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Hydrogels that couple nitrogen-enriched graphene with Ni(OH)₂ nanosheets for high-performance asymmetric supercapacitors

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ABSTRACT

Nitrogen-enriched graphene coupled with nickel hydroxide nanosheets $(Ni(OH)_2/NG)$ hydrogel is successfully synthesized through a facile one-pot hydrothermal method. Comprehensive investigations reveal that the nitrogen atoms are successfully inserted into graphene and that the nickel hydroxide nanosheets (-30–50 nm) are anchored on NG homogeneously. With the enhanced electroactivity caused by nitrogen doping and the synergy effect from Ni(OH)₂ nanosheets and NG, the Ni(OH)₂/NG hydrogel electrode displays much better electrochemical properties than two individual electrodes. It features a specific capacitance as high as 896 F g⁻¹ at 0.5 A g⁻¹ and even 504 F g⁻¹ at 12 A g⁻¹ showing a high rate capability (56.3% retention with 24 times higher current density). An asymmetric supercapacitor device on the basic of Ni(OH)₂/NG hydrogel and activated carbon (AC) was assembled and delivered a high energy density of 28.7 W h kg⁻¹ at the power energy density of 0.36 kW kg⁻¹. Such results indicate that the Ni(OH)₂/NG hydrogel could be considered as a promising candidate for electrochemical supercapacitors.

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1. Introduction

In recent years, an increasing need for energy storage and conversion techniques has stimulated intense research on new energy devices [1]. Supercapacitors with the characteristics of a high power density, short charging time, long lifetime, and environmental friendliness have attracted extensive interest [2,3]. The electrode materials for supercapacitors can mainly be classified into three categories, i.e., carbon materials, metal oxides/hydroxides and conducting polymers. Carbon materials for nonfaradaic electric double capacitors store charges based on the reversible adsorption/ desorption of ions, which enables a wide potential window and a high power density but at the cost of a low specific capacitance and energy density [4]. By comparison, metal oxides/hydroxides and conducting polymer materials for pseudocapacitors exhibit a relatively high specific capacitance and energy density but have the disadvantages of a low cycling stability and rate capability [5,6]. To solve these problems, researchers have combined nonfaradaic and faradaic electrode materials to design hybrid supercapacitors [7]. Moreover, such a combination is an effective strategy to obtain a synergistic effect and achieve improved electrochemical performances [8,9].

Currently, numerous transition-metal oxide/hydroxide electrode materials with an active redox performance, such as RuO_2 [10], NiO/Ni(OH)₂ [11,12], MnO₂ [13], and Co₃O₄ [14], have been explored for use in pseudocapacitors. Among them, Ni(OH)₂ is a promising candidate because of its high theoretical capacitance value (2584 F g⁻¹) and low cost [15]. However, in practical applications with Ni(OH)₂, the obtained capacitance is far lower than the theoretical value due to the low conductivity and tendency to aggregate [16]. Recently, it was found that incorporating nickel hydroxide into carbon materials could combine the traits of all the components to obtain an improved overall capacitive performance [17,18]. Among various carbon materials, graphene has become a popular research topic because of its large surface area, excellent electric conductivity, and remarkable chemical stability [19]. To







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date, significant efforts have been made to prepare nickel hydroxide and graphene composite materials [20,21]. For instance, Lee et al. prepared Ni(OH)₂/reduced graphene oxide (rGO) via a nonaqueous method, and this material exhibited an excellent cycle life and rate capability. The enhanced properties are ascribed to the deposition of nickel hydroxide sheets on graphene, which decrease the π - π interactions between the sheets [22]. Due to the comparable atomic size, nitrogen doping should further improve the capacitive performance of graphene [23]. Nitrogen-doped graphene (NG), with the π electronic conjugated structure of graphene and the lone pair electrons of the nitrogen atom, can effectively modify the local electronic structure and alter the electronic properties of graphene [24]. Additionally, the insertion of nitrogen into the honeycomb-like graphene structure can improve the conductivity significantly and offer a support for anchoring welldispersed metal nanoparticles [25]. Additionally, the flexible nitrogen-doped graphene can work as a highly conductive support for generating strong adhesion. Therefore, a high-performance electrode material can be expected by combining nickel hydroxide with nitrogen-doped graphene.

