A high-energy, long cycle-life hybrid supercapacitor based on graphene composite electrodes

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ABSTRACT

Hybrid supercapacitors consisting of a battery-type faradaic electrode/capacitive electrode couple could achieve significantly improved energy density compared to that of the state-of-the-art supercapacitors due to the extended voltage window and introduction of a battery-type electrode with high capacity. However, their commercial application is still hampered by lacking of proper electrode materials and structures. Here, a series of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ -reduced graphene oxide (rGO) nanocomposites are derived from a facile process at room temperature using hydrous hydrazine and different ratios of Co(II) to Ni(II) to tune the composition and morphology. In particular, an architectural composite electrode consisting of porous $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ disks wrapped by rGO achieves high capacity, rate capability (743 and 545 C g^{-1} at 1 A g^{-1} and 20 A g^{-1} , respectively), and long cycling life. When coupled with a p-phenylenediamine (PPD)-modified rGO, the resulting hybrid supercapacitor exhibits superior energy densities of 72 and 44 W h Kg^{-1} at a power density of 797 W Kg^{-1} and 16.7 kW Kg^{-1} , respectively, and excellent cycling stability for 20,000 cycles at 20 A g^{-1} , implying that it is a very promising device for portable power and next-generation energy storage.

KEYWORDS

graphene, composites, hybrid supercapacitors, hydroxides, organic molecular

1. Introduction

Supercapacitors (or electrochemical capacitors) have attracted intense attention due to their higher power density and longer cycle-life than existing rechargeable batteries [1-4]. They are well suited for applications requiring rapid power delivery and recharging, such as regenerative braking, short-term energy storage, hybrid electric vehicles, large industrial equipment, and portable devices. However, commercially available supercapacitors are still based on activated carbon materials, known as electrical double-layer capacitors (EDLCs), and have much less energy density than rechargeable batteries, which severely limit their potential for many applications [1].

During the past few years, asymmetric/hybrid supercapacitors with much higher energy density than that of EDLCs, due to the extended voltage window and the significantly enhanced capacitance, are considered a promising energy storage device to meet the demands for many emerging applications [5-18]. The term “asymmetric supercapacitors” is suggested by Brousse et al. to be used for the devices with only capacitive/pseudocapacitive electrodes (e.g., MnO_2 /graphene//carbon nanotubes [5]) to avoid confusion with “hybrid” devices in-between a supercapacitor and a battery. [19]. Compared to asymmetric supercapacitors, hybrid supercapacitors consisting of a battery-type faradaic electrode (for high energy density) and a capacitive electrode (for high power density and long cycle life) could achieve even higher energy density because the hybridization of these two electrodes can significantly broaden the operating voltage and increase the capacitance of the hybrid capacitor [20, 21]. The electrochemical performance of hybrid supercapacitors is sensitive to the nature of the electrode materials, which are the key to developing a long cycle-life hybrid supercapacitor with high energy and power density. In a typical hybrid supercapacitor, the capacitive electrode is usually

activated carbon[11-14, 22] or graphene[15, 18, 23, 24], and the battery-type electrode is lithium intercalation compounds [7, 8] or transition metal compounds[16, 17, 22, 24, 25].

Recently, Ni and/or Co-based oxides/hydroxides have been reported as one of the most promising candidates for battery-type electrodes in hybrid supercapacitors due to their attractive theoretical specific capacity and potentially high rate capability in aqueous electrolyte (e.g., KOH). These oxides/hydroxides that were reported as advanced “pseudocapacitive” materials[26-28], have been recently considered as “extrinsic pseudocapacitors” [29] (with other examples including V_2O_5 [29] and metal sulfides[30, 31]), which do not exhibit pseudocapacitance but battery-type behavior in the bulk state due to phase transformations during ion storage, but an improved capacitive behavior in nanosize with increased surface area especially at high current density. Now these Ni and/or Co-based oxides/hydroxides have been termed as battery-type faradaic electrode materials based on their electrochemical behavior in aqueous electrolytes [2, 19, 32], which have gained significant credence. However, these oxides/hydroxides suffer from relatively poor electronic conductivity, leading to limited rate capability and cycling stability. Growth of these Ni and/or Co-based oxides/hydroxides on conductive substrates such as carbon fiber paper[27], or nickel foam[33-35] have been demonstrated as an effective approach to improve the electronic conductivity, further resulting in an improved rate capability and cycling performance. Compared to commercial carbon fiber papers and nickel foams, the formation of composites with graphene is preferred. Graphene-based materials have been widely reported with attractive electrical/electrochemical properties [36-41]. The much higher surface area and ultrathin thickness of graphene results in significantly enhanced mass loading of active materials (i.e., Ni and/or Co-based oxides/hydroxides), and further improved capacity based on the total mass of active materials/conductive substrates. To

date, numerous efforts have been devoted to engineering the microstructures of Ni and/or Co-based oxides/hydroxides for improved electrochemical performance[24-26, 42-44]. However, advanced architecture with stable cycling performance as well as high rate capability derived from a facile method is still rarely reported. Porous microstructures in micrometer-size derived from a facile method are significantly preferred for commercial applications.

Figure 1. Schematic illustration of the hybrid supercapacitor device with a $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ @reduced graphene oxide (rGO) composite as a battery-type faradaic electrode and a p-phenylenediamine (PPD)-modified rGO composite as a capacitive electrode.

In this work, we report our findings on the synthesis and characterization of a series of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ -reduced graphene oxide (rGO) nanocomposites prepared by a facile process at room temperature where hydrous hydrazine was used as the OH^- source and reducing agent. Different ratios of initial Co(II) to Ni(II) and different amounts of hydrazine have been used to tune the composition and morphology. Specifically, a porous disk-like $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ structure wrapped by rGO was prepared, in which the unique porous structures facilitate rapid access of liquid electrolyte to electrode materials and rGO offers effective electron paths for fast energy

storage. The resulting composite electrode exhibited a high specific capacity, rate capability, and cycling stability. More importantly, when coupled with a high-performance p-phenylenediamine-modified rGO (PPD/rGO) capacitive electrode, the hybrid supercapacitor (Figure 1) delivered greatly enhanced gravimetric/volumetric energy density and cycle-life compared to those of recently reported advanced hybrid/asymmetric supercapacitors[22-25, 45-49]. The simple preparation process and high performance make the hybrid supercapacitor attractive for a wide variety of applications.

2. Experimental Section

Materials synthesis: Graphite oxide was synthesized by a modified Hummers' method [50]. The as-prepared aqueous suspension of graphite oxide was diluted with deionized water under ultrasonication for 5 h to obtain an exfoliated graphene oxide (GO) suspension ($\sim 1 \text{ mg mL}^{-1}$). 50 mL of mixed $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ solution with 30 mmol of total metal ions was poured into a 50 mL of GO suspension (1 mg mL^{-1}) and stirred for 10 min, and then 1.5 ~ 4.5 mL of hydrazine monohydrate (N_2H_4 64-65 %, reagent grade, 98%, Sigma-Aldrich) was dropped into the solution, followed by stirring for 36 h at room temperature. The as-obtained composite was washed repeatedly with deionized water by vacuum filtration until the filtrate had a neutral pH and the filtrate became colorless. The collected black solids were dried at room temperature in air under fume hood.

By adding 1.5 mL of hydrazine monohydrate, a series of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ composites with different $\text{Co}^{2+}:\text{Ni}^{2+}$ ratios but fixed total metal ion amount (30 mmol) were prepared and named CNOHa:b (a:b means that the mole ratio of Co(II):Ni(II) in the raw materials). By fixing the initial Ni(II) to Co(II) ratio as 1:1, the increased amounts of hydrous hydrazine (3.0 and 4.5

mL) were further used to synthesize the $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ -rGO nanocomposites, which were named CNOH1:1-II, and CNOH1:1-III, respectively. A pure rGO was also prepared in a similar fashion by using 4.5 mL of hydrous hydrazine as the reducing agent only without adding $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$.

To prepare the PPD/rGO material, 50 mg of GO was dispersed in 35 mL of deionized water. Then, 54 mg of PPD was dissolved in 15 mL of deionized water and added into the GO suspension. The mixture was stirred for 30 min and reacted in a Teflon-lined stainless steel autoclave at 180°C for 12 h. After the reaction, the composite was washed repeatedly with deionized water and dried at 55 °C for 24 h.

Basic characterization: The X-ray diffraction (XRD) patterns were recorded with an X'Pert PRO Alpha-1 X-ray diffractometer. A scanning electron microscope (SEM, LEO 1530) coupled with an energy dispersive X-ray spectrometer (EDX) was used to analyze the morphologies and element distribution/ratio of samples. A high-resolution transmission electron microscope (TEM, FEI G2 Tecnai F30) was used to analyze the microstructures and morphologies of samples. Prior to TEM analysis, the samples were ultrasonically dispersed in ethanol for several hours. The nitrogen adsorption–desorption isotherm of the sample was measured at the boiling point of liquid nitrogen (77 K) using a Micromeritics ASAP 2020 analyzer. Thermogravimetric analysis (TGA) was carried out with an SDTQ-600 (TA Instruments Co.) apparatus in air with a heating rate of 10 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) was measured on a Thermo K-Alpha XPS spectrometer (Thermo Fisher Scientific) equipped with a monochromatic Al-K α X-ray source ($h\nu = 1468.6$ eV). Raman spectroscopic measurement was performed using a

Renishaw RM1000 microspectroscopic system. A He-Ne laser with a wavelength of 633 nm (Thorlab HRP-170) was applied as excitation laser through a 20x/0.40 objective.

