Graphene-assisted synthesis of three-dimensional Ni/Co hydroxide nanowire network with enhanced electrochemical capacitive performance

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Abstract

Three-dimensional (3D) electrodes, which are composed of thin inorganic pseudocapacitive nanowire networks, show high electrochemical capacities and excellent cyclic performance because of their high surface area, convenient ion/electron transport and mechanical stability. Herein, we reported the hydrothermal preparation of a 3D ultra-thin Ni/Co basic carbonate nanowire network with the aid of a small amount of graphene oxide (GO) (6 wt%) as both the binder and the conductive filler. Through using an electrochemical cyclic process, the Ni/Co basic carbonate nanowires were subsequently *in-situ* converted to Ni/Co hydroxide nanowires with high electrochemical capacitance. The specific capacitance of the Ni/Co hydroxide nanowire/rGO hybrid networks achieved 1434 F g^{-1} at 0.5 A g^{-1} . Furthermore, the specific capacitance of the sample has no loss during the 5000 charge/discharge cycles. This Ni/Co hydroxide nanowire/rGO composite can be used to prepare asymmetric supercapacitors with high performance.

Keywords: Ni/Co hydroxide nanowire; three-dimensional electrode; conversion process; supercapacitors; graphene.

1. Introduction

The increase of energy requirements and the environmental pollutions has largely accelerated the development of clean energy conversion and storage.[1,2] Among different energy storage devices, supercapacitor exhibits various advantages in practical applications, such as high power density, long life-time, safety, low price, et al, thus was considered as a promising candidate for energy supplying of portable electronic devices.[3,4] However, the electrodes of commercialized supercapacitors were prepared by mixing electrochemical active materials and carbonous conductive fillers (carbon black, carbon nanotube (CNT), graphene, et al) together with polymer binder. This structure cannot achieve uniform dispersion of conductive fillers in the active materials or form abundant channels for electrolyte ion diffusion into the electrode. Furthermore, the introducing of polymer binder decreased the internal conductivity of the electrodes. These characteristics largely limited the practical electrochemical performance of the electrodes. An ideal three-dimensional electrode structure should have high loading-mass of active materials, large specific area, well-distributed conductive network and open-porous structures for the effective electrolyte diffusion in the electrode. Recently, two strategies were usually used to design three-dimensional electrodes for supercapacitors. The one is to grow electrochemical active materials on the surface of nano-sized conductive fillers such as metallic nanostructures and carbon nanomaterials (carbon nanotube (CNT) and reduced graphene oxide (rGO)) [5-8], and the other is to directly grow active materials on three-dimensional conductive scaffolds such as carbon fiber cloth,[9,10] CNT paper/sponge[11] and CVD grown graphene foam with nickel foam as the template.[12,13] However, the two strategies could not solve the problem of three-dimensional electrode designs. The former was limited by the full covering of active

materials onto the conductive nanoparticles, which usually made it necessary for the use of excess conductive fillers to construct the conductive network in the whole electrodes,[14,15] while the latter was limited by the low loading mass of active materials on the scaffolds with low specific areas, which reduced the practical capacitance of the electrodes.

Graphene oxide (GO) nanosheet was usually used to construct three-dimensional nanostructures for electrodes of energy storage devices by a hydrothermal process, which can reduce GO nanosheets to rGO with high conductivity. This process could achieve uniform dispersion of conductive rGO in it to form a conductive network for electrodes. Different kinds of electrochemical active materials have already been embedded into this rGO based nanostructure by hydrothermal method,[16] such as Fe_2O_3 , [17] MoS_2 , [18] Co_3O_4 , [19] $\text{Ni}(\text{OH})_2$, [20] SnO_2 , [21] and TiO_2 . [22] However, most of these inorganic nanostructures loaded on graphene networks were nanospheres, nanoparticles and nanosheets. These morphologies could not achieve both keeping open channels for electrolyte diffusion and large mass loading. A one-dimensional inorganic nanostructure with ultra-thin diameter can form a 3D stable network.[23] Although some nanowires could form hydrogel by dispersion in aqueous solution and subsequently hydrothermal treatment,[24,25] even one-step process including growth and hydrogel assembly in hydrothermal environment,[26] it's still a challenge to assembling electrochemical capacitive nanowires to hydrogel with high performance for the electrodes of electrochemical energy storage devices, such as supercapacitor.