Here, we prepared a hydrogel (Ni(OH)₂/NG) that couples nitrogen-enriched graphene with nickel hydroxide nanosheets by a facile one-pot hydrothermal route. Ethylenediamine acted as both the nitrogen source and the reductant, and thus the nitrogen doping and reducing processes of graphene oxide proceeded simultaneously. Owing to the synergy between nitrogen-doped graphene and nickel hydroxide, the Ni(OH)₂/NG hydrogel exhibits a high specific capacitance (896 F g^{-1} at 0.5 A g^{-1}), high rate capability $(504 \text{ Fg}^{-1} \text{ at } 12 \text{ Ag}^{-1})$ and long-cycle performance (85.9%) remaining after 5000 cycles). Moreover, the asymmetric Ni(OH)₂/ NG//AC supercapacitor device exhibits a high energy density of 28.7 W h kg⁻¹ at 0.36 kW kg⁻¹ and maintains 19.78 W h kg⁻¹ even when the power density is increased to 4.00 kW kg⁻¹, which can illuminate a light emitting diode (LED) by two cascaded devices after being charged. Such excellent results highlight the synergy for maximizing the utilization of nickel hydroxide and NG for energy storage devices.

2. Experimental

2.1. Raw materials

Graphite powder was purchased from Sinopharm Chemical Reagent Co., Ltd. Nickel dichloride hexahydrate (NiCl₂·6H₂O) and ethylenediamine (EDA) were obtained from Aladdin Industrial Corporation. Nickel foam with an areal density of 350 g cm^{-2} and a thickness of 1.0 mm was supplied by Tianjin EVS Chemicals Science and Technology Ltd. All the other reagents were of analytical grade and used as received without any further purification.

2.2. Synthesis of NG and the Ni(OH)₂/NG hydrogel

Graphene oxide (GO) was prepared by the modified Hummers method [26]. The GO dispersion (4 mg mL^{-1}) was obtained by dispersing dry graphene oxide (400 mg) into deionized water (100 mL) under ultrasonic conditions. For the preparation of nitrogen-doped graphene, 34 mL of the GO dispersion and 1 mL of EDA were mixed and sealed in a 50-ml reaction kettle at 180 °C for 12 h. After cooling naturally, the cylindrical-shaped NG hydrogel was immersed into water to remove impurities and then freezedried. Reduced graphene oxide (rGO) was produced without adding EDA following the same processes.

The Ni(OH)₂/NG hydrogel was prepared by the following onestep route. Briefly, 0.69 g NiCl₂· $6H_2O$ was added into 34 mL of the GO suspension and then stirred intensely for 50 min. The pH value was adjusted to 10 by a sodium hydroxide solution, and EDA (1 mL) was dropped into the hybrid solution over 20 min under magnetic stirring. Then, the solution was transferred into a reaction kettle at 180 °C for 12 h. Finally, the cylindrical hydrogel was purified by washing with excessive amounts of deionized water and freeze dried. As a control, pure nickel hydroxide was prepared using the above-described method without GO.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Panalytical X' Pert X-ray diffractometer (Holland). Raman spectra were obtained on a Renishaw in Via Raman microscope with a 532-nm laser beam. The elementary compositions of the samples were analyzed by X-ray photoelectron spectroscopy (XPS) with a Thermo Fisher 250XI spectrometer. The morphologies were determined by field emission scanning electron microscopy (TEM, JEM-2100F, JEOL).

2.4. Electrochemical measurements

The working electrodes were fabricated as follows. The asprepared active material powders, polytetrafluoroethylene and conducting carbon were mixed in a weight ratio of 80:10:10 and ground in a mortar. A small amount of N-methy-2-pyrrolidione was dropped into the hybrid materials to form a uniform paste. A certain quantity of the mixed slurry was used to cover a piece of Ni foam (1.5 cm \times 1.5 cm) and dried at 60 °C for 16 h; nearly 2 mg of electroactive material was loaded on the electrode. Electrochemical tests were performed in a three-electrode cell. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and galvanostatic charge/discharge (GCD) measurements were performed on a CHI660E electrochemical workstation.

