Bio-inspired synthesis of NaCl-type $\text{Co}_x\text{Ni}_{1-x}\text{O}$ ($0 \leq x < 1$) nanorods on reduced graphene oxide sheets and screening for asymmetric electrochemical capacitors†

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Received 20th February 2012, Accepted 24th April 2012

DOI: 10.1039/c2jm31057k

A bio-inspired approach has enabled the first synthesis of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ ($0 \leq x < 1$) nanorods on reduced graphene oxide (RGO) sheets. The key is the crystallization process from amorphous precursors in a disordered and hydrated state being able to take compositions arbitrarily different from that of the known stable mixed oxide NiCo_2O_4 . This success has permitted further screening of the compositions for electrochemical capacitors. $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposite electrodes achieve a peak specific capacitance when the Co/Ni molar ratio is close to 1. For example, $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposite electrode has exhibited a specific capacitance up to 823.0 F g^{-1} (based on the total active materials mass) and 909.4 F g^{-1} (based on the oxide mass) at 1 A g^{-1} , which are among the highest for Co/Ni oxides. Also revealed was their superior cycling stability compared to the $\text{Co}_3\text{O}_4/\text{RGO}$ and NiO/RGO nanocomposites, with a surprising increase of the specific capacity in the initial 100 cycles before flattening out. In addition, testing of $(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})//\text{RGO}$ asymmetric cells yielded an energy density up to 35.3 Wh kg^{-1} at a cell voltage of 1.5 V , much higher than those of the symmetric cells $(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})//(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})$ (20.2 Wh kg^{-1}) and RGO/RGO (4.5 Wh kg^{-1}). Even at a high power density of 3614.0 W kg^{-1} , the asymmetric cell could still maintain an energy density of 28.0 Wh kg^{-1} . There was only a $<4\%$ loss of the initial specific capacitance after 1000 cycles of charge/discharge at 2 A g^{-1} .

Introduction

Intensive efforts have recently been focused on searching for cheap transition metal oxides for electrochemical capacitor electrodes, such as MnO_2 ,^{1–4} Co_3O_4 ,^{5–7} NiO ,^{8–14} and their mixed versions,^{15,16} to replace RuO_2 due to the sheer high cost and rareness of the latter. NiCo_2O_4 is considered to be one of the most promising electrode materials among the oxides for electrochemical capacitors, largely due to its good electronic conductivity, at least two orders of magnitude higher than those of the monometallic NiO and Co_3O_4 , as well as its tendency to form a variety of high electroactive surface area nanostructures.^{17,18} This has been confirmed by the previous work of our group and Hu's group.^{15,16} However, the spinel crystalline NiCo_2O_4 is stoichiometric and has a molar ratio of Co/Ni fixed at $2 : 1$, and thus the study of the properties of Co/Ni oxides at other compositions has been out of reach, until now. In this regard, two thought provoking questions come to the fore: can we prepare $\text{Co}_x\text{Ni}_{1-x}\text{O}$ ($0 \leq x < 1$) nanostructures with a continuously variable x ? If the answer to that question was

“yes”, how would the variable compositions influence the supercapacitor properties? The present work is intended to address these questions.

It is instructive to weigh up why the stoichiometric Co/Ni ratio for a spinel crystal structure is fixed at $2 : 1$, *i.e.*, NiCo_2O_4 . What is important here are the two different asymptotic crystal structures of Co_3O_4 (spinel, $Fd3m$) and NiO (NaCl-type structure, $Fm3m$). Since Ni^{2+} ions can only replace Co^{2+} in the spinel structure, the stoichiometric formula NiCo_2O_4 is expected. On the other hand, Co^{2+} and Ni^{2+} could co-exist in any molar ratio in the NaCl-type crystal structure, leading to the possible formation of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ crystals. Single phase NaCl-type $\text{Co}_x\text{Ni}_{1-x}\text{O}$ compounds are usually prepared by physically mixing CoO and NiO at different molar ratios, which are then thermally treated for the cobalt and nickel ions to inter-diffuse, forming a homogeneous solid.^{19,20} By classical crystallization it is difficult, if not impossible, to obtain a single phase NaCl-type $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanocrystal in aqueous solution. Such single phase oxide nanocrystals, however, may be synthesized *via* an amorphous precursor pathway. We submit that appropriately chosen amorphous precursors in disordered states and with high solubility could allow the co-existence of Co^{2+} and Ni^{2+} in any molar ratio. The amorphous precursors could then be crystallized and thermally decomposed into single phase $\text{Co}_x\text{Ni}_{1-x}\text{O}$ (NaCl-type crystal structure) with various molar ratios of Co/Ni.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2jm31057k

Considering their relatively high theoretical specific capacitance, the transition metal oxides obtained so far have exhibited low specific capacitance in experiments largely due to the poor electrical conductivity and large crystallite size. So the way forward now should be to reduce the crystal size and increase the electrical conductivity. Efforts have been expended to increase the electrical conductivity by dispersing them into carbonaceous materials such as activated carbon, carbon nanotubes and most recently, graphene, which not only improve the conductivity, but also suppress the crystal size, thus improving the electrochemical capacitor performance. Graphene is a palpable choice owing to its excellent electronic conductivity and high theoretical surface area ($2630 \text{ m}^2 \text{ g}^{-1}$).^{21–23} Recently, Wang *et al.*²⁴ used positively charged Co–Ni layered double hydroxide nanosheets intercalated by *p*-amino-benzoate ions and negatively charged graphene oxide (GO) sheets as building blocks to construct their composite *via* electrostatic interactions. The subsequent thermal treatment led to the transformation of the layered double hydroxide nanosheets into spinel NiCo_2O_4 nanosheets followed by the reduction of graphene oxide to finally form the $\text{NiCo}_2\text{O}_4/\text{RGO}$ composite. However, NiCo_2O_4 was not directly tethered onto RGO, which hindered the electron transport from NiCo_2O_4 to graphene and hence limited the supercapacitor performance. To overcome this problem, we made direct use of the rich carboxyl and hydroxyl functional groups of graphene oxide as an organic matrix to tether the oxide nanoparticles in much the same way as in the biomineralization process.

In this work, we adopt and augment this bio-inspired method to directly disperse $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorods on RGO sheets, making it possible to tune the molar ratio of Co/Ni in a continuous fashion. This has allowed us to screen $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites for the electrodes of supercapacitors. We have found that the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites afford a maximum specific capacitance and excellent cycling stability as the Co/Ni molar ratio is close to 1, *e.g.* $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposites. To further amend the disadvantageously low energy densities of supercapacitors (normally $\leq 10 \text{ Wh kg}^{-1}$) compared to batteries, we tested an asymmetric cell configuration. This can raise the cell voltage (*V*) besides improving cell capacitance (*C*) and thereby boost the energy density more effectively according to the equation $E = 1/2 CV^2$.²⁵ Asymmetric electrochemical capacitors can provide a wider operating potential window than symmetric ones because they are composed of a battery-like Faradic electrode (as energy source) in addition to a capacitive electrode (as power source). For demonstration of principle, we use the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposites for the battery-like Faradic electrode and graphene for the capacitive electrode to compose the asymmetric cell, and this has extended the cell voltage to 1.5 V in an aqueous electrolyte, resulting in high energy density, high power density and excellent cycling stability all together.

Experimental

Preparation of $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{reduced graphene oxides (RGO)}$ nanocomposites

Graphite flakes (natural, ~ 325 mesh, Alfa Aesar), potassium permanganate (KMnO_4 , Riedel-de Haën), hydrogen peroxide solution (30 wt%, H_2O_2 , BDH), nickel chloride hexahydrate

($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Fisher), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), sodium hydrogen carbonate (NaHCO_3 , BDH), and hydrazine monohydrate (min. 98.0 wt%, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, Wako) were used without further purification. Graphene oxide (GO) sheets were prepared from natural graphite powder (Sigma-Aldrich) by oxidation with potassium permanganate according to the procedure reported by Hummers *et al.*²⁶ Then, GO sheets are dispersed in DI water at a concentration of $\sim 1 \text{ mg mL}^{-1}$. Firstly, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 40 mM NaHCO_3 are added into 90 mL of DI water. The total concentration of nickel and cobalt ions is 20 mM. The above solutions are flushed with gaseous CO_2 for 2 h to form a transparent solution. Then, 10 mL of GO solution is added into the transparent solution. After 24 h of stirring at room temperature, the precipitates are slowly formed, accompanied with the escape of CO_2 . Followed by hydrothermal treatment at 100°C for 12 h, 0.1 mL of N_2H_4 was then added into the above solution, and refluxed at 100°C for 10.0 h to partially recover the electrical conductivity of graphene. The precipitates were washed with DI water three times and dried by freeze drying. Finally, the products were thermally decomposed at 300°C at a heating rate of 5°C min^{-1} under an N_2 atmosphere for 3 h.

General materials characterization

The product morphologies were directly examined by scanning electron microscopy (SEM) using a JEOL JSM-6700F at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) observations were carried out on a JEOL 2010 microscope operating at 200 kV. X-Ray diffraction (XRD) was performed on a Philips PW-1830 X-ray diffractometer with $\text{Cu K}\alpha$ irradiation ($\lambda = 1.5406 \text{ \AA}$). The step size and scan rate are set as 0.05° and $0.025^\circ \text{ s}^{-1}$, respectively. Brunauer–Emmett–Teller (BET) surface areas were carried out on a Coulter SA 3100 surface area analyzer. X-Ray photoelectron spectroscopy (XPS) was measured on a Perkin-Elmer model PHI 5600 XPS system with a resolution of 0.3–0.5 eV from a monochromated aluminium anode X-ray source with $\text{K}\alpha$ radiation (1486.6 eV). X-Ray fluorescence spectroscopy (XRF) was carried out on a JEOL JSX-3201Z instrument to determine the Co/Ni molar ratio. Raman spectroscopy was carried out on a micro-Raman system (RM3000, Renishaw) with an Ar^+ laser (20 mW) and a Ge detector. Fourier transform infrared spectroscopy (FT-IR) was carried out with KBr discs in the region of $4000\text{--}400 \text{ cm}^{-1}$ on a Perkin Elmer (Spectrum one) spectrometer with a resolution of 4 cm^{-1} . Thermogravimetric analysis (TGA) was performed from 30 to 600°C on a TGA Q5000 (TA Instruments Ltd.) at a heating rate of 5°C min^{-1} under an air flow of 25 mL min^{-1} .

Electrochemical measurements

The working electrode was prepared with the active material, acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 80 : 10 : 10. The slurry was coated on graphite paper and dried under vacuum at 100°C for at least 12 h. The electrolyte used was a 1.0 M KOH aqueous solution. The capacitive performance of the samples was evaluated on a CHI 660D electrochemical workstation using cyclic voltammetry, chronopotentiometry, and A. C. impedance tests with

a three-electrode cell where Pt foil served as the counter electrode and Ag/AgCl (saturated KCl solution) as the reference electrode. To construct an asymmetric electrochemical capacitor, the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposite used for the positive electrode was prepared by mixing 80 wt% $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$, 10 wt% acetylene black, and 10 wt% PVDF binder, and the negative electrode was prepared by the same procedure with 90 wt% RGO and 10 wt% PVDF. The loading mass ratio of $(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})/\text{RGO}$ was estimated to be 0.46 from the specific capacitance in a three-electrode cell. The cyclic voltammetry and galvanostatic charge–discharge tests of the symmetric electrochemical capacitors (RGO//RGO, $(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})//(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})$) and the $(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})/\text{RGO}$ asymmetric electrochemical capacitors, separated by a cellulose acetate membrane with a pore size of 200 nm, were performed in a two-electrode cell at the 1.0 M KOH electrode.

The specific capacitance values were calculated from the galvanostatic charge and discharge curves, using the following equation: $C = (I\Delta t)/(m\Delta V)$, where I is the charge or discharge current, Δt is the discharge time, m indicates the mass of electroactive materials, and ΔV represents the voltage change after a full charge or discharge. The energy density (E_c) was derived from the discharge curve: $E_c = \int VdQ = \int Vd(It) = I \int Vdt$. The power density (P) was calculated from the following equation: $P = E_c/\Delta t$, where E_c is the energy density and Δt is the time for a discharge segment.

Results and discussion

Fabrication and characterization of $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites

Drawn in Fig. 1 is a flowchart for the bio-inspired growth of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanostructures on the RGO surface. As in the biomineralization of, for example, CaCO_3 , the first step here was intended to form amorphous Co–Ni salts on the surfaces of GO. In this process, Co^{2+} and Ni^{2+} cations were attached to the dense functional groups (such as carboxyl, hydroxyl, *etc.*) of GO sheets as the nucleation sites. Then, with the gradual escape of CO_2 , amorphous Co–Ni carbonate hydroxide precursors were gradually nucleated and uniformly grown on the GO surfaces with an increasing degree of supersaturation (Step I in Fig. 1). The subsequent Ostwald ripening process turned the amorphous precursors into a more ordered Co–Ni carbonate hydroxide nanostructure (Step II in Fig. 1). To bring back the electrical conductivity of graphene, the GO sheets were reduced into RGO sheets using hydrazine at 100 °C (Step III in Fig. 1). Finally, the Co–Ni nanomaterials were thermally decomposed under an N_2 atmosphere into the oxides with the original morphology conserved (Step IV in Fig. 1).

The Co^{2+} and Ni^{2+} aqueous solution containing GO was flushed with gaseous CO_2 for 2 h to form a supersaturated solution. Then, the Co–Ni salts gradually nucleated on the GO surfaces with the slow escape of CO_2 from the supersaturated solution. As can be seen from Fig. 2A and B, nuclei of less than 10 nm in size were fully and uniformly attached to the GO surface, forming a sandwich-like structure. The XRD profile (Fig. 2C) presents a broad featureless bump, suggesting that they are indeed in the amorphous phase. Furthermore, the FT-IR

Fig. 1 Schematic illustrating the formation process of $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites. (I) The dense carboxyl and hydroxyl groups of graphene oxide (GO) acted as the nucleation sites for amorphous precursors (purple color), which were formed upon the slow escape of CO_2 from the supersaturated solution. (II) The amorphous precursors were converted into ordered Co–Ni carbonate hydroxide nanorods (yellow color) in the subsequent Ostwald ripening process. (III) The GO was reduced to RGO to partially recover its electrical conductivity. (IV) The Co–Ni carbonate hydroxide nanorods were thermally decomposed into the target oxides (cyan color), forming the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites with the original rod morphology being conserved.

spectrum in Fig. 2D reveals some information about the composition. A band at 1620 cm^{-1} is attributable to the bending vibrations of water molecules.^{27,28} The bands at $1500\text{--}1400$, 1073 , 833 , and 687 cm^{-1} can be assigned to the ν_3 , ν_1 , ν_2 , and ν_4 vibration of carbonate ions, respectively. The bands at 742 cm^{-1} can be ascribed to the O–H bending mode of carboxyl groups,²⁹

Fig. 2 Characterization of amorphous Co–Ni carbonate hydroxide precursors/GO nanocomposites: (A and B) SEM images, (C) XRD pattern, and (D) FT-IR spectrum.

while that at 520 cm^{-1} can be assigned to the $\nu_{\text{M-O-H}}$ vibration.³⁰ Thus, the result proves that the amorphous Co–Ni carbonate hydroxide precursors have been nucleated at the dense functional groups of GO from the supersaturated $\text{Co}^{2+}/\text{Ni}^{2+}$ solution accompanied by the slow escape of CO_2 , in much the same way as the nucleation of amorphous CaCO_3 particles from a supersaturated $\text{Ca}(\text{HCO}_3)_2$ solution in mimicking the biomineralization process.

By the hydrothermal treatment at $100\text{ }^\circ\text{C}$ for 12 h, the amorphous precursors were transformed into more ordered crystalline nanorods. The nanorods are in the known $\text{Co}_x\text{Ni}_{1-x}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ phase (JCPDS 48-0083) as revealed by the XRD pattern in Fig. SI-1†. The SEM images in Fig. 3A and B show that the nanorods are densely and uniformly dispersed on the surfaces of GO. In confirming those SEM images, the TEM image in Fig. 3C provides a more detailed view about the dense and uniform dispersion of the Co–Ni carbonate hydroxide nanorods of around 10 nm in diameter on the GO surfaces. These nanorods appear to be single crystalline as visualized from the high-resolution TEM image in Fig. 3D. The lattice spacings of 0.25 and 0.29 nm match up well with the interplanar spacings of (040) and (300), respectively, suggesting that the nanorods grow along the [100] direction in much the same way as the needle-like cobalt carbonate hydroxide nanorods we reported previously.¹⁵ In the absence of CO_3^{2-} anions, Co^{2+} and Ni^{2+} ions reacted with hydroxides to form layered double hydroxide nanosheets.²⁴ However, in our case, upon the introduction of CO_3^{2-} anions, the Co^{2+} and Ni^{2+} ions coordinate with CO_3^{2-} and OH^- to form $\text{Co}_x\text{Ni}_{1-x}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$ nanorods from amorphous precursors. This suggests that the carbonate anions act to inhibit selectively the crystal growth in the direction of the side planes of the rods.^{31,32} The EDX patterns in Fig. SI-2† also verify the even and indiscriminative coverage of the Co and Ni elements within the nanorods.

Fig. 3 Structural characterization of $\text{Co}_x\text{Ni}_{1-x}(\text{CO}_3)_{0.5}(\text{OH})$ nanorods/GO nanocomposites, which are obtained from the amorphous Co–Ni carbonate hydroxide precursors after the Ostwald ripening process. (A, B) SEM images at different magnifications. (C, D) TEM and HRTEM images.

These nanocomposites were obtained after hydrazine reduction followed by thermal decomposition under N_2 atmosphere. This can be seen clearly from the XRD patterns in Fig. 4. The $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ nanorods have been converted to Co_3O_4 after releasing CO_2 and H_2O vapor in accordance with the standard pattern (JCPDS 65-3103). Interestingly, the decomposition of $\text{Co}_x\text{Ni}_{1-x}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ ($0 \leq x < 1$) resulted in $\text{Co}_x\text{Ni}_{1-x}\text{O}$, which from the XRD pattern is in the NiO phase (JCPDS 47-1049). In parallel, the underlying GO sheets have been reduced to RGO and this should at least partially restore the electrical conductivity of graphene. As shown in Fig. SI-3†, this was verified by the increased Raman D/G intensity ratio (1.70) of RGO (where D denotes the defect peak arising from inter-valley scattering and G refers to the graphene G peak) relative to that of the pristine GO (1.48), a signature of a decrease in the average size of the crystalline graphene domains during GO reduction but an increase in the number of GO sheets.³³

It is clear from the SEM and TEM images in Fig. 5 that the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites have inherited the nanorod morphology of the predecessor Co–Ni carbonate hydroxide. This is despite the fact that during the calcination process, much of the constituent material has been driven out in the form of CO_2 and H_2O gases. As a gratifying result, the $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorods are, in the same way as their predecessor, uniformly and densely distributed on the RGO surfaces (Fig. 5B and C). Even more incredible, the $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorods are grown along the [110] axis direction from the HRTEM image in Fig. 5D.

To gain further information on the structure and composition of the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites, we resort to X-ray photoelectron spectroscopy (XPS) measurements and the result is shown in Fig. 6. The high energy shoulder of the C 1s peak at 288.9 eV may be ascribed to COOR (Fig. 6A), while the high energy (532.0 eV) and low energy (530.0 eV) peaks in the O 1s XPS spectrum correspond to the O atoms in the RGO sheets and in the O–Co/Ni bonding structure, respectively.³³ With regards to the Co 2p XPS spectrum, there are two characteristic peaks at 780.6 and 790.8 eV, corresponding to the $2p_{3/2}$ and $2p_{1/2}$ spin-orbit peaks of Co^{2+} (Fig. 6C).^{19,34,35} The peaks at around 786.5 and 803.5 eV are associated with the shake-up type peaks of the $2p_{3/2}$ and $2p_{1/2}$ edges, respectively (Fig. 6C). Finally, our Ni XPS

Fig. 4 XRD patterns of the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites (JCPDS 65-3103: Co_3O_4 ; JCPDS 47-1049: NiO), which were formed by thermal decomposition of the carbonate hydroxide precursors.

Fig. 5 (A and B) SEM, and (C and D) TEM images of the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites.

Fig. 6 (A) C 1s XPS, (B) O 1s XPS, (C) Co 2p XPS, and (D) Ni 2p XPS of the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites.

spectrum has revealed that the main $2p_{3/2}$ peak is at 855.5 eV, which is close to 854.9 eV for Ni^{2+} but much lower than 857.1 eV for Ni^{3+} .^{19,36} Therefore, we are confident that Ni is in the divalent state. Also, there are two shake-up type peaks of nickel at the high binding energy side of the Ni $2p_{3/2}$ and $2p_{1/2}$ edge (Fig. 6D).

Table 1 summarizes some of the structural characteristics obtained for the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites. Notably, the molar ratios of Co/Ni in the oxides determined from the XPS and XRF results are almost the same as those added in the reactants. Note that the RGO contents in the nanocomposites were calculated from the TGA curves in Fig. SI-4†. The weight loss from 30 to 600 °C may belong to free water and RGO, since $\text{Co}_x\text{Ni}_{1-x}\text{O}$ compounds are stable during this temperature zone. Notice that before the TGA tests, the samples had been thermally treated at 300 °C under N_2 atmosphere to form the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ composites. Thus, the first weight loss was due to the escape of free water, and the second weight loss at >200 °C may be ascribed to the decomposition and combustion of RGO. According to this analysis, the mass percentages of RGO are 8.6

($\text{Co}_3\text{O}_4/\text{RGO}$), 8.7 ($\text{Co}_{0.76}\text{Ni}_{0.24}\text{O}/\text{RGO}$), 8.9 ($\text{Co}_{0.6}\text{Ni}_{0.4}\text{O}/\text{RGO}$), 9.5 ($\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$), 8.4 ($\text{Co}_{0.34}\text{Ni}_{0.66}\text{O}/\text{RGO}$), 11.5 ($\text{Co}_{0.17}\text{Ni}_{0.83}\text{O}/\text{RGO}$) and 11.2 wt% (NiO/RGO). Using the adsorption–desorption isotherms obtained from the Brunauer–Emmett–Teller (BET) measurements, the specific surface areas were calculated for the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites, and are listed in Table 1. The adsorption and desorption isotherms can be categorized as type II/IV (Fig. SI-5†), associated with the mesoporous structure.³⁷ The measured specific surface areas of the nanocomposites are all higher than those of the porous sea-urchin like NiCo_2O_4 we reported previously ($198.9 \text{ m}^2 \text{ g}^{-1}$).¹⁵ This has benefitted from the high surface area of the graphene sheets on which the $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanomaterials are grown. Moreover, by virtue of the dense functional groups of the GO sheets as the nucleation sites as well as by way of amorphous precursor transformation, the as-obtained $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorods are quite small in diameter (around 10 nm), only one-tenth of that in porous sea-urchin like NiCo_2O_4 . Next, the determined pore diameters in the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites span from 5 to 50 nm with an average of ~ 10 nm. Such a sheet–nanorod motif with a high specific surface area and different sized mesopores is auspicious for obtaining both a high main pseudocapacitance of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ and a high electric double-layer capacitance of graphene since the hydrate ions in the electrolyte can get easy access to the exterior and interior pore surfaces.³⁸

There are several prodigious features of the amorphous precursor approach for generating $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorods on graphene sheets. First, this approach can easily control the molar ratios of Co/Ni in the oxides, which are otherwise impossible to achieve by the conventional precipitation method. Since the amorphous Co–Ni carbonate hydroxide precursors are in a disordered state with high solubility, they allow the co-existence of Co^{2+} and Ni^{2+} in any possible molar ratio, which make their way into the final NaCl-type $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorod crystals. Second, graphene oxides with rich functional groups such as carboxyl and hydroxyl groups provide numerous nucleation sites for growing Co–Ni carbonate hydroxide directly on the surface. This tends to favor the formation of small sized nanocrystals, the Co–Ni carbonate hydroxide nanorods in our case here, in a solution of a given supersaturation.

Electrochemical characterization

Supercapacitor electrodes made of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorods/RGO nanocomposites. To test the supercapacitor performance, the electroactive $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites were deposited on graphite paper as the working electrode in a three electrode system. Cyclic voltammetry (CV) curves in Fig. 7A were obtained by sweeping the voltage from 0 to 0.5 V at a scanning rate of 5 mV s^{-1} . Distinctive pairs of redox peaks can be clearly observed in the anodic and cathodic waves sitting on a broad background. For example, the $\text{Co}_3\text{O}_4/\text{RGO}$ and NiO/RGO electrodes show redox peak pairs at 0.43 V/0.38 V and 0.39 V/0.29 V, respectively, ascribed to the redox couples of $\text{Co}_3\text{O}_4/\text{CoOOH}$ and NiO/NiOOH .¹⁵ The CV curves thus demonstrate that the capacitance of the nanocomposites is mainly derived from the pseudocapacitance with its root in the redox pairs of $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$, rather than purely the electric double-layer charging/discharging of RGO at the electrode/electrolyte interfaces. Compared with the

Table 1 Experimental data summary for the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites

Co/Ni molar ratio added in the reactants	Co/Ni molar ratio in the oxides ^a	Co/Ni molar ratio in the oxides ^b	RGO content (wt%)	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume (mL g^{-1})
1 : 0	—	—	8.6	204.2	0.58
4 : 1	0.76 : 0.24	0.78 : 0.22	8.7	202.7	0.50
2 : 1	0.60 : 0.40	0.64 : 0.36	8.9	209.9	0.79
1 : 1	0.45 : 0.55	0.47 : 0.53	9.5	226.8	0.70
1 : 2	0.34 : 0.66	0.37 : 0.63	8.4	226.6	0.55
1 : 4	0.17 : 0.83	0.19 : 0.81	11.5	287.4	0.57
0 : 1	—	—	11.2	272.7	0.53

^a The Co/Ni molar ratio in the oxides are determined by XPS results. ^b The Co/Ni molar ratio in the oxides are determined by XRF results.

Fig. 7 Electrochemical characterization of the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites in a three-electrode configuration. (A) CV curves. (B) Galvanostatic discharge curves at a current density of 1 A g^{-1} . (C) Specific capacitance as a function of charge–discharge current density. (D) Normalized specific capacitance versus cycle number at a galvanostatic charge–discharge current density of 10 A g^{-1} .

$\text{Co}_3\text{O}_4/\text{RGO}$ and NiO/RGO electrodes, the cathodic and anodic peaks of the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ electrodes are conspicuously broadened due to the interaction between the $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ redox pairs. Moreover, the peak current density increased as the molar ratio of Co/Ni in the oxides is close to 1, indicative of better charge transfer kinetics.^{18,39}

Shown in Fig. 7B are galvanostatic charge–discharge curves of the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites at a discharge current density of 1 A g^{-1} . Notably, the discharge curves also show characteristics of pseudocapacitance, in agreement with the CV curves. More interestingly, as the Co/Ni molar ratios are close to 1, the charge and discharge segments of the curves become more and more symmetrical, meaning that the charge/discharge processes tend to be more and more reversible towards those of the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposite. Moreover, the difference between the cathodic and anodic peak potentials gradually decreases, revealing a reversible trend of the redox reactions as the molar ratio of Co/Ni approaches 1, in consonance with the galvanostatic charge–discharge curves. The pseudocapacitance for each of these samples can be estimated from those curves. The total capacitance for the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ electrodes contains a contribution from the redox pseudocapacitance of cobalt and

nickel oxides coupled with the double-layer capacitances of cobalt and nickel oxides and RGO sheets, which is averaged as follows:

$$C_s = \frac{[m_{\text{Co}_x\text{Ni}_{1-x}\text{O}}(C_{\text{p,Co}_x\text{Ni}_{1-x}\text{O}} + C_{\text{dl,Co}_x\text{Ni}_{1-x}\text{O}}) + m_{\text{RGO}}C_{\text{dl,RGO}}]}{(m_{\text{Co}_x\text{Ni}_{1-x}\text{O}} + m_{\text{RGO}})}$$

where m_{RGO} and $m_{\text{Co}_x\text{Ni}_{1-x}\text{O}}$ are respectively the masses of RGO sheets and $\text{Co}_x\text{Ni}_{1-x}\text{O}$ in the electrodes, $C_{\text{dl,RGO}}$ and $C_{\text{dl,Co}_x\text{Ni}_{1-x}\text{O}}$ are their corresponding double-layer capacitances, and $C_{\text{p,Co}_x\text{Ni}_{1-x}\text{O}}$ is the pseudocapacitance of $\text{Co}_x\text{Ni}_{1-x}\text{O}$. In the actual case here, $C_{\text{dl,RGO}}$ and $C_{\text{dl,Co}_x\text{Ni}_{1-x}\text{O}}$ can be neglected compared with the dominant $C_{\text{p,Co}_x\text{Ni}_{1-x}\text{O}}$.

The specific capacitances of the series of $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites as a function of charge–discharge current densities are shown in Fig. 7C. Most obvious is the increasing order of the specific capacitance: $\text{Co}_3\text{O}_4/\text{RGO} < \text{Co}_{0.76}\text{Ni}_{0.24}\text{O}/\text{RGO} < \text{NiO}/\text{RGO} < \text{Co}_{0.17}\text{Ni}_{0.83}\text{O}/\text{RGO} < \text{Co}_{0.34}\text{Ni}_{0.66}\text{O}/\text{RGO} < \text{Co}_{0.60}\text{Ni}_{0.40}\text{O}/\text{RGO} < \text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$. In particular, the specific capacitance achieves the maximum value when the molar ratio of Co/Ni is close to 1, i.e., for the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposites, which obtained a specific capacitance up to 823.0 F g^{-1} (based on the total active material mass) and 909.4 F g^{-1} (based on the mass of the oxides) at a current density of 1 A g^{-1} . Referring to the CV curves in Fig. 7A, as the molar ratio of Co/Ni approaches 1, the redox peaks of the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposites are broadened and at the same time, the peak current density hits the highest point, resulting from the collective action of the redox pairs of $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$. As a result, the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposite exhibits the highest specific capacitance of all the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites we have tested. As usual, the specific capacitance decreases gradually with increasing current density (Fig. 7C) due commonly to (I) the limitation of electron/electrolyte transport and (II) the activation and concentration polarization, resulting in the low utilization of the electroactive materials. However, impressively, the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposites still has a specific capacitance of 643.3 F g^{-1} even at a current density of 10 A g^{-1} again due to its singular structural characteristics brought up above.

Cycle stability is another key parameter in relation to the electrochemical performance of a supercapacitor and relevant results are presented in Fig. 7D. Overall, bimetallic $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ ($0 < x < 1$) nanocomposites have better cycle stability performance than monometallic $\text{Co}_3\text{O}_4/\text{RGO}$ and NiO/RGO nanocomposites. Specifically, during the repetitive

charge–discharge processes at a current density of 10 A g^{-1} , $\text{Co}_3\text{O}_4/\text{RGO}$ and NiO/RGO nanocomposites have lost 3.0% and 7.0% of their initial specific capacitance, respectively. The bimetallic $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ ($0 < x < 1$) nanocomposites, on the contrary, actually gained specific capacitance in the initial 100 cycles, perhaps due to activation, and suffered no capacitance loss at all in the subsequent charge–discharge processes. As is known, the electrochemical cycle stability is closely related to the charge transfer kinetics and mechanical robustness of the electrode materials involved, *e.g.*, structural stability and flexibility and insolubility, *etc.*, under the electrochemical conditions.⁴⁰ The $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanocomposites, being of the same structure as NiO , are expected to be stable; their thermal stability has indeed been observed by their existence under the TGA conditions (Fig. SI-4†). More importantly, on top of the high conductivity of RGO introduced into the nanocomposites, the bimetallic $\text{Co}_x\text{Ni}_{1-x}\text{O}$ materials themselves exhibit much faster charge transfer kinetics than the monometallic oxides Co_3O_4 and NiO as will be demonstrated immediately below, further contributing to the cycle stability performance.

To understand the electrochemical performance characteristics of the $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanocomposites, we resorted to electrochemical impedance spectroscopy (EIS) carried out at open circuit potential with an ac perturbation of 5 mV in the frequency range of 1000 kHz–0.01 Hz. Fig. 8A shows the Nyquist plots thus obtained. The EIS data were fitted based on an equivalent circuit model consisting of bulk solution resistance R_s , charge-transfer resistance R_{ct} , double-layer capacitance C_{dl} , and Warburg resistance (W), and the result is shown in Fig. 8B. The bulk solution resistance R_s and charge-transfer resistance R_{ct} can be estimated from the intercepts of the semicircle with the real axis at high and low frequencies, respectively.^{41–43} A most striking difference lies in the semicircle corresponding to the charge-transfer resistance (R_{ct}) caused by the Faradic reactions and the double-layer capacitance (C_{dl}) on the grain surface. The slope of the linear portion of the curve on the right of the semicircle is called the Warburg resistance (W), which is a result of the frequency dependent ion diffusion/transport in the electrolyte

towards the electrode surface.⁴⁴ In this way, R_s of the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites is found to be around 2.4Ω , whereas R_{ct} decreases gradually from 5.83 (NiO/RGO) to 2.29Ω ($\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$) as the molar ratio of Co/Ni approaches 1. This clearly demonstrates that the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites display an increasingly favorable charge-transfer kinetics as the molar ratio of Co/Ni increases towards 1, in excellent agreement with the trend of their largely enhanced specific capacitances (Fig. 7C).

Asymmetric supercapacitor cells of $(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})//\text{RGO}$. The commonly low energy density of electrochemical capacitors could be improved in an asymmetric electrode scheme by combining a battery-like Faradic electrode (as energy source) and a capacitive electrode (as power source) so as to increase the operation voltage. Our $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposites with the highest specific capacitance are an ideal choice for the positive electrode of the asymmetric cell. In this regard, RGO could be used as the negative electrode. Fig. 9A shows a schematic of the assembled structure for such asymmetric electrochemical capacitors. To avoid damage of the cell under high-voltage levels during early cycles, it is necessary to polarize each electrode and thus to estimate the stable electrochemical windows before cycling the hybrid cell. Fig. 9B shows cyclic voltammogram (CV) measurements of these two electrode materials in a 1.0 M KOH aqueous solution using a three electrode system. The RGO and $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ electrodes are measured within a potential window of -1.0 to 0 V and 0 – 0.5 V vs. Ag/AgCl (sat. KCl) at a scan rate of 5 mV s^{-1} . The CV curve of the RGO electrode exhibits a nearly ideal rectangular shape, and no peaks for oxidation and reduction are observed, indicating a typical characteristic of electrical double layer capacitor (EDLC) behavior. Calculated from the discharge segments (Fig. SI-6†), the specific capacitances of RGO are 188.4, 147.9, 134.3, 125.9, 119.6, 99.8, and 83.2 F g^{-1} at a current density of 1, 2, 3, 4, 5, 10, and 20 A g^{-1} , respectively. The CV curve of the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ electrode in the potential range of 0 – 0.5 V vs. Ag/AgCl (sat. KCl), in a way different from that of the RGO EDLC, displays obvious redox peaks because the overall capacitance derives from the combined contributions of mainly the redox pseudocapacitance of $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}$ and in part the EDLC of RGO in the nanocomposites. From the CV curves measured in the three electrode configuration, the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ positive electrode displays an O_2 evolution potential of $>0.5 \text{ V}$ due to a large overpotential of positive polarization, and the RGO negative electrode also presents a H_2 evolution of $<-1.0 \text{ V}$ due to a large overpotential of negative polarization. Also, the two CV curves are slightly overlapped at around 0 V . Thus it is expected that the operating cell voltage of the $(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})//\text{RGO}$ (CNG//RGO) asymmetric capacitor can be safely extended to about 1.5 V in 1.0 M KOH solution from that of the symmetric RGO//RGO cell (1.0 V).

The CV and galvanostatic charge–discharge measurements were used to evaluate the stable electrochemical windows of the asymmetric cell and the results are shown in Fig. 10. Indeed, the stable electrochemical window has been expanded to 1.5 V . The high operating voltage of the asymmetric electrochemical capacitor is due to the perfect combination of the positive and negative potential stabilities of the two respective electrodes.

Fig. 8 (A) EIS Nyquist plots for the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposite electrodes. (B) Equivalent circuit diagram proposed for analysis of the EIS data in (A).

Fig. 9 (A) Layout of the asymmetric electrochemical capacitor consisting of the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposite as cathode and reduced graphene oxide as anode (inset: exploded view of the assembled asymmetric electrochemical capacitor); (B) CV curves of the reduced graphene oxide and $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ electrodes obtained in a three-electrode configuration in a 1 M KOH electrolyte solution (scan rate of 5 mV s^{-1}).

Fig. 10A shows a typical CV of the asymmetric electrochemical capacitor with a voltage of 1.5 V at various scan rates. In comparison with the CV curve of the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposites (Fig. 9B), the asymmetric electrochemical capacitor tends to show ideal capacitor behavior with a nearly rectangular CV shape. In keeping with that, the galvanostatic charge–discharge curves (Fig. 10B) exhibit potentials of charge–discharge that are nearly proportional to the charge or discharge time, another characteristic of an ideal capacitor. The specific capacitances, calculated from the galvanostatic charge–discharge curves at various current densities according to the equation ($C = I\Delta t/m\Delta V$), are 113.0, 111.1, 110.3, 106.5, 102.6, and 99.4 F g^{-1} at current densities of 0.5, 1, 2, 3, 4, and 5 A g^{-1} , respectively. Note that the specific capacitances are nearly 3 times those for the $\text{NiO}/\text{activated carbon (AC)}$ cell.^{45,46} Furthermore, the asymmetric electrochemical capacitor exhibits excellent cycling stability. After 1000 charge–discharge cycles, the specific capacitance incurs only less than 4% decay at a current density of 2 A g^{-1} (Fig. 10C). In contrast, the specific capacitance of the NiO/AC asymmetric cell has decreased by 50% after 1000 cycles.⁴⁶ Even for the $\text{MnO}_2/\text{graphene}$ nanocomposites/graphene asymmetric cell, after 1000 cycles, the specific capacitance only retained $\sim 79\%$ of the initial capacitance at a current density of 0.5 A g^{-1} .⁴⁷

Fig. 10 Electrochemical characterization of the $(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})//\text{RGO}$ (CNG//RGO) asymmetric electrochemical capacitor. (A) CV curves in a voltage range of 1.5 V at various scan rates; (B) galvanostatic charge–discharge curves at various current densities; (C) the cycle stability at a current density of 2 A g^{-1} ; and (D) Ragone plots of energy vs. power density of the CNG//RGO asymmetric capacitor and the $(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})//(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})$ (CNG//CNG) and RGO//RGO symmetric capacitors.

To facilitate the performance assessment of the CNG//RGO asymmetric electrochemical capacitors, Ragone plots relating the corresponding energy and power density are calculated from the galvanostatic discharge curves, in the range of current densities from 0.5 to 5 A g^{-1} (Fig. 10D). First of all, the maximum energy density obtained for the CNG//RGO asymmetric electrochemical capacitor is 35.3 Wh kg^{-1} , which is considerably higher than those of the symmetric electrochemical capacitors, $(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})//(\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO})$ (CNG//CNG) (20.2 Wh kg^{-1}), RGO//RGO (4.5 Wh kg^{-1}). This is a gratifying result of raising the cell voltage to 1.5 V by using the asymmetric cell architecture, besides the high specific capacitance of the $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ nanocomposite. Second, in comparison with some best performing MnO_2 -based asymmetric capacitors reported previously, *e.g.*, $\text{MnO}_2/\text{graphene}$ nanocomposites/graphene asymmetric capacitors,⁴⁷ the CNG//RGO cell enjoys a higher energy density, although the cell voltage (1.5 V) of the latter is lower than the former (2.0 V) due to the much higher specific capacitance of the positive $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ electrode, almost 4 times that of the MnO_2 -based asymmetric cell reported previously (31.0 F g^{-1} at a current density of 0.5 A g^{-1}). Moreover, this asymmetric electrochemical capacitor can still deliver an energy density of 28.0 Wh kg^{-1} at a high power density of 3613 W kg^{-1} , whereas the MnO_2 -based asymmetric cell only has an energy density of around 10 Wh kg^{-1} .

Several contributing factors can be considered for the high specific capacitance, remarkable rate capability and excellent cycle stability of the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites based electrochemical capacitors, especially the one based on $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$. First, in comparison with the monometallic oxides Co_3O_4 and NiO , the $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanocomposites, due to the introduction of Co or Ni, are superior in terms of their charge transfer kinetics.^{15–18} Second, the unique sheet–nanorod mosaic taken by the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites can effectively

forestall the aggregation of graphene and $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorods and consequently provide a high specific surface area and hierarchical mesoporous structure favorable for the migration of hydrated ions in the electrolyte to the surface of both the $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorods and graphene. Third, the excellent electrical conductivity of graphene can significantly decrease the internal resistance of an electrode by the construction of a conductive network. Finally, the adoption of the asymmetric configuration for the supercapacitors has widened the voltage window to 1.5 V and thus the energy density because the energy density of electrochemical capacitors is proportional to the square of the cell voltage. Thus, the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites characterized by the sheet–nanorod mosaic have rich redox reactions, excellent electrical conductivity, and fast electrolyte transportation, and consequently have achieved outstanding electrochemical capacitor performance, establishing them as viable positive electrodes for supercapacitors.

Conclusions

We have adopted a bio-inspired route to successfully synthesize $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorods around 10 nm in diameter from amorphous precursors on RGO sheets. The disordered and hydrated state of the amorphous precursors has allowed Co^{2+} and Ni^{2+} ions to co-exist in any molar ratio, enabling the synthesis of mixed oxide composites with variable Co/Ni molar ratios by a simple transformation from the amorphous precursors. These novel nanomaterials have provided the basis for electrochemical capacitor studies of this interesting system. Significantly, the specific capacitance is found to be dependent on the Co/Ni molar ratio, maxing out at a molar ratio of Co/Ni close to 1. Much to our surprise, not only are the cycle stabilities of the nanocomposite superior to that of monometallic NiO/RGO and $\text{Co}_3\text{O}_4/\text{RGO}$, but the specific capacitance is actually increased substantially in the initial 100 cycles, due to the cycling activation, and essentially suffers no decay in the following repetitive charge–discharge cycles of our tests. The asymmetric cell based on the positive electrode of $\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$ and the negative electrode of RGO has extended the cell voltage to 1.5 V and attained an energy density up to 35.3 Wh kg^{-1} , significantly higher than those of the symmetric ones ($\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$)/($\text{Co}_{0.45}\text{Ni}_{0.55}\text{O}/\text{RGO}$) (20.2 Wh kg^{-1}) and RGO/RGO (4.5 Wh kg^{-1}). The specific capacitance decayed by less than 4% after 1000 cycles at a current density of 2 A g^{-1} , which is superb in comparison to the best asymmetric cells reported previously such as $(\text{MnO}_2/\text{RGO})/\text{RGO}$ (around 21% decay after 1000 cycles at a current density of 0.5 A g^{-1}).⁴⁷ Thus, