Three-dimensional Ni(OH)$_2$ nanoflakes/graphene/nickel foam electrode with high rate capability for supercapacitor applications

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**Abstract**

Supercapacitor, known as an important energy storage device, is also a critical component for next generation of hydrogen fuel cell vehicles. In this study, we report a novel route for synthesis of three-dimensional Ni(OH)$_2$/graphene/nickel foam electrode by electrochemical depositing Ni(OH)$_2$ nanoflakes on graphene network grown on nickel foam current collector and explore its applications in supercapacitors. The resulting binder-free Ni(OH)$_2$/graphene/nickel foam electrode exhibits excellent supercapacitor performance with a specific capacitance of 2161 F/g at a current density of 3 A/g. Even as the current density reaches up to 60 A/g, it still remains a high capacitance of 1520 F/g, which is much higher than that of Ni(OH)$_2$/nickel foam electrode. The enhanced rate capability performance of Ni(OH)$_2$/graphene/nickel foam electrode is closely related to the presence of highly conductive graphene layer on nickel foam, which can remarkably boost the charge-transfer process at electrolyte-electrode interface. The three-dimensional graphene/nickel foam substrate also significantly improves the electrochemical cycling stability of the electrodeposited Ni(OH)$_2$ film because of the strong adhesion between graphene film and electrodeposited Ni(OH)$_2$ nanoflakes. Results of this study provide an alternative pathway to improve the rate capability and cycling stability of Ni(OH)$_2$ nanostructure electrode and offer a great promise for its applications in supercapacitors.

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**Abbreviations:**
NF, nickel foam; 3D NF, three-dimensional NF; Ni(OH)$_2$/G/NF, Ni(OH)$_2$/graphene/NF; XRD, X-ray diffraction; CVD, chemical vapor deposition; CV, cyclic voltammetry; $R_{ct}$, charge-transfer resistance at the electrode-electrolyte interface; $R_{ct}$, electron charge-transfer resistance; FESEM, field-emission electron microscopy; G, graphene.

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Introduction

The increasing monetary cost and pollution arisen from the nonrenewable fossil fuels have triggered tremendous research efforts for the storage and conversion of renewable energy sources. Electrochemical capacitors, also known as supercapacitors, are considered as promising candidates for energy storage device due to their high specific power and energy densities, fast charge and discharge rates, and long cycle life. As an important energy storage device, supercapacitors can be broadly used in portable electronics, backup power supply, regenerative braking system, laser and energy management system. Besides, supercapacitors are also the critical components in the next generation of all-electrical cars and hybrid vehicles based on fuel cell that use the hydrogen or alcohol as the clean energy media [1]. Traditional metal oxides and hydroxides, including RuO$_2$, NiO, Co$_3$O$_4$, MnO$_2$, Ni(OH)$_2$, and Co(OH)$_2$, are typical supercapacitive materials and possess high specific capacitance because of their reversible redox transition at the electrode surface [2–6]. Among them, Ni(OH)$_2$ is more attractive in view of its low cost and well-defined electrochemical redox activity [7–9]. Although Ni(OH)$_2$-based supercapacitive materials perform well at relatively low discharge rate, they can not fully engaged in the electrochemical reaction at large discharge rate due to the semiconducting or even insulating property of nickel compounds, resulting a very low storage capacity [10]. To address this problem, chemical and structural modification strategies were adopted to fabricate the electrochemically active Ni(OH)$_2$ nanostructures with high specific surface area and electrical conductivity. Recent studies indicate that the discharge performance of nanostructured Ni(OH)$_2$ materials at large current density is significantly improved and high specific capacitance of 700–2000 F/g has been obtained based on different Ni(OH)$_2$ nanostructures (nanoporous, spherical superstructure, sponge-like, etc.) with high specific surface area [11–17]. However, for traditional slurry-derived electrode, the non-uniform distribution of aggregated Ni(OH)$_2$ nanoparticles on current collector prevents the electrolyte ions accessing the active electrode surface, resulting in a relatively slow redox reaction rate and thus a passable rate capability. The use of non-conductive binder and the inferior interface between Ni(OH)$_2$ and current collector would also certainly increase charge-transfer resistance and significantly influence the performance of supercapacitors. To further improve their supercapacitive performance, novel design of the binder-free Ni(OH)$_2$-based electrodes instead of “dead surface” in traditional slurry-derived electrodes is highly desired. Yang et al. reported a high specific capacitance of 3152 F/g at a current density of 4 A/g and a capacitance of 280 F/g at a current density of 16 A/g for loosely packed α-Ni(OH)$_2$ nanoflake structure on three-dimensional nickel foam (3D NF) electrode [18]. Although the high specific capacitance is achieved, Ni(OH)$_2$-based supercapacitor devices still suffer from the cycling stability during the charge-discharge process due to the weak adhesion between the active material and current collector. Moreover, the inferior electrical contact between NF and deposited Ni(OH)$_2$ leads to a worse rate capability due to presence of native oxide layer on NF which is difficult to removed even after etching by HCl solution [19]. Recently, Tang et al. reported a binder-free Ni(OH)$_2$/CNT/NF electrode with improved supercapacitor performance compared to that of Ni(OH)$_2$/NF electrode [20]. Chen et al. reported a 3D porous graphene/Ni(OH)$_2$ hybrid hydrogel nanostructure with high specific capacitance, excellent rate capability and cycling stability, benefiting from the usage of highly conductive 3D graphene network and the hierarchical porosity of hybrid hydrogels [21,22]. All these imply that the good electrical contact and strong interfacial adhesion between active material and current collector are critical for the development of high performance supercapacitor devices. Until now, although there are numerous research works focusing on Ni(OH)$_2$-based supercapacitors, the report for highly conductive 3D Ni(OH)$_2$-based composite electrode with excellent rate capability has rarely been conducted.