To assemble an asymmetric supercapacitor (ASC) device, active materials and active carbon (AC) were deposited onto a piece of Ni foam (1.5 cm \times 1.5 cm) and used as the positive and negative electrodes, respectively. A piece of cellulosic paper as the separator was placed between the positive and negative electrodes. All the tests were conducted in a 6 M KOH solution.

3. Results and discussion

3.1. Microstructure characterization

Fig. 1 illustrates the preparation process of the Ni(OH)₂/NG hydrogel synthesized through a facile one-pot hydrothermal route, during which NiCl₂·6H₂O was used as the nickel source, and EDA served as the reducing and doping agent. To prevent the Ni(OH)₂ nanosheets from spontaneous nucleation and growth in the solution, which may cause the formation of independent Ni(OH)₂ separated with graphene, Ni²⁺ was first anchored with the help of the oxygen-containing functional groups of GO by electrostatic adherence under an ultrasonic treatment. Then, the pH was adjusted to 10, and Ni²⁺ was transformed into nickel hydroxide. After the introduction of EDA, the mixed solution underwent the hydrothermal treatment to generate the Ni(OH)₂/NG hydrogel. During this period, the amino (-NH₂) group in EDA can not only react with the carbonyl or epoxy groups located on the same side of GO as a mechanism of the cyclization-removal reaction but also reacts with hydroxyls by an immediate removal reaction to form hydroxylamine, which leads to a nitrogen-doped structure [27].

The XRD patterns of GO, NG, pure Ni(OH)₂ and Ni(OH)₂/NG are given in Fig. 2a. The characteristic diffraction peak of GO at ~11.4° is attributed to the presence of oxygen-containing groups, suggesting



Fig. 1. Schematic diagram for the formation process of Ni(OH)₂/NG hydrogel.

the successful oxidation of graphene. For NG, the broad peak at ~26.2° corresponds to the (002) reflection of the NG sheet structure, suggesting that during the hydrothermal reduction process, the π -conjugated structure is recovered, and the framework is restacked because of the van der Waals interaction [28]. For the pure nickel hydroxide and Ni(OH)₂/NG, the diffraction peaks at ~ 19.2°, 32.9°, 38.6°, 52.1°, 59.0°, 62.5°, 70.5° and 72.8° can be indexed to the (001), (100), (101), (102), (110), (111), (103) and (201) crystal planes, respectively. The reflections are in good agreement with those of β -Ni(OH)₂ (JCPDS:14-0117) [15]. The peaks of Ni(OH)₂/NG are similar to those of Ni(OH)₂, except that the reflection at approximately 11.4° from GO almost disappeared, implying that the exfoliation of graphene in the Ni(OH)₂/NG composite took place [29]. Moreover, due to the more disordered and homogeneous dispersion of NG in the composite, no peaks at ~26.2° from NG can be found in the diffraction pattern of Ni(OH)₂/ NG [28,30].

Fig. 2b displays the Raman spectra of rGO, NG, and Ni(OH)₂/NG. It can be observed that two typical D and G peaks of rGO are present at 1322 and 1567 cm⁻¹, respectively. The D peak is related to the disorder and the defects caused by the vibrations of sp³ carbon atoms, and the G peak is related to the vibration of sp² carbon atoms [31]. It is noteworthy that the G peaks at 1587 cm⁻¹ for NG and Ni(OH)₂/NG show a slight blueshift compared with rGO, revealing that nitrogen doping was successful [28,32]. The band intensity ratio of I_D/I_G was used to assess the disorder degree of graphene; the I_D/I_G values were 1.26, 1.44, and 1.63 for rGO, NG, and $Ni(OH)_2/NG$, respectively. The significant enhancement in the I_D/I_G value of Ni(OH)₂/NG demonstrates an increase in a number of defects and indicates a formation of a more disordered carbon structure, which are ascribed to the incorporation of nitrogen atoms and Ni(OH)₂ into the graphene sheets. Nitrogen doping can increase the amount of defects in graphene, possibly supplying more active sites for electron storage and benefiting an enhanced electrochemical performance.

To reveal more details about the chemical components and chemical bonds in the Ni(OH)₂/NG hydrogel, XPS measurements were also performed. Fig. 2c shows the survey scan spectrum of the Ni(OH)₂/NG hydrogel. The peaks centered at 284.7, 400.5, 530.4 and 856.2 eV correspond to C 1s, N 1s, O 1s and Ni 2p, respectively,

revealing that nitrogen atoms were inserted into the hydrogel by the hydrothermal process. Fig. 2d depicts the four deconvoluted peaks of the C 1s spectrum, which were assigned to C=C at 284.7 eV, C-O & C=N at 285.8 eV, C=O & C-N at 286.9 eV and O-C=O at 288.9 eV. The peaks of C-O and C=O usually overlap with the C=N and C-N bonds, respectively [28]. The incorporation of nitrogen atoms through the reaction of GO with EDA can be confirmed by the presence of the C=N (285.8 eV) and C-N peaks (286.9 eV) in the C 1s spectrum. Furthermore, the hydrophilic functional groups can serve as anchoring sites, which enable nickel hydroxide to directly grow on graphene [33]. As clearly exhibited in Fig. 2e, the N 1s spectrum can be presented as a superposition of three peaks centered at 398.3, 399.3 and 400.7 eV, corresponding to pyridinic N, pyrrolic N and graphitic N, respectively. These results indicate that during the hydrothermal process, the EDA acting as the nitrogen source reacts with the hydrophilic functional groups in GO to form the N-doped structure. Fig. 2f shows the Ni 2p XPS spectrum with two peaks assigned to Ni 2p_{3/2} (855.5 eV) and Ni $2p_{1/2}$ (873.1 eV), implying that the nickel ion is bivalent. The characteristics of the nickel hydroxide phase with a spin-energy separation of 17.6 eV agree well with previous reports [28,34]. In addition, two satellite peaks located at 861.1 and 879.1 eV around the Ni 2p_{1/2} and Ni 2p_{3/2} peaks can be noticed. The above XPS results prove that Ni(OH)₂/NG has been successfully prepared.

The morphologies of NG and Ni(OH)₂/NG were studied by SEM and TEM measurements, as displayed in Fig. 3. From Fig. 3a, it is evident that the surface of large NG sheets is rough and irregular, which can be attributed to the increased number of edges and defects appearing due to nitrogen doping. It was reported that structural defects can supply more nucleation sites for electron storage, which is significant for the improvement of the capacitive performance [35]. The structure of NG remains almost unchanged after the deposition of nickel hydroxide, and the highly dispersed nickel hydroxide nanosheets are anchored on the surface of NG, as shown in Fig. 3b. Thus, NG can serve as a substrate on which nickel hydroxide can grow, and the deposition of nickel hydroxide can effectively stem the agglomeration and restacking of graphene. Thus, the composite has the potential to greatly improve the overall performance when used as an electrode material.

Further insights into the microstructure of NG and Ni(OH)₂/NG



Fig. 2. (a) XRD patterns of GO, NG, pure Ni(OH)₂ and Ni(OH)₂/NG. (b) Raman spectra of rGO, NG and Ni(OH)₂/NG. XPS spectra of Ni(OH)₂/NG: (c) survey spectrum, (d) high-resolution C 1s spectrum, (e) high-resolution N 1s spectrum and (f) high-resolution Ni 2p spectrum.

can be achieved by TEM measurements. The transparent thin layer with crumpled silk waves and rumples in Fig. 3c corresponds to NG. Fig. 3d and Fig. S1 show that all the nickel hydroxide sheets are anchored on NG, and no freestanding nanosheets can be observed in NG, even after a powerful ultrasonication, suggesting the existence of a strong interaction between nickel hydroxide and NG [36]. Furthermore, the selected area electron diffraction (SAED) pattern (inset of Fig. 3d) demonstrates that Ni(OH)₂ is highly crystalline. HRTEM images were used to characterize the well-defined structure of Ni(OH)₂/NG shown in Fig. 3e. The interplanar distance in NG is measured as 0.35 nm, which is close to the reported interlayer distance in graphene (0.34 nm) [37], and the lattice distance of 0.23 nm corresponds to the (101) plane of β -Ni(OH)₂ [21]. These results demonstrate that the composite was successfully prepared, and this agrees with the XRD results. The EDS results of Ni(OH)₂/NG in Fig. 3f indicate that the observed elements include nickel, nitrogen, oxygen and carbon, which is in accordance with the XPS results.

3.2. Electrochemical analyses

To examine the electrochemical properties of the materials, CV tests were performed. Fig. 4a and b shows the CV curves of pure Ni(OH)₂ and Ni(OH)₂/NG from 5 to 100 mV s⁻¹. Two redox peaks can be clearly observed for all the curves, which are related to the pseudocapacitive behavior of nickel hydroxide. The well-defined redox peaks suggest that the capacitance originates from the redox reaction. The anodic peaks correspond to an oxidation reaction of Ni(OH)₂ to form NiOOH, and the cathodic peaks display the inverse process. The reversible reaction between Ni²⁺ and Ni³⁺ can be described as follows [38,39]:

 $Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$

The anodic and cathodic peak positions of $Ni(OH)_2/NG$ are centered at 0.341 and 0.213 V at 5 mV s⁻¹, respectively, which generates a potential gap of 0.128 V. The potential gap of $Ni(OH)_2$



Fig. 3. SEM images of (a) NG and (b) Ni(OH)₂/NG. TEM images of (c) NG and (d) Ni(OH)₂/NG. Inset: the SAED pattern. (e) HRTEM image of Ni(OH)₂/NG. (f) EDS analysis of the Ni(OH)₂/NG hydrogel.

(Fig. 4a) at the same scan rate is 0.173 V based on the anodic position of 0.415 V and the cathodic peak position of 0.242 V. The smaller peak potential gap of Ni(OH)₂/NG demonstrates a much better reversibility [29]. The redox current clearly increases with increasing scan rate, signifying its good rate ability [28,31]. Furthermore, the redox peaks of Ni(OH)₂/NG show slight shifts towards more positive and negative directions with increasing scan rate, which results from the limitation of the ion diffusion rate during the reaction [9,40] and reveals the existence of a fast faradaic redox reaction between the electroactive material and the electrolyte [41]. The CV curves comparison of pure Ni(OH)₂ and Ni(OH)₂/NG and the CV curve of NG are shown in Fig. S2, showing the largest enclosed area of the Ni(OH)₂/NG electrode, which indicates that the Ni(OH)₂/NG electrode exhibits the largest specific capacitance. In addition, the pure Ni foam substrate was examined, and the effect was shown to be almost negligible (Fig. S3).

Fig. 4c shows the GCD curves of Ni(OH)₂ and Ni(OH)₂/NG at 1.5 Ag^{-1} , and the inset is the GCD curve of NG at the same current density. NG displays an approximate triangle curve in the charge-discharge process. The curves of pure Ni(OH)₂ and Ni(OH)₂/NG electrodes are not ideal straight lines in the charging and discharging process, further confirming the pseudocapacitive behavior of the electrodes [36]. The discharge time of the Ni(OH)₂/NG electrode is much longer than that of the other two individual

electrodes, indicating an improved specific capacitance after the integration.

Fig. 4d exhibits the GCD curves of the Ni(OH)₂/NG hydrogel at diverse current densities. The obvious plateaus indicate the presence of faradaic redox reactions, which is consistent with the redox activities from the CV results shown in Fig. 4b. A similar phenomenon can also be observed from the GCD curves of nickel hydroxide in Fig. S4a. Fig. S4b shows the GCD curves of NG and rGO marked with triangles. The calculated specific capacitances from the discharge curves are plotted with the corresponding current density in Fig. 4e. The specific capacitances of the Ni(OH)₂/NG electrode are determined as ~ 896, 798, 736, 657, 599, 507 and $504 \, F \, g^{-1}$ at 0.5, 1, 2, 4, 8, 10 and 12 Ag^{-1} , respectively. Pure Ni(OH)₂ (450 F g⁻¹ at 1.5 A g⁻¹) and NG (465.9 F g⁻¹ at 1 A g⁻¹) deliver lower specific capacitances than the Ni(OH)₂/NG composite. The specific capacitance of the Ni(OH)₂/NG hydrogel decreases slowly with an increase in current density as compared to the other two individual electrodes. Even when the current density is as high as 12 Ag^{-1} , the specific capacitance still reaches $504 \,\mathrm{Fg}^{-1}$, showing a capacitance retention of 56.3%, which demonstrates that the composite has a good rate capability. Compared to previous reports on the electrode materials of supercapacitors based on nickel hydroxide and graphene composites [42], transition-metal oxides/hydroxides and nitrogen-doped graphene [33,43], and pure nitrogen-doped



Fig. 4. CV curves of (a) pure Ni(OH)₂ and (b) Ni(OH)₂/NG electrodes at different scan rates. GCD curves of (c) pure Ni(OH)₂ and Ni(OH)₂/NG at 1.5 A g⁻¹. Inset: the GCD curve of NG at 1.5 A g⁻¹, (d) Ni(OH)₂/NG at different current densities. (e) Specific capacitance of pure Ni(OH)₂, NG and Ni(OH)₂/NG at different current densities. (f) Cycling stability of Ni(OH)₂/NG at 4 A g⁻¹. Inset: GCD curves of the first and final five cycles.

graphene [44,45], the Ni(OH)₂/NG hydrogel in this work shows a higher capacitance and a good rate capability (Table S1).

The advantageous properties of the Ni(OH)₂/NG hydrogel benefit from the following two major aspects: (i) the positive synergistic effect between the metal hydroxide and nitrogen-doped graphene. NG offers more surface area to improve electron transport and acts as a scaffold for the growth of the Ni(OH)₂ sheets. The Ni(OH)₂ supported by NG is beneficial to the reaction kinetics. (ii) The nitrogen-doped site, particularly the pyridinic site, is a strong bonding site to grow the metal hydroxide, which contributes to the pseudocapacitance [46]. NG with more wrinkles can provide not only more electronic and ion-conductive channels to enable effective electrolyte diffusion but also more nucleation sites to enhance the metal hydroxide-graphene interaction [28,36]. Moreover, the extra pair of electrons from the nitrogen atom can increase the electron density of graphene, leading to an enhanced conductivity [47].

A long cycle life is crucial for the practical applications of supercapacitors. The cycling properties of the $Ni(OH)_2/NG$ hydrogel were estimated by GCD at $4 A g^{-1}$, and the results are shown in Fig. 4f. The capacitance increases slightly after the initial cycles and then decreases gradually with the following cycles. The increased capacitance after the initial cycles is attributed to the activation of

the electrode [31,48]. The values of the specific capacitance before and after 5000 cycles are 656.8 and $564.8 \,\mathrm{Fg}^{-1}$ from the inset, respectively. The capacitance retention of the Ni(OH)₂/NG hydrogel is 85.9% after 5000 cycles. This cycling stability is comparable to the best reported long-life value among similar hybrid electrode materials (Table S1).

To investigate the ion diffusion and the electron transport of the electrode, EIS is also carried out with an open circuit voltage and a 10 mV sinusoidal amplitude (Fig. S5). Each plot starts from a semicircle in the high frequency range and rises along the imaginary impedance axis in the low frequency range. The plots are fitted by an equivalent circuit, as shown in the inset of Fig. S5. W, C_{dl}, R_{ct}, R_s, and C represent the Warburg impedance, electrochemical double layer capacitance, charge transfer resistance, equivalent series resistance and Faradaic charge-discharge resistance, respectively [31,33]. The R_s and R_{ct} of the Ni(OH)₂/NG hydrogel are 0.7685 and 0.2164 Ω , respectively, which are smaller than those of pure nickel hydroxide (R_s value of 1.348 Ω and R_{ct} value of 3.437 Ω), suggesting a lower intrinsic resistance. The Ni(OH)₂/NG electrode shows a more vertical line in the EIS plot, suggesting fast ion diffusion and electron transport take place. The results further indicate that the Ni(OH)2/NG hydrogel is more conducive to electrochemical applications.

Since the best overall properties were demonstrated by the Ni(OH)₂/NG electrode, an asymmetric supercapacitor (ASC) device was fabricated to further study the possible real applications by integrating Ni(OH)₂/NG as the positive electrode, active carbon (AC) as the negative electrode, and a piece of cellulosic paper as the separator in an electrolyte. The CV curves of the two electrode materials were obtained at 100 mV s^{-1} to further evaluate the potential windows, see Fig. 5a. The Ni(OH)₂/NG electrode was measured in a range -0.2-0.6 V, while AC was measured from -1.0to 0V. Employing the different potential windows, the operating cell voltage of the fabricated device can be enhanced up to 1.6 V. The CV and GCD curves with diverse working voltages are depicted in Fig. 5b and Fig. S6, respectively. As expected, the device can operate normally in an enhanced potential window and almost maintain the same shape, implying a desirable capacitive performance. The CV curves in the range of $20-500 \text{ mV s}^{-1}$ almost maintain the same profile in Fig. 5c, indicating the excellent reversibility of charge and discharge. The GCD curves at diverse current densities are exhibited in Fig. 5d, and accordingly, the capacitances are 80.8, 73.1, 65.2, 61.5, 58.5 and 55.6 F g⁻¹ at 0.5, 1, 2, 3, 4 and 5 A g⁻¹, respectively. The energy density and the power density are estimated from the GCD curves using the formulas given in the supporting information. On the basis of the GCD curves, the Ragone plots of the ASC are built and are shown in Fig. 5e. The Ni(OH)₂/NG//AC device delivers a maximum energy density of 28.73 W h kg⁻¹ at 0.36 kW kg⁻¹ and maintains 19.78 W h kg⁻¹, even when the power density is increased to 4.00 kW kg⁻¹. Importantly, the Ni(OH)₂/NG//AC device outperforms the supercapacitors described in the reference data, such as 3D a-Ni(OH)₂//AC (14.9 W h kg⁻¹ at 0.14 kW kg⁻¹) [49], NiCo₂O₄/rGO//AC (23.3 W h kg⁻¹ at 0.32 kW kg⁻¹) [50], Ni–Co binary hydroxides//CG (26.3 W h kg⁻¹ at 0.32 kW kg⁻¹) [52], and NiCo₂S₄//AC (25.5 W h kg⁻¹ at 0.33 kW kg⁻¹) [53]. Finally, a LED can be easily illuminated by two devices in series after being charged, as shown in the inset of Fig. 5e. The cycling stability of the ASC examined at 1.5 A g⁻¹ is shown in Fig. 5f. A capacitance retention of 74.3% is achieved after 5000 cycles, suggesting that the device has an excellent electrochemical stability.



Fig. 5. (a) CV curves comparison of AC and Ni(OH)₂/NG at 100 mV s⁻¹. (b) CV curves of the ASC measured in different voltage windows at 100 mV s⁻¹. (c) CV curves of the ASC at different scan rate at 1.6 V. (d) GCD curves of the ASC at different current densities. (e) Ragone plot of the ASC device, the inset is optical image of lighting LEDs driven by two ASC devices in series. (f) The long-term cycling performance of the ASC device, Inset: GCD curves of the first and final five cycles.

4. Conclusions

In conclusion, a facile one-pot hydrothermal route was employed to successfully fabricate the Ni(OH)₂/NG hydrogel. Due to the synergistic effect between the metal hydroxide and nitrogendoped graphene, the Ni(OH)₂/NG hydrogel electrode displays improved electrochemical behaviors as compared with the individual Ni(OH)₂ and NG components. The Ni(OH)₂/NG electrode delivers a high specific capacitance of 896 F g⁻¹ at 0.5 A g⁻¹ with a good rate capability (56.3% retention with a 24-fold increase in the current density). At the same time, 85.9% of the initial capacitance remains after 5000 long-term cycles. A Ni(OH)₂/NG/AC ASC device is assembled and delivers a high energy density and a good cycle stability. This strategy provides an alternative route to simply fabricate electrode materials and could be extended to more metal hydroxides or oxides/NG hydrogels.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jallcom.2018.12.188.

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