Transition metallic hydroxides with nickel and cobalt showed ultra-high specific capacitance.[27,28] However, it was difficult to prepare Ni/Co hydroxide nanowires for the special layered crystal structures of these hydroxides.[29] Ni/Co basic carbonates

prepared with the assistance of urea usually showed nanowire morphologies.[30] In this research, a three-dimensional ultra-thin Ni/Co basic carbonate nanowire/rGO network was synthesized by using a low content (6 wt%) of graphene oxide (GO) as both the binder and the conductive filler in a hydrothermal process. The basic carbonate nanowires in this network were subsequently *in-situ* converted to relative hydroxide nanowires with high capacitance in an electrochemical cyclic process. This as-converted hybrid network exhibits superior electrochemical capacitance with excellent rate performance. This result provides a new way to obtain Ni-Co hydroxide nanowires with high electrochemical performance, which could be a promising candidate for the design of 3D electrode for supercapacitors.

2. Experimental section

2.1. Materials

Single-layered GO was purchased from Tianjing Plannano Technology Co., Ltd, P. R. China. Carboxylated CNT was purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. All of other chemical reagents were analytical reagents and purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis

The 3D hybrid network was prepared by on-step hydrothermal process. Typically, 30 mg GO powder or CNT powder was dispersed into 20 ml water by ultrasonic treatment for 30 min. 0.39615 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.7931 g CoCl_2 and 0.62 g urea were subsequently dissolved into the carbon nanomaterial dispersion. The mixed solution was removed into a polytetrafluorethylene (Teflon)-lined autoclave (volume 24 ml). After hydrothermal treatment at 120 °C for 12 h, the autoclave was naturally cooled to room temperature; the obtained carbon nanomaterial/metallic basic carbonate hybrid hydrogel was taken out and

freezing dried. As a comparison, the mixed solution without carbon nanomaterials was also treated in the same hydrothermal environment.

2.3. Characterization and tests

The morphology and microstructure of the samples were systematically investigated by field emission scanning electron microscopy (FE-SEM, Quanta 400 FEG, FEI), high resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 S-Twin, FEI), X-ray diffraction (XRD, D8 Advance Powder X-ray diffractometer, Bruker AXS) and thermo gravimetric analyzer (TGA, TG 209 F1 Libra®, NETZSCH). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 Automatic Physisorption Analyzer (Micromeritics, USA), before measurements, the samples were degassed in a vacuum at 160 °C for at least 5 h. The Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) model were utilized to calculate the BET specific surface areas and the pore size distributions, respectively. Electrochemical experiments were carried out in CHI-660C electrochemical workstation and LANHE CT2001A electrochemical cell test equipment. A three-electrode system was chosen to test the electrochemical performance of the materials. A platinum wire was used as the counter electrode, and a calomel electrode was used as the reference electrode. 6 M KOH aqueous solution was chosen as the electrolyte.

3. Results and discussion

Figure 1 shows the scheme of Ni-Co hydroxide nanowire/rGO hybrid nanostructure preparing process. GO nanosheets in hydrothermal environment were acted as both separating agents and nucleation centers for the growth of Ni-Co basic carbonate nanowires. As a result, the introducing of GO induced the formation of a 3D Ni-Co basic

carbonate nanowire/rGO hybrid network. The inserted images of Figure 2(a) and 2(c) show the optical images of the samples composed of pure Ni/Co basic carbonate and Ni/Co basic carbonate/rGO, respectively. The sample without rGO is pink powder. However, the Ni-Co basic carbonate nanowire/rGO hybrid materials assembled to aerogel-like forms. Similarly, CNTs with the same content can be used to replace GO for the formation of the 3D nanostructures as shown in Figure S1. Both of them with carbon nanomaterials are black even the content of carbon nanomaterials in them are low to 6 wt%. The Ni/Co basic carbonate nanowire grown without carbon nanomaterials exhibits a much large diameter with a sea urchin-like assembling structure as shown in Figure 2(a) and (b). Figure 2(c) and (d) show the rGO/Ni-Co basic carbonate nanowire hybrid structure, which was composed of ultra-thin nanowires. These nanowires form a 3D network structure which is inserted into the rGO network. CNTs can also assist the formation of the thin nanowire network as shown in Figure S1(a) and (b), but the diameters of these nanowires are slightly larger than them formed with rGO. As shown in Figure S2, energy dispersive X-ray spectroscopy (EDX) mapping revealed that Co and Ni are uniformly distributed on these nanowires.

According to the microstructure analysis, the introducing of carbon nanomaterials is a key to the 3D nanostructures of thin Ni-Co basic carbonate nanowires. The carbon nanomaterials in the hydrothermal condition served as nano-sized partition to prevent the formation of large-sized basic carbonate nanowires and their sea urchin-like nanoflowers. Furthermore, the carbon nanomaterials with abundant oxide-contained functional groups on their surface largely reduced the nucleation center for the nanowire growth and induced the growth of thin nanowires. While the solution without carbon nanomaterials

formed large particles of basic carbonate, which served as the crystal nucleus for the growth of large-diameter nanowires and the formation of sea urchin-like nanoflowers.

The crystal structures of the Ni/Co basic carbonate nanowires and their composite with rGO were investigated by XRD pattern analysis. The results are shown in Figure 3(a). The pink powder shows a typical pattern of $\text{Co}_2(\text{OH})_2\text{CO}_3$. The introducing of rGO didn't affect the crystal structure of the mixed metallic basic carbonate. Furthermore, these thin nanowires show higher thermal stability in air after the introducing of rGO as shown in TG curve (Figure 3(b)). The pristine Ni/Co basic carbonate nanoflowers were decomposed at the temperature lower than 200 °C, and only 47% of the total mass was left when the temperature was higher than 600 °C. However, more than 70% of the total mass in the composite with rGO was left. The introducing of rGO may decrease the content of water of crystallization, thus the decomposing temperature of the composite with rGO was improved. BET analysis was used to investigate the specific surface area and porous structure of the samples. The results are shown in Figure 3(c) and (d). The introducing of rGO largely increased the specific surface area from 7.24 $\text{m}^2 \text{g}^{-1}$ of pristine Ni/Co basic carbonate nanoflowers to 54.74 $\text{m}^2 \text{g}^{-1}$ for the 3D nanowire network with rGO (see Figure 3(c)). Furthermore, the nanowire network with rGO shows an open-pore porous structure with most of its pore diameter between 100~500 nm (see Figure 3(d)). This porous structure was beneficial for electrolyte diffusion, thus could effectively improve the mass utilization of the electrochemical active materials in the electrodes. To the electrode for supercapacitors, the electrochemical redox reaction usually happened on the surface of the materials, thus the large specific surface area was valuable for increasing the specific capacitance of the electrodes.

Ni/Co basic carbonate has poor initial capacitance as the electrode of supercapacitors, but it can be converted to hydroxide with high capacitance.[31] As mentioned in our previous research, electrochemical cycles can be used to achieve this conversion in 6 M KOH aqueous electrolyte via both cyclic voltammetry (CV) and charge/discharge cycles.[32] Figure 4(a) shows the CV curves of pristine Ni/Co basic carbonate nanowire/rGO composite and its converted Ni/Co hydroxide nanowire/rGO composite. The as-converted composite exhibited largely enhanced encircling area comparing with pristine Ni/Co basic carbonate/rGO composite, which indicated high capacitance. This conversion process can be exhibited in CV cycles as shown in Figure S3(a), in which the encircling area of the curves continuously enlarged in the first 50 cycles with a scan rate of 5 mV s^{-1} . Although Ni foam as the current collector also has capacitance in alkaline electrolytes, Figure S3(b) reveals that its contribution to the total capacitance of the composite is low even after several electrochemical cycles. TEM analysis reveals that the basic carbonate nanowires with rGO have small diameter (diameter range 10~20 nm) (Figure 4(b)). Furthermore, these nanowires are single crystal which grew along (020) lattice plane. The morphologies of the converted Ni/Co hydroxide nanowires in the composite with rGO are shown in Figure 4(c) and (d). The results show that the conversion process did not change the morphologies of these nanowires. However, the HRTEM image of the nanowire reveals that it is not a single crystal after the conversion reaction (Figure 4(c)). The selected area electron diffraction in the inserted image of Figure 4(d) confirms that the single crystal Ni/Co basic carbonate nanowire has already been converted to multi-crystal Ni/Co hydroxide with the diffraction rings of $\beta\text{-Co(OH)}_2$ (corresponding to the crystal faces of (101), (111) and (112)). The electrochemical

conversion mechanism can be demonstrated as the equations bellow, which has been discussed in our previous reports [31]:

This phase change did not occur by the immersion of Ni/Co hydroxide nanostructure into 6 M KOH aqueous solution without electrochemical process, even the immersing time was more than 72 h. The results are shown in Figure S4(a) and (b).

Figure 5(a) shows the CV curve comparison of the samples with and without carbon nanomaterials in a scan rate of 5 mV s⁻¹. The three samples were all electrochemically converted to hydroxide. The samples with 6wt% carbon nanomaterials show much larger encircling area in CV curve than the pure converted Ni/Co hydroxide nanowire. The CV curves of the three samples all show a pair of visible redox peaks, which should be attributed to the reversible oxidation-reduction reaction of Co²⁺/Co³⁺ and Ni²⁺/Ni³⁺. Here both the samples with rGO and CNT exhibit similar encircling area at the scan rate of 5 mV s⁻¹. The rate performance comparison in Figure 5(b), which was calculated from charge/discharge curves, reveals the difference of the three samples. The converted Ni/Co hydroxide nanowire/rGO composite electrode shows much larger specific capacitance than the pure converted Ni/Co hydroxide nanowire. Its specific capacitances at the current density of 0.5 A g⁻¹ and 10 A g⁻¹ are 1434 F g⁻¹ and 1057 F g⁻¹, respectively, with a good rate performance. While these of the pure converted Ni/Co hydroxide nanowire are 604.8 F g⁻¹ and 264.2 F g⁻¹, respectively, with a large fading of more than 50%. The sample with CNTs shows the highest specific capacitance at 0.5 A g⁻¹ (1747 F g⁻¹), but its rate performance was poor. Its specific capacitance at 20 A g⁻¹ was only 602 F g⁻¹. A comparison of this performance with other literatures can be shown in Table S1 of the

supplementary materials. As shown in Figure S5(a), the energy density of converted Ni/Co hydroxide/carbon nanomaterials composites can show 50-60 Wh kg⁻¹, and still keeps higher than 20 Wh kg⁻¹ when the power density is higher than 5 kW kg⁻¹. As a comparison, the energy density of pure converted Ni/Co hydroxide was only around 5-21 Wh kg⁻¹.

The charge/discharge curves of the converted Ni/Co hydroxide nanowire/rGO composite electrode at different current densities are shown in Figure 5(c). The charge/discharge curve shows highly symmetrical triangle shape at low current densities, close to electrochemical double layer capacitive electrode materials but with a much larger charge/discharge time, which means higher specific capacitance. The shape of the charge/discharge curves keeps stable when increasing the current densities, which brings stable Coulombic efficiency at large current densities. Comparing with the pure converted hydroxide, the converted Ni/Co hydroxide nanowire/rGO (or CNT) composite has a fuller shape close to a rectangle, which means higher specific capacitance and excellent Coulombic efficiency. The superior electrochemical performance of converted Ni/Co hydroxide nanowire/carbon nanomaterial composites to pure converted Ni/Co hydroxide nanowire should be attributed to the increase of specific area and the enhancement of conductivity for the electrode. The diameter of the nanowire without graphene is as large as 200 nm as shown in Figure 2(a) and (b), while the nanowires formed assisted by rGO and CNT have the diameter usually smaller than 50 nm, even only 10 nm (see Figure 2(c), (d) and Figure S1(a), (b)). As a result, the latter electrodes have much larger contact area with electrolyte than the former sample, which is beneficial for increasing the utilizing efficiency of these nanowires as electrochemical active materials in the electrode. Furthermore, the conductivity of the three samples is

clearly compared in Figure 2(b), 2(d) and S1(b). The nanowires without graphene shows a severe charging effect, which usually happened on the surface of insulating samples for SEM observation. While the images of the sample with rGO and CNT (Figure 2(d) and S2(b)) are much clear, which indicates that the introducing of carbon nanomaterials largely increases the electric conductivity of the composites, even their content in the composite electrode is low to 6wt%. This characteristic can effectively enhance the electrochemical conversion of basic carbonate to relative hydroxide, and is a key to keep high specific capacitance of the electrode at large current densities. This result indicates that the carbon nanomaterials uniformly dispersed in the 3D network may serve as micro current collectors to enhance the electron transportation and exchange in the electrode. Comparing with CNT, reduced GO nanosheet has large contact area with converted Ni/Co hydroxide nanowire, thus could enhance the conductivity of the nanowire. This characteristic can be exhibited as the high value of specific capacitance at large current densities, in another word, good rate performance. While CNT with one-dimensional nanostructure has small contact with the hydroxide nanowire, although it could also decrease the diameter of basic carbonate nanowires and promote the formation of 3D network.

Figure 5(d) shows the cyclic performance of Ni/Co basic carbonate nanowire/rGO hybrid network and pure Ni/Co basic carbonate nanoflowers at the current density of 2 A g^{-1} . The two curves reveal that the electrochemical performance of Ni/Co basic carbonate nanowire both with and without rGO increased along with the charge/discharge cyclic process. However, the specific capacitance of thin nanowires with rGO largely increases 5 times than the initial value after 5000 cycles, which suggests a phase change during this process. Furthermore, there's no capacitance decrease of specific capacitance during the

5000 cycles of converted Ni/Co hydroxide/rGO composite. While pure Ni/Co basic carbonate nanoflower has a slight increase of specific capacitance after 5000 cycles, which should be attributed to the large diameter of nanowires without effective conductive fillers in it. These thick nanowires may decrease the specific area of the materials and the lack of conductive fillers decrease the conversion efficiency of these basic carbonate nanowires, thus prolong the phase change process. This characteristic makes the converted Ni/Co hydroxide/rGO composite being valuable for the electrode of high-performance supercapacitors.

Electrochemical impedance spectroscopy (EIS) was used to investigate electron and ion transfer properties of the converted Ni/Co hydroxide nanowires with and without rGO. Figure 5(e) shows Nyquist plots of the two samples. A typical Nyquist plot consisted of a semicircle in the high-frequency region and a straight line with a slope around $45\sim90^\circ$ in the low-frequency region. The semicircle is related to Faradaic reactions, which denotes exhibited the charge transfer resistances (R_{ct}) of the electrochemical active materials in the electrodes. The straight line is related to the electrochemical double layer capacitance on the surface of porous electrodes. The transition region between the semicircle and the straight line reflects the Warburg resistance, which roots in the diffusion of electrolyte into the porous electrodes. The sample with rGO shows an idea Nyquist plot with lower R_{ct} and Warburg resistance than it without rGO, which reflects excellent electron conductive performance and electrolyte ion diffusion performance of the 3D network. The Bode plots in Figure 5(f) shows that both of the two samples have a higher phase angle, which indicates the formation of stable electrochemical double layers (EDLs) on the surface of the porous electrodes. The EDLs was beneficial for the adsorption of electrolyte ions on the surface of porous

electrodes and thus accelerated the pseudocapacitive reactions. As a result, the specific capacitances of the two samples are both increased after cyclic measurements. Furthermore, the phase angle of the sample with rGO is 10 ° higher (80 °) than it without rGO (70 °), which means higher specific capacitance.

An asymmetric supercapacitor was assembled based on converted Ni/Co hydroxide nanowire/rGO composite as one electrode and active carbon/15% carbon black as another electrode. The mass ratio of the two electrodes is 1/3 according to the equation:

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \quad \text{---Eq.3}$$

In this equation, m is the mass of one electrode; C is the specific capacitance, and ΔV is the potential window of the electrode. Figure 6(a) shows the structure and morphology of the assembled device. Its potential could be increased to 1.5 V to drive a time meter. There is largely difference in CV curves of the asymmetric supercapacitor between it before cyclic test and after 300 cycles at the current of 500 mA g⁻¹, as shown in Figure 6(b). The latter has much fuller shape and larger encircling area than the former one, which means a large increase of the capacitance in cyclic test process. It also indicates the conversion of the pseudocapacitive electrode from Ni/Co basic carbonate nanowire/rGO composite to Ni/Co hydroxide nanowire/rGO composite in the long-time electrochemical charge/discharge cyclic process. The charge/discharge curves of the supercapacitor at different current densities after 300 cycles test is shown in Figure 6(c). Figure 6(d) shows the rate performance of the supercapacitor calculated from charge/discharge curves. The specific capacitance of the device decreases from 74 F g⁻¹ at 100 mA g⁻¹ to 42 F g⁻¹ at 2000 mA g⁻¹. As shown in Figure S5(b), the as-assembled asymmetric supercapacitor shows an energy density higher than 10 Wh kg⁻¹, and even

high to 23.5 Wh kg^{-1} , different from active carbon based symmetric supercapacitors. The performance of the asymmetric supercapacitor could be further enhanced by modifying the structure of the device and the chemical composing of the electrolyte.

4. Conclusion

In summary, 3D nanostructure based on Ni-Co hydroxide nanowires was constructed by a one-step hydrothermal method and the subsequently electrochemical converting process. A small amount of carbon nanomaterials (6 wt%) plays a key role in the formation of ultra-thin Ni/Co basic carbonate nanowires and their 3D network. The electrochemical charge/discharge process could *in-situ* convert Ni/Co basic carbonate nanowire into continuous multi-crystal Ni/Co hydroxide nanowire with superior electrochemical performance. This 3D Ni/Co hydroxide nanowire/rGO network has no specific capacitance fading during 5000 cycles of charge/discharge at the current density of 2 A g^{-1} . Furthermore, it shows a specific capacitance high to 1434 F g^{-1} at 0.5 A g^{-1} , and keeps it to 1057 F g^{-1} when the current density is increased to 10 A g^{-1} , displays good capacitance retention. The asymmetric supercapacitor based on this composite and active carbon also exhibited high electrochemical performance. The synthesis strategy here we used for the hybrid network will be valuable for the design of 3D nanostructure network electrodes in high-performance energy storage devices.

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Figure 1 The scheme of materials preparing process.

Figure 2 SEM images of pure Ni/Co basic carbonate nanoflowers (a, b) and Ni/Co basic carbonate nanowire/rGO hybrid network (c, d) (inserted images of (a) and (c): corresponding optical images).

Figure 3 XRD patterns (a), TG curves (b), adsorption/desorption isotherm curves (c) and corresponding pore-size distribution (d) of Ni/Co basic carbonate nanowire/rGO hybrid network and pure Ni/Co basic carbonate nanoflowers.

Figure 4 CV curve comparison (5 mV s^{-1}) of Ni/Co basic carbonate nanowire/rGO hybrid network before and after electrochemical conversion (a); HRTEM of pristine Ni/Co basic carbonate nanowire (b) and converted Ni/Co hydroxide nanowire (c, d), inserted image of Fig. 4(d): selected area electron diffraction.

Figure 5 The electrochemical performance: CV curve (at the scan rate of 5 mV s^{-1}) (a) and rate performance (b) comparison of converted Ni/Co hydroxide nanowire/rGO hybrid network, converted Ni/Co hydroxide nanowire/CNT hybrid network and pure converted Ni/Co hydroxide nanoflowers; charge/discharge curves (c) of converted Ni/Co hydroxide nanowire/rGO hybrid network at different scan rates/current densities; comparison of cyclic performance (d), Nyquist plots (e) and Bode plots (f) for Ni/Co hydroxide/rGO composites and pure converted Ni/Co hydroxide.

Figure 6 The electrochemical performance of asymmetric supercapacitor based on converted Ni/Co hydroxide nanowire/rGO and active carbon: structure and optical image of asymmetric supercapacitor (a); CV curve comparison of asymmetric supercapacitor before and after 300 cycles at the scan rate of 5 mV s^{-1} (b); charge/discharge curves at different current densities (c); rate performance (d).