3D graphene, an interconnected network structure, possesses the low density (10–20 mg/cm$^3$) and high electrical conductivity (~1.3 × 10$^6$ S/m at 300 K) [23,24]. It can be directly grown on NF by CVD method under reducing atmosphere and high temperature. This special synthesis condition can reduce the native oxide layer on NF before growth of graphene film and leads to a low resistance interfacial contact between graphene film and NF [19,25]. The growth of graphene on NF can protect it from being oxidized again in air and simultaneously afford a good electrical contact for charge-transfer from deposited active material to current collector in supercapacitors. Additionally, the negatively charged functional groups on 3D graphene formed after plasma treatment will help to adsorb the electrolyte anions during the electrochemical deposition and anchor the metal hydroxide on graphene surface [26], and finally enhance the interfacial adhesion between the active material and current collector. Inspired by these considerations, in this study, we report a binder-free Ni(OH)$_2$/graphene/NF (Ni(OH)$_2$/G/NF) electrode by
electrochemically depositing Ni(OH)₂ nanoflakes on 3D graphene network grown on NF and investigate its electrochemical properties. The as-prepared Ni(OH)₂/G/NF electrode shows a high specific capacitance of 2161 F/g at a current density of 3 A/g and still remains a high capacitance of 1520 F/g as current density reaches up to 60 A/g, showing the good rate capability and promising its potential application in supercapacitors.

Experimental details

All chemicals were of analytical grade and directly used as received. NF with a thickness of ~1.6 mm (Changsha Lyrun Co. Ltd., China) was used as the substrate for growth of graphene film and also employed as the current collector of supercapacitor electrode. The whole fabrication process of Ni(OH)₂/G/NF supercapacitor electrode is demonstrated in Fig. 1. Prior to experiment, NF was sequentially cleaned with 2% hydrochloric acid, acetone, and deionized water within an ultrasonic bath followed by drying with flow N² gas. 3D graphene was synthesized via a chemical vapor deposition (CVD) process by using NF as substrate and ethanol as carbon source, as described elsewhere [25]. Briefly, NF was placed into the center of a quartz tube furnace and annealed at 1000 °C for 5 min with a gas flow rate of H₂/Ar (H₂:Ar = 20:100 sccm) under atmosphere pressure, in order to reduce the native oxide layer on the surface of NF [19]. Then ethanol was bubbled into the tube by Ar flow to grow the graphene film. After 10 min of growth, the sample was rapidly cooled down to the room temperature at a cooling rate of 100°C/min under H₂/Ar flow. The deposition of Ni(OH)₂ was performed using a commercialized CHI660D electrochemical workstation (Shanghai Chenhua Instrument Co., China) in a three-electrode cell with a saturated calomel electrode (SCE) as reference electrode, a platinum plate as counter electrode and the as-prepared G/NF substrate as working electrode. The electrolyte was an aqueous solution of 0.1 M Ni(NO₃)₂. The electrochemical deposition experiments were conducted via a potentiostatic mode with a cathodic potential of −0.7 V and total passed charge quantity of 0.25 C. After deposition, the as-prepared Ni(OH)₂/G/NF electrode was thoroughly rinsed with deionized water for several times and dried at 120°C for 2 h. For the purpose of comparison, the Ni(OH)₂/NF electrode was also fabricated via the same electrochemical deposition procedure.

Raman spectra were recorded at ambient temperature on a WITech CRM confocal microscopy Raman system (WITech, Germany) with 532 nm wavelength laser. X-ray diffraction (XRD) was carried out on a Digaku D/max-2400 diffractometer using a Cu Kα radiation source at a wavelength of 0.1541 nm. The surface morphologies and microstructure of as-prepared electrode were examined by a field-emission electron microscopy (FESEM, JSM-6701, JOEL) system. Cyclic voltammetry (CV) and galvanostatic charge/discharge measurement were performed using above mentioned electrochemical workstation with a three-electrode cell containing 1 M KOH aqueous solution. Electrochemical impedance spectroscopy was carried out at 0.27 V (near open circuit potential) in an alternating current frequency ranging from 0.01 to 3 × 10⁴ Hz with an excitation signal of 5 mV.

Results & discussion

Fig. 2(a) and (b) shows the FESEM images of NF after ethanol-CVD process. It can be seen that NF still remains its 3D cross-linked network structure after high temperature treatment. High magnification FESEM image indicates that a thin layer of carbon film with some ripples and wrinkles is uniformly grown on NF surface. Considering its successful applications in fast and non-destructively detecting the structure and property of carbon film, Raman microscopy was also utilized to characterize the as-grown carbon film in our experiment. The typical Raman spectra recorded from the surface of NF, as shown in Fig. 3, clearly demonstrate the two characteristics carbon bonding bands, i.e., the G-band around 1580 cm⁻¹ related to in-plane vibrations and the 2D band around 2700 cm⁻¹ related to inter-valley double resonance Raman scattering. The intensity ratio of I₂D/I_G and shape of 2D band are sensitive to the number of graphene layers and usually are used to distinguish the graphene film from bulk graphite [27]. The increase in the number of graphene layers would lead to the significant decrease of I₂D/I_G ratio and the
asymmetric broadening of 2D band. In this study, the shape of 2D band is almost symmetric and the intensity ratio of $I_{2D}/I_G$ is calculated to be 0.3–1. These indicate that the as-grown carbon film consists of single- to few-layer (less than 5 layers) graphene. The ripples and wrinkles observed on NF surface are mainly related to the different thermal expansion coefficient of nickel and graphene during the cooling down process. In some area, the ripples and wrinkles are observed to propagate over the crystal boundary of NF, which further indicate the continuous growth and high crystallinity of graphene on NF surface.

After deposition of Ni(OH)$_2$, surface morphology of the samples changes greatly. Fig. 4(a) shows the FESEM image of electrodeposited Ni(OH)$_2$ nanostructure on 3D cross-linked G/NF surface. High magnification FESEM image, as shown in Fig. 4(b), demonstrates that Ni(OH)$_2$ nanoflakes are vertically packed on NF, forming a 3D porous surface morphology. The surface morphology of Ni(OH)$_2$/NF, as shown in Fig. 4(c), is similar to that of Ni(OH)$_2$/G/NF electrode because of same deposition procedure and same deposition parameters. XRD measurement was carried out to determine the crystal structure of two as-prepared electrodes. As shown in Fig. 5, besides the diffraction peaks of graphene and nickel foam, both of two XRD patterns show four broad diffraction peaks at $2\theta = 11.35$, 22.74, 34.17 and 59.98, which can be assigned to the (001), (002), (101)/(012) and (110) planes of $\alpha$-Ni(OH)$_2$, respectively. This implies that the crystal structure of Ni(OH)$_2$ nanoflakes on the two electrode is same. The broadening of peaks in XRD pattern is closely related with the small crystallite size of Ni(OH)$_2$, nanoflakes, which is believed to have a high electrochemical activity in literature [28–30].

Fig. 6(a) and (b) shows the CV curves of the as-prepared Ni(OH)$_2$/G/NF and Ni(OH)$_2$/NF electrodes in a potential window of 0–0.5 V at scan rates ranging from 5 to 100 mV/s. As noted, both of two CV curves present a pair of large redox peaks which corresponds to the reversible redox reaction of $\alpha$-Ni(OH)$_2$/-NiOOH generated by the proton intercalation and deintercalation [31]. This clearly demonstrates that the charge storage mechanism of two electrodes is mainly ascribed to the pseudocapacitance resulted from the Faradaic processes of the high specific surface area of 3D porous surface morphology. The anodic and cathodic peaks of two CV curves

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**Fig. 3** – Raman spectra of single-, double- and few-layer graphene films recorded on the 3D NF.

**Fig. 4** – (a) low magnification, (b) high magnification FESEM images of Ni(OH)$_2$ nanoflakes on 3D G/NF and (c) FESEM image of Ni(OH)$_2$ nanoflakes on NF.
show a highly symmetric characteristics, suggesting a high redox reversibility of the electrodeposited Ni(OH)$_2$ nanoflakes. Although the redox transformation is same for both two electrodes, after a careful comparison, it can be found that, for Ni(OH)$_2$/G/NF electrode, the anodic peak of CV curve is relatively sharper, implying a fast charge-transfer process and good redox reversibility, which are believed to be the two critical factors for high performance rechargeable batteries. While for Ni(OH)$_2$/NF electrode, the anodic peak of CV curve have a remarkable diffusion tail, especially for that at scan rate of 100 mV/s, indicating a relatively lower charge-transfer process.

Series of charge/discharge measurements were performed on the two as-prepared electrodes at different current densities via a chronopotentiogram mode. Fig. 7 gives the specific capacitance of two electrodes at different current densities. The two insets are corresponding discharge curves. As demonstrated, both of the Ni(OH)$_2$/G/NF and Ni(OH)$_2$/NF electrodes present a high specific capacitance more than 2000 F/g at current density of 3 A/g. Surprisingly, the specific capacitance Ni(OH)$_2$/G/NF electrode still remains as high as 1520 F/g as current density reaches up to 60 A/g with a visible lower capacitance loss of 29.7%, in contrast to 58.8% capacitance loss of Ni(OH)$_2$/NF electrode at the same current density in this study, 91.1% capacitance loss of Ni(OH)$_2$/NF electrode at current density of 16 A/g [18], and 55.6% capacitance loss of Ni(OH)$_2$/graphite/NF electrode at current density of 60 A/g in previous reports [32]. This clearly indicates that the as-prepared Ni(OH)$_2$/G/NF has a superb rate capability and can provide reliable capacitive performance at different current densities, even at super-high current density. Besides the specific capacitance and rate capability, cycling stability is another critical important requirement for supercapacitor electrode. Fig. 8 shows the cycling characteristics of the two as-prepared electrodes at current density of 3 A/g. It can be seen that after 500 cycles the specific capacitance of Ni(OH)$_2$/G/NF maintains 63% value of the first cycle, in contrast to 84.5% capacitance loss of Ni(OH)$_2$/NF electrode at same

Fig. 5 – XRD pattern of the electrodeposited Ni(OH)$_2$ nanoflakes.

Fig. 6 – CV curves of (a) Ni(OH)$_2$/G/NF electrode and (b) Ni(OH)$_2$/NF electrode at scan rates ranging from 5 to 100 mV/s.

Fig. 7 – Specific capacitance of Ni(OH)$_2$/G/NF electrode and Ni(OH)$_2$/NF electrode at current densities ranging from 1 to 60 A/g. Insets are corresponding discharge curves of two electrodes at different current densities.
measurement conditions in this study, 48% capacitance loss of Ni(OH)$_2$/NF electrode after 300 cycles at current density of 4 A/g [18], and 54% capacitance loss of Ni(OH)$_2$ nanoflake electrode during the first 400 cycles at current density of 5 mA/cm$^2$ (1.6 A/g) in previous reports [33]. These clearly demonstrate that the introduction of graphene film is beneficial to the enhancement of cycling stability of Ni(OH)$_2$/G/NF electrode. Surface morphology of two as-prepared electrodes after 500 cycles is presented in Fig. 9. As demonstrated in Fig. 9(a), the Ni(OH)$_2$/G/NF electrode still keeps its original porous morphology. No exfoliation or accumulation of graphene/Ni(OH)$_2$ film is observed, indicating a good adhesion between graphene and Ni(OH)$_2$ nanoflakes as well as between graphene and NF. The good combination between graphene and NF is possibly related with the formation of sp$^2$−C−Ni bond (Fig. 10(a)) due to the diffusion of carbon into the NF substrate during the growth of graphene [32]. While the good adhesion between graphene and Ni(OH)$_2$ is possibly related with the oxygen-containing functional groups on graphene surface (Fig. 10(b)), which combine with Ni$^{2+}$ or OH$^−$ through the electrostatic and/or chemical bonds and strongly anchor the Ni(OH)$_2$ nanoparticles on its surface. These two aspects enable a stable electrode condition and thus an enhanced cycling stability of the electrode during the charge-discharge process. For comparison, the surface morphology of Ni(OH)$_2$/NF electrode after 500 cycles is also characterized and given in Fig. 9(b). As demonstrated, the original porous morphology (Fig. 4(c)) completely disappears and serious aggregation of Ni(OH)$_2$ nanoparticles, as indicated by arrows in Fig. 9(b), is obviously observed on electrode surface, implying a weak adhesion between NF and Ni(OH)$_2$ nanoflakes, and thus a bad cycling stability of electrode.

The cycling stability of the electrode at large current density, which can more precisely reflect the service performance of supercapacitor, is also investigated in this study. As shown in Fig. 11, after 500 cycles, the Ni(OH)$_2$/G/NF electrode delivers a specific capacitance of 819 F/g at a current density of 60 A/g, demonstrating a capacitance retention of 51%. It should be noted that although the capacitance retention at 60 A/g is not very high, the specific capacitance of Ni(OH)$_2$/G/NF electrode after 500 cycles is almost identical to that of Ni(OH)$_2$/NF electrode at first cycle, and still much higher than those previously reported at same current density or lower current density [12,14,15,18,34–36]. All these demonstrate that the rate capability and cycling stability of Ni(OH)$_2$/G/NF electrode are greatly improved due to the incorporation of graphene between NF and electroactive Ni(OH)$_2$ nanoflake structure.

To further explore the nature of the good rate capability of Ni(OH)$_2$/G/NF electrode, we perform the impedance measurements of the two as-prepared electrodes. As shown in Fig. 12, both two impedance spectra consist of a partial semicircle in the high- and medium-frequency region and a nearly straight line in the low-frequency region. The semicircle in the high-frequency region corresponds to a typical Faradic process and is related with a charge-transfer
resistance at the electrode-electrolyte interface ($R_{\text{ct}}$) due to the conductivity difference between solid electrode (electronic conductivity) and liquid electrolyte phase (ionic conductivity). From the inset of Fig. 12, it can be seen that the $R_{\text{ct}}$ value of Ni(OH)$_2$/G/NF electrode is obviously lower than that of Ni(OH)$_2$/NF. This is closely related to the lower electronic conductivity of the G/NF substrate and good contact between graphene and Ni(OH)$_2$, which enable the faster charge-transfer process from active materials to current collectors via the underlying graphene network, and thus induce the better rate capability of Ni(OH)$_2$/G/NF electrode than that of Ni(OH)$_2$/NF electrode in this study and those electrodes in previous reports [18,32]. The impedance behavior of the two as-prepared electrodes at the medium-frequency region corresponds to the typical redox reaction process and is related with an electron charge-transfer resistance ($R_{\text{ct}}$). The linear straight line in the low-frequency region is the typical characteristics of the Warburg impedance and corresponds to the diffusion of OH$^-$ ions into the pores of the Ni(OH)$_2$ nanoflakes during the redox reactions. The slope of EIS plot of Ni(OH)$_2$/G/NF electrode is stiffer than that of Ni(OH)$_2$/NF, demonstrating the lower diffusion resistance of OH$^-$ ions into Ni(OH)$_2$/G/NF electrode. By and large, the impedance measurements substantiate the lower inherent resistance of Ni(OH)$_2$/G/NF electrode compared with that of Ni(OH)$_2$/NF electrode, which leads to the good rate capability of Ni(OH)$_2$/G/NF electrode in KOH electrolyte. Even with the high specific capacitance and good rate capability, the performance of Ni(OH)$_2$/G/NF electrode still cannot completely reach the requirement of practical application because of the inferior intrinsic cycling stability of Ni(OH)$_2$. Further efforts are still needed to enhance the cycling stability of Ni(OH)$_2$ by constructing the Ni(OH)$_2$-based hybrid materials on G/NF electrode in future.
Conclusions

3D Ni(OH)₂ nanoflakes/G/NF electrode has been successfully prepared by a combination of CVD process and electrochemical deposition method. The as-prepared Ni(OH)₂/G/NF electrode delivers a high capacitance, remarkable rate capability and cycling stability, significantly outperforming those of Ni(OH)₂ nanoflakes/NF electrode. The improved rate capability and cycling stability is closely related to the presence of graphene layer between the Ni(OH)₂ nanoflakes and NF, which greatly boosts the charge-transfer at the electrode-electrolyte interface and simultaneously increases the adhesion between Ni(OH)₂ nanoflakes and current collector. This study provides an alternative pathway to improve the rate capability and cycling stability of Ni(OH)₂-based supercapacitive materials.

REFERENCES