Electrochemical measurement: The electrochemical performances of the as-obtained $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ materials were investigated under a three-electrode configuration in a beaker with a 2 M KOH aqueous solution as electrolyte at room temperature. A Ag/AgCl electrode prefilled with 4 M KCl aqueous solution saturated with AgCl and a Pt mesh electrode were used as the reference and the counter electrodes, respectively. The working electrode was prepared as follows: the $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ materials and Super P Li powders (TIMCAL Graphite & Carbon) were ground and sieved through a 170-mesh sieve before using; a free-standing film (5/16 in. in diameter) was made from a mixture of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ materials, Super P Li and polytetrafluoroethylene (PTFE) at a mass ratio of 85:10:5 with assistance of ethanol; the working electrode was obtained by pressing the free-standing film between two nickel foams (3/8 in. in diameter). Besides acting as a conductive additive, the Super P Li powders was also used as additive to assist the preparation of free-standing electrode films; it appears that we were unable cast the $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ into a free-standing electrode film without adding Super P Li powders. The typical mass loading of the active material (i.e., $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$) in the electrode is $2.7 \sim 3.3 \text{ mg cm}^{-2}$. The working electrode was soaked in a 2 M KOH aqueous solution under vacuum for $> 8 \text{ h}$ before the electrochemical measurement.

The electrochemical performances of the hybrid supercapacitor were investigated under a two-electrode configuration in a split test cell (MTI Corporation). The free-standing film mixture of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ materials, Super P Li and PTFE at a mass ratio of 85:10:5 was used as the

positive electrode. The negative electrode was a free-standing film of mixture of PPD/rGO materials and PTFE at a mass ratio of 95:5. Carbon fiber papers (7/16 in. in diameter) were used as current collectors by only physical contact with the working electrode. A 2 M KOH aqueous solution was used as electrolyte, and a NKK separator (MPF30AC-100, Nippon Kodoshi Corporation, Kochi, Japan) was used as the separator. The electrodes were soaked in the electrolyte solution for approximately 1 h under vacuum and were assembled in a split test cell under ambient atmosphere. The cell was tightened by 4 nuts and bolts, and was standing for another 9 h under atmospheric pressure before the electrochemical measurement.

Cyclic voltammograms were recorded on a Solartron electrochemical workstation (Solartron SI 1287 electrochemical interface). The galvanostatic charge/discharge measurements were carried out using an Arbin testing system (BT-2143) at room temperature. At the beginning of the electrochemical measurement, the working electrode or cell was always activated via cyclic voltammetry test at a scan rate of 30 mV s⁻¹ for 5-10 cycles until cyclic voltammograms became relatively stable. The cycling performance of three-electrode system or two-electrode device was carried out after the initial activating process and rate capability testing.

The specific capacity (C g⁻¹) of Co_xNi_{1-x}(OH)₂-rGO electrode based on the galvanostatic discharge curve was calculated using the following equation:

$$Q = It/m \quad (1)$$

where I (mA) is the discharge current, It (s) is the discharge time, and m (mg) is the mass of the active material (i.e., Co_xNi_{1-x}(OH)₂-rGO). The specific capacity is based on the total mass of the Co_xNi_{1-x}(OH)₂-rGO composite.

The mass ratio of positive electrode to negative electrode in the hybrid supercapacitor device was determined to better balance the obtainable charge of the two electrodes ($q_+ = q_-$). The charge of the positive electrode (q_+) was calculated with that of the negative electrode (q_-) based on the cyclic voltammograms acquired from a cell with a three-electrode configuration.

$$q = \int i m dV / \nu \quad (2)$$

where q (C) is the charge, i ($A\ g^{-1}$) is the current density, m (mg) is the mass of the active material, V (V) is the voltage, ν ($mV\ s^{-1}$) is the scan rate, and $\int i dV$ is the integral area of the cyclic voltammogram.

To achieve $q_+ = q_-$, the mass ratio of positive electrode active material to negative electrode active material is determined from the following equation:

$$m_+ : m_- = (\int i dV / \nu)_- : (\int i dV / \nu)_+ \quad (3)$$

The mass ratio of the positive electrode active material ($Co_xNi_{1-x}(OH)_2$ -rGO) to the negative electrode active material (PPD/rGO) was calculated to be 1:2.28 for the hybrid supercapacitor, as determined from the cyclic voltammograms acquired at $10\ mV\ s^{-1}$ (Figure 4a) for both electrodes.

The energy density ($W\ h\ kg^{-1}$) of the hybrid supercapacitor device was calculated based on the galvanostatic discharge curve using the following equation:

$$E = I \int V dt / 3.6 (m_{Co_xNi_{1-x}(OH)_2-rGO} + m_{PPD/rGO}) \quad (4)$$

The constant 3.6 is adopted when the energy density (E) is in $W\ h\ kg^{-1}$, the current (I) is in mA, the voltage (V) is in V, the time (t) is in seconds, and the mass (m) is in mg. The mass used in the

calculation for hybrid supercapacitor device was based on the total mass of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ composite and PPD/rGO composite.

The power density (W kg^{-1}) is calculated using the following equation:

$$P = E/\Delta t \quad (5)$$

3. Results and Discussion

The preparation processes of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ composites are schematically illustrated in Figure 2a. Co(II)/Ni(II) -containing aqueous solution was mixed with GO suspension, followed by adding 1.5 mL of hydrous hydrazine, stirring for 36 h at room temperature. A series of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ composites with different Co(II):Ni(II) ratios were prepared and named CNOHa:b (a:b means that the mole ratio of Co(II):Ni(II) in the raw materials; the actual ratios in the as-prepared samples were also tested by EDX analysis with results shown in Table S1, which were similar to initial ratios by adding 1.5 mL of hydrous hydrazine). After washing, the morphologies of the as-obtained $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ composites (Figure S1) were very similar, although the degree of aggregation may appear somewhat different. The morphological features are dominated by wrinkled graphene sheets, suggesting that the as-prepared $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ are small nanoparticles, as reflected by the relatively low intensity of X-ray diffraction (XRD) peaks (Figure S2). The XRD patterns of CNOH3:0, CNOH2:1, CNOH1:1, and CNOH1:2 samples were similar with four broad peaks corresponding to $\alpha\text{-Ni(OH)}_2$ - and $\alpha\text{-Co(OH)}_2$ -like structures [51]. No diffraction peak corresponding to metallic Ni or Co was observed. The CNOH0:3 sample without Co(II) was almost amorphous instead of the $\alpha\text{-Ni(OH)}_2$ -like structure, which may be attributed to some special reaction with hydrous hydrazine in absence of Co(II) . The XRD

peak intensity of the CNOH3:0 sample without Ni(II) was much lower than those of the CNOH2:1, CNOH1:1, and CNOH1:2 samples. These results suggest that the presence of both Co(II) and Ni(II) ions in the alkaline solution (hydrous hydrazine) improves the crystallinity of the hydroxides. The absence of the obvious diffraction peak corresponding to rGO could be attributed to the distinctly reduced layer-to-layer interaction between adjacent graphene sheets

Figure 2. (a) Schematic illustration of the preparation of Co_xNi_{1-x}(OH)₂-rGO composites via a facile hydrazine-induced process at room temperature. (b, c, d) BF-TEM images of (b) CNOH1:1, (c) CNOH1:1-II, and (d) CNOH1:1-III (i.e., Co_xNi_{1-x}(OH)₂-rGO composite; 1:1 means that the mole ratio of Co(II):Ni(II) in the raw materials is 1:1; I, II, and III represent the sample prepared

with different amounts of hydrous hydrazine); (e) DF-TEM, and (f) HRTEM images of CNOH1:1-III obtained from the selected rectangle region with orange border (dotted line), and red border (solid line) in (d), respectively; (g) HAADF STEM image of CNOH1:1-III; the arrows in (f) indicate layered graphene structure; the arrows in (g) indicate the graphene sheet structures, the circles (dotted line) indicate the typical pores in the unique architecture. (h) XRD patterns, (i) XPS spectra of C 1s, and (j) XPS spectra of Ni 2p of as-prepared samples using different amounts of hydrous hydrazine: CNOH1:1, CNOH1:1-II, and CNOH1:1-III; XPS spectrum of C 1s in GO sample was also given in (i); “Sat.” in (j) means satellite.

which could be an indication that the surface of rGO was mostly covered by as-formed $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$.

The hydrous hydrazine in the synthesis process plays two key roles: offering OH^- for the formation of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ and acting as the reducing agent for reducing GO. We systematically varied the used amount of hydrous hydrazine to explore the effect on the material properties (Figure 2a). With increasing amount of hydrous hydrazine from 1.5 to 3.0 mL, the morphology of as-obtained sample (named CNOH1:1-II) (Figure S3a) still remained similar, but somewhat looser compared to that of the CNOH1:1 sample (Figure S3b). When the amount of hydrous hydrazine was increased to 4.5 mL, many $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ disk-like structures of micrometer-size appeared in the as-prepared sample (named CNOH1:1-III), as shown in Figure S3c. More importantly, it seems that the $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ disks were wrapped by graphene sheets. The Co:Ni ratios in the samples measured by EDX analysis increased from 44:56 for CNOH1:1 sample to 65:35 for CNOH1:1-II sample, and 69:31 for CNOH1:1-III sample, respectively, with increasing amount of hydrous hydrazine (Table S1). As seen from the transmission electron microscopy (TEM)/scanning TEM (STEM) images shown in Figure 2b-g, a significant amount of folding

graphene sheets were observed for the samples. The bright-field (BF)-TEM image of CNOH1:1-II sample (Figure 2c) confirmed that it had relatively loose microstructure compared to that of CNOH1:1 sample (Figure 2b). Figure 2d presents a typical $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2@\text{rGO}$ disk, in which the $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ disk appeared to be wrapped by graphene sheets. Dark-field (DF)-TEM images demonstrate that the as-formed $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ in CNOH1:1-III (Figure 2e), CNOH1:1-II (Figure S4) and CNOH1:1 (Figure S5) samples were actually ultrafine nanocrystals. These nanocrystals were relatively uniformly distributed in the composites especially for CNOH1:1-II and CNOH1:1. Figure 2f and S6 show two typical high-resolution TEM (HRTEM) images of the border of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2@\text{rGO}$ disk, in which the periodic lattice fringe corresponding to $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ phase were wrapped by clear graphene sheets with 3-5 layers. High-angle annular dark-field (HAADF) STEM image (Figure 2g) confirmed that the $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ disk was wrapped by graphene sheets. Importantly, the as-obtained $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ disks were porous with a significant quantity of mesopores from the observation of HAADF STEM (Figure 2g and S7). The porosity of the samples was further analyzed by nitrogen adsorption-desorption measurements, confirming the mesoporosity in CNOH1:1-III sample (Figure S8). Such porous structure would facilitate the access of liquid electrolyte to electrode materials for fast ionic transport while the wrapped graphene sheets promote effective electron transport and current collection.

The phase structures of these as-prepared nanocomposites were almost the same, as reflected by the XRD patterns shown in Figure 2h. No diffraction peaks corresponding to metallic Ni or Co were observed even when the amount of hydrous hydrazine was increased to 4.5 mL. The character of broad peaks in XRD patterns was consistent with the ultrafine nanocrystal nature as observed by DF-TEM (Figure 2e, S4, and S5). As determined by thermogravimetric analysis (TGA) (Figure S9), the content of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ in the composite

increased with increasing amount of hydrous hydrazine from CNOH1:1 to CNOH1:1-II sample and almost remained unchanged for the CNOH1:1-III sample.

Figure 2i shows X-ray photoelectron spectroscopy (XPS) spectra of C1s in different samples with fitted results. After the synthesis process, the intensity of C-O-type carbon (286.8 eV, including C-OH and C-O-C (epoxide groups)) significantly decreased, confirming that the GO was successfully reduced by hydrous hydrazine. The peak shift of C-O-type carbon was attributed to the sharp reduction of C-O-C groups in C-O-type carbon. With increasing amount of hydrous hydrazine, the content of C=O- and O-C=O-type carbon somewhat increased. This result is anomalous since hydrous hydrazine is a well-known reducing agent. The result may be due to the competition between the formation of metal hydroxide and the reduction of graphene oxide. In the Ni 2p spectra (Figure 2j), expected Ni 2p_{1/2} (873.3 eV) and Ni 2p_{3/2} (855.7 eV) signals were observed with two corresponding satellites for all the samples, consistent with that of Ni(OH)₂ [52, 53] and Ni-Co hydroxide [28]. No Ni 2p_{3/2} peak centered at ~852.6 eV was observed, confirming that no metallic Ni formed under this reducing environment. The Co 2p_{3/2} was centered at 780.8 eV (Figure S10), suggesting the formation of cobalt hydroxide [54]. The spin-orbit splitting value of Co 2p_{1/2} and Co 2p_{3/2} was 15.6 eV, and the intensity of the Co 2p_{3/2} satellite line was low, indicating the presence of both Co³⁺ and Co²⁺ in these Co_xNi_{1-x}(OH)₂-rGO samples[28, 52]. The formation of Co_xNi_{1-x}(OH)₂-rGO composite was further supported by Raman analysis (Figure S11).

To characterize the electrochemical performance, the as-prepared Co_xNi_{1-x}(OH)₂-rGO composites were tested using a three-electrode configuration in a 2 M KOH aqueous solution. Shown in Figure 3a are some typical cyclic voltammetric (CV) curves of Co_xNi_{1-x}(OH)₂-rGO composite electrodes derived from different Co(II) to Ni(II) ratios and 1.5 mL of hydrous

hydrazine. While one pair of redox peaks were observed for all samples, the oxidation peak of the as-prepared composite electrodes shifted in the positive potential direction while increasing the initial Ni(II) content. The CNOH2:1 and CNOH1:1 samples exhibited the largest integral area, indicating the highest specific capacities. Figure 3b shows the galvanostatic charge-discharge curves of the $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ composite electrodes at 1 A g^{-1} ; the electrochemical

Figure 3. (a) CV curves at a scan rate of 2 mV s^{-1} , (b) 5th galvanostatic charge-discharge curves at 1 A g^{-1} , (c) specific capacities of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ composite electrodes with different initial Co(II) to Ni(II) ratios using 1.5 mL of hydrous hydrazine. (d) 5th galvanostatic charge-discharge curves at 1 A g^{-1} , and (e) rate performance of as-prepared samples using different amounts of hydrous hydrazine: CNOH1:1, CNOH1:1-II, and CNOH1:1-III, the inset in (e) is discharge curves of the CNOH1:1-III electrode at different current densities (1-20 A g^{-1}), the rectangular triangles shown in the figure are used for clearly understanding the different slopes of the curves at 1 (red) and 20 A g^{-1} (violet). (f) Cycling performance of the CNOH1:1-III electrode at 20 A g^{-1} .

behaviors are consistent with the CV results. The corresponding discharge capacities were summarized in Figure 3c. The capacities of the CNOH2:1 and CNOH1:1 electrodes were similar, demonstrating 692 and 707 C g⁻¹ (based on the total mass of Co_xNi_{1-x}(OH)₂-rGO composite), respectively, much better than those of the CNOH1:2, CNOH3:0 and CNOH0:3 electrodes. The substitution of Ni with an appropriate amount of cobalt definitely increased the specific capacity, consistent with the reported results [25, 51, 55]. Based on the slightly higher capacity and higher redox potentials (better for hybrid device) of CNOH1:1 electrode compared to those of CNOH2:1 electrode, the initial Co(II) to Ni(II) ratio of 1:1 was selected to study the effect of the amounts of hydrous hydrazine.

The galvanostatic charge-discharge curves of the CNOH1:1, CNOH1:1-II, and CNOH1:1-III electrodes at 1 A g⁻¹ are shown in Figure 3d. The different potential plateaus suggest the difference of Co to Ni ratio in these samples, which was consistent with EDX analysis (Table S1). The corresponding typical rate capability results are summarized in Figure 3d. With increasing amount of hydrous hydrazine, the capacities at low current density were somewhat increased due to the increased content of Co_xNi_{1-x}(OH)₂ in the composite. The rate capability was also enhanced with increasing amount of hydrous hydrazine. This effect is likely due to the improved microstructures of CNOH1:1-II and CNOH1:1-III samples, where more open channels promote easy ion access whereas the graphene allows fast current collection. In particular, specific capacities of 743 and 545 C g⁻¹ were achieved, respectively, at 1 A g⁻¹ and 20 A g⁻¹ for the CNOH1:1-III electrode. For comparison, a CNOH1:1-III sample without graphene was also prepared in a similar fashion with typical electrochemical performance shown in Figure S13. The CNOH1:1-III electrode exhibited significantly improved specific capacity and rate

performance compared to that of the CNOH1:1-III without graphene electrode, suggesting the presence of a synergistic effect of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ and graphene in the composite.

Figure 3e shows the typical discharge curves of the CNOH1:1-III electrode at different current densities (1 to 20 A g^{-1}). A potential plateau between 0.15 and 0.05 V with relatively small slope prevails over a wide capacity range, although the slope increased with increasing current density, suggesting an increase in the contribution of capacitive behavior to capacity. A high capacitive contribution is more beneficial to cycling stability [56, 57]. When evaluated at 20 A g^{-1} , the CNOH1:1-III electrode demonstrated an attractive capacity retention of ~91% after 5,000 cycles (Figure 3f). The morphology stability of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ disks in the CNOH1:1-III electrode was verified by SEM observation of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ disks grown on nickel foam before and after 5,000 cycles (Figure S14). Additionally, the Co:Ni ratio in the sample was found to be a key factor for cycling stability; the composite sample with a Co:Ni ratio of ~2:1 had a better electrochemical stability compared to that of the composite sample with a Co:Ni ratio of ~1:1 (Figure S15). The high specific capacity, rate capability, and superior cycling stability could be attributed to the proper Co:Ni ratio, unique porous disk-like architecture, the wrapped rGO, and the high contribution of capacitive behavior to capacity at high current densities.

To further enhance the energy density, the operation voltage of the capacitor should be broadened using a hybrid cell configuration. We built a hybrid device using a high-performance PPD/rGO composite as the negative electrode and the CNOH1:1-III as the positive electrode, as schematically illustrated in Figure 1. Some typical CV curves of the two electrodes are presented in Figure 4a. Clearly, the CNOH1:1-III electrode exhibited a pair of redox peaks within a potential window of -0.15~0.45 V whereas the PPD/rGO electrode showed a typical capacitive behavior between -1.15 and -0.15 V (Figure 4a and S16) with electrical double-layer capacitive

contribution from rGO and amine groups-derived pseudocapacitive contribution from PPD. The PPD/rGO composite achieved a much higher specific capacitance than that of the pure rGO sample (Figure S16). Since the specific surface area of PPD/rGO is $7.7 \text{ m}^2 \text{ g}^{-1}$ and that of rGO is $188.7 \text{ m}^2 \text{ g}^{-1}$ (Figure S17), the PPD in the PPD/rGO composite contributes the most to the pseudocapacitance of the sample. However, a comparison of the CV curve of pure rGO with that of the PPD/rGO electrode at the same scan rate (Figure S16) indicates that the double-layer contribution from PPD/rGO electrode was still higher than that from pure rGO electrode, suggesting that the PPD also functions as a molecular spacer to prevent the graphene sheets from restacking. An operation voltage of 1.6 V could be achieved for the hybrid

Figure 4. (a) CV curves of the CNOH1:1-III electrode and PPD/rGO electrode at a scan rate of 10 mV s^{-1} obtained in a three-electrode system; (b) CV curves at different scan rates (5 – 100 mV s^{-1}), (c) galvanostatic discharge curves at different current densities (1 – 20 A g^{-1}) of hybrid

supercapacitor device with CNOH1:1-III//PPD/rGO couple; (d, e) Ragone plot of the CNOH1:1-III//PPD/rGO hybrid supercapacitor device compared to that of traditional EDLCs and LIBs based on the mass of active materials [34], and recently reported advanced hybrid/asymmetric supercapacitors [22-25, 45-49] with electrode materials shown in (e); all the energy/power density was calculated based on the mass of active materials; The inset time is obtained by dividing the energy density by the power density, which is a time constant of the devices; (e) is an enlarged image of (d); and (f) cycling stability at current density of 20 A g^{-1} between 0 and 1.6 V of the CNOH1:1-III//PPD/rGO hybrid supercapacitor device, the inset shows the corresponding galvanostatic charge/discharge curves of the 9990-10000th and last 10 cycles; the inset digital photo is a GT logo consisting of 32 green LEDs in parallel powered by two hybrid supercapacitor devices in series.

supercapacitor. The corresponding CV curves and galvanostatic discharge curves of the hybrid supercapacitor are shown in Figure 4b and 4c. The shapes of CV curves were well maintained as the scan rate was increased from 5 to 100 mV s^{-1} , suggesting reasonably high rate capability of the hybrid supercapacitor, attributed to the electrochemical properties of both the positive and negative electrodes. The galvanostatic discharge curves of the hybrid supercapacitor (Figure 4c) appear to be battery-type with a marked sloping plateau at low current densities, but seems to be capacitor-like behavior at high current densities (inset in Figure 4f). The rate performance was summarized in Figure S18.

Shown in Figure 4d and 4e (the Ragone plot) are the gravimetric energy and power densities of the hybrid supercapacitor calculated from the discharge curves (Figure 4c), demonstrating a high energy density of 72 W h kg^{-1} at a power density of 797 W kg^{-1} . Even at a

power density of 16.7 kW kg^{-1} , energy density of 44 W h kg^{-1} still remains. The energy and power densities of the traditional EDLCs and lithium-ion batteries (LIBs) based on the mass of active materials [34] were also presented in Figure 4d for comparison. The hybrid supercapacitor delivered much higher energy density compared to that of EDLCs at the same power density and much higher power density compared to that of LIBs at the same energy density. The energy densities of the hybrid supercapacitor are comparable to those of the LIBs at the same power density. Furthermore, the gravimetric energy and power densities of the hybrid supercapacitor were superior to that of recently reported advanced hybrid/asymmetric supercapacitors, including NiCo_2S_4 ball-in-ball hollow spheres//graphene/carbon spheres [45], NiCo_2S_4 /N-doped carbon (C) foam//ordered mesoporous C/N-doped C foam[46], $\text{Co}_{0.5}\text{Ni}_{0.5}(\text{OH})_2$ /graphene(G)/CNTs//activated carbon (AC)[25], Ni-Co-Fe hydroxide//AC[22], MnO_2 /GO//porous C[47], Co-Al hydroxide/dodecyl sulfate anions/G//sandwiched G/porous C[48], Fe_2O_3 /functionalized G// MnO_2 /functionalized G[49], NiO-porous C hollow sphere//N-doped G[23], $\text{Ni}(\text{OH})_2$ /G//porous G[24]. Additionally, the volumetric energy and power densities of the presented hybrid supercapacitor were also evaluated with results shown in Figure S19, which were comparable or even superior to that of recently reported advanced hybrid/asymmetric supercapacitors [6, 33]. Moreover, a simple application example of the hybrid supercapacitor is presented. A GT (Georgia Institute of Technology) logo consisting of 32 green LEDs in parallel can be powered by two hybrid supercapacitor devices in series after being charged to 3.2 V (inset in Figure 4f). Cycling performance, which is an important property for a supercapacitor, of the hybrid supercapacitor at 20 A g^{-1} between 0 and 1.6 V is shown in Figure 4f. An excellent cycling stability without undergoing decay compared to the initial Q_m was achieved even after 20,000 cycles at a high current density of 20 A g^{-1} , which is much better than

that of LIBs and superior to those of recently reported advanced hybrid/asymmetric supercapacitors (Table S2)[22-24, 45-49]. The corresponding Coulombic efficiency was around 99% for the initial 2,000 cycles, and was above 99% (close to 100%) for the subsequent 18,000 cycles (Figure S20). Furthermore, the corresponding galvanostatic charge/discharge curves of the 9990-10000th and the last 10 cycles are given in Figure 4f (inset). There is little observable change in these curves, confirming the excellent cycling stability of the hybrid supercapacitor.

4. Conclusion

In summary, a high-energy, long cycle-life hybrid supercapacitor was constructed using graphene-based hybrid materials: $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ and PPD/rGO. We have successfully prepared a series of $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2\text{-rGO}$ nanocomposites via a facile hydrazine-induced process and studied the effect of different Co(II) to Ni(II) ratios and hydrous hydrazine amounts on the phase structure, microstructure, and the electrochemical performance. In particular, a porous $\text{Co}_x\text{Ni}_{1-x}(\text{OH})_2$ disks@rGO nanocomposite delivered outstanding specific capacities, rate capability, and cycling stability. When coupled with a capacitive-type PPD/rGO electrode, the hybrid supercapacitor achieved superior energy and power density, and a stable cycling performance for 20,000 cycles at 20 A g^{-1} . The attractive electrochemical performance and simple preparation process make the hybrid supercapacitor a promising candidate for commercial applications. Furthermore, the unique architecture with porous micrometer-sized disks wrapped by rGO provides new insight into the design of better electrode materials. The facile preparation strategy further opens a general avenue to the development of cost-effective fabrication of high-performance supercapacitors based on transition metal hydroxides for many applications.

Supporting Information.

SEM images and XRD patterns of CNOH_a:_b; SEM, TEM images, N₂ adsorption–desorption results, TGA curves, XPS spectra and Raman results of CNOH1:1, -II, -III samples; CV curves of blank Ni foam; electrochemical performance of CNOH1:1-III without graphene; microstructure stability of CNOH1:1-III; cycling performance of the CNOH2:1, CNOH1:1, CNOH1:1-II; CV curves and rate performances of PPD/rGO and pure rGO; volumetric energy/power density of the CNOH1:1-III//PPD/rGO device; EDX analysis of Co_xNi_{1-x}(OH)₂-rGO; comparison of the cycling stability of the supercapacitors.

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Graphical Abstract