that the CV curves for the second and third cycles in this work are obviously different from those of Co(OH)2 with large area in the previous work,11 where both anodic and cathodic peaks of the second and third cycles are nearly consistent with those of the first cycle, indicating the different mechanism of lithium storage. This may be attributed to the size of active materials just as shown in the work of Tarascon et al.,31 which suggested that Li-ion storage mechanism of bulk iron oxide is different from that of nanoscale iron oxide. However, the exact reason for the difference is unclear due to limited report for Li-storage in Co(OH)2.9,12 so investigation in detail is needed in the following work.

In further, we evaluated the cyclic stability and rate-performance of Co(OH)2 and Co(OH)2 array/GNSs by charge-discharge measurements. Fig. 6b shows the first discharge/charge voltage profiles of Co(OH)2 array/GNSs and pure Co(OH)2 at current density of 50 mAg−1. Their discharge/charge curves are very alike, where one long discharge plateau from 1.2 to 0.8 V, and three obvious charge plateaus (1.0-1.5 V, 1.5-2.0 V and 2.0-2.5 V) are clearly observed, which are consistent with the CV measurements. For pure Co(OH)2, the initial discharge (Li-insertion) and charge (Li-desertion) capacities are 1787 and 1120 mAhg−1, respectively. Rate-performance of pure Co(OH)2 nanoplates is also exhibited in Fig. 6c. The delivered capacities of Co(OH)2 nanoplates at 100, 500, and 1000 mAg−1 are ca. 788, 321, and 124 mAhg−1, respectively. After the current density returns to 50 mAg−1, the specific capacity can recover to ca. 743 mAhg−1 and keep at 697 mAhg−1 after 60 cycles, which is ca. 62 % of the first reversible capacity. Compared with previous reports,9,12 it can be concluded that specific capacity and rate-performance of Co(OH)2 plates with nanoscale length are also better than that of large area Co(OH)2 sheets. For example, the work by He et al.9 showed that the reversible capacity of Co(OH)2 sheets with discal size of ca. 0.65 μm diameter was ca. 660 mAhg−1 and no corresponding rate-performance was measured. At Huang’s paper10, reversible capacity of pure Co(OH)2 sheets with size of ca. 1-3 μm was 912 mAhg−1 at first cycle and 63 mAhg−1 after 50 cycles at 58 mAg−1, and decreased to ca. 30 mAhg−1 at 1160 mAg−1. These results indicate that the plates with nanoscale diameter possess higher electrochemical activity and are more in favour of diffusion of Li-ion.

Compared with the electrochemical performance of pure Co(OH)2 sheets, Co(OH)2 array/GNSs composites exhibit not only high cyclic stability, but also better high-rate performance. At 50 mAg−1, the first charge and discharge capacities are 1654 and 977 mAhg−1, respectively. At higher current densities of 100, 500, and 1000 mAg−1, the reversible capacities can reach up to 925, 696 and 496 mAhg−1, which maintain about 95, 71 and 51 % of capacities at 50 mAg−1, respectively. After the current density returns to 50 mAg−1, the reversible capacity can be still up to ca. 980 mAhg−1, and there is no any capacity fade after 65 cycles. It can also be calculated that the capacity contributed by Co(OH)2 is ca.1237 mAhg−1 by capacities of composite (980 mAhg−1) and GNSs (381 mAhg−1 after 50 cycles, see the ESI, Fig. S5), and
weight content of Co(OH)₂, indicating that GNSs can be beneficial for large improvement of electrochemical activity of Co(OH)₂.

Moreover, Fig. 6d reveals the cyclic performance of Co(OH)₂ array/GNSs at various current densities using three new cells. At 50 mAg⁻¹, there is still no capacity fade, indicating better repeatability of Co(OH)₂ array/GNSs. When the cell is discharged/charged directly at a higher current density of 500 mAh⁻¹, the first reversible capacity still reach to 734 mAh⁻¹, and reversible capacity keeps at ca. 508 mAh⁻¹ after 100 cycles, which is ca. 69 % of the first reversible capacity. At 1 Ag⁻¹, the first reversible capacity still reach to 615 mAh⁻¹, and reversible capacity keeps at ca. 321 mAh⁻¹ after 50 cycles, which is ca. 52 % of the first reversible capacity. It can be seen that both the specific capacity and cyclic stability of Co(OH)₂array/GNSs at high rate are also superior to the reported values of Co(OH)₂ nanosheets as well as graphene-based Co(OH)₂ hybrids. 9-12 And the electrochemical performance Co(OH)₂array/GNSs is even comparable with those of graphene-based cobalt oxide anode materials. 32

Figure 7. EIS spectra of Co(OH)₂ and Co(OH)₂array/GNSs after 50 cycles at current density of 50 mAg⁻¹ and equivalent circuit for EIS simulation (inset in the Figure).

Measurements of Electrochemical impedance spectroscopy (EIS) reveal the kinetic information of Li-ion storage in pure Co(OH)₂ sheets and Co(OH)₂ array/GNSs composites (Fig. 7). EIS is constituted of two semicircles in the high frequency region and an inclined line at low frequency. Generally, the radius of the semicircle represents contact and charge-transfer impedances and the slope of the line reflects Warburg resistance, which reveals the diffusion of redox species in the electrolyte. The elements in the equivalent circuit include the ionic resistance of electrolyte (Rₑ), the intrinsic resistance of SEI-solid electrolyte interface (Rₛ) and charge-transfer resistance (Rₜ) between the electrode and electrolyte. According to the simulation by equivalent circuit (inset in Fig. 7), the value of Rₛ of Co(OH)₂array/GNSs and Co(OH)₂ is 7.8 and 9.2Ω, while their Rₜ values are 11.7 and 35.8 Ω, respectively. Rₑ value of Co(OH)₂array/GNSs is much lower than that of Co(OH)₂, indicating that GNSs addition and the interfacial interaction between GNSs and Co(OH)₂ improve largely the conductivity of Co(OH)₂. In addition, the hexagonal structure of Co(OH)₂ as well as the special conjugation between Co(OH)₂ and GNSs should also help to improve the electrochemical stability of composite.

Conclusions

In present work, we prepared graphene-based Co(OH)₂ composite nanosheets by a facile in-situ reaction between Co(NO₃)₂ on GNSs and KOH. The composites own very interesting structure that the hexagonal Co(OH)₂ nanoplates stand on graphene basal plane rather than lay flat on graphene, and (001) crystal planes of Co(OH)₂ nanoplates are preferentially vertical orientation versus graphene basal plane and interact with graphene by Co-C covalent bonds. The Co(OH)₂array/GNSs composite exhibits high specific capacitance and better rate-performance. We attribute promising electrochemical performance to the particular structure of Co(OH)₂ as well as synergistic effect between Co(OH)₂ and graphene. Therefore, Co(OH)₂array/GNSs are expected to have potential applications in LIB.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures; TG and DSC curves of the Co(OH)₂array/GNSs composites, FTIR spectra of original GNSs and GNSs oxidized by HNO₃, SEM image schematic illustration of hexagonal Co(OH)₂ nanoplates on HNO₃-oxidizing GNSs, data for Raman spectra and C1s XPS spectra, and cyclic performance of GNSs as anode materials. See DOI: 10.1039/b000000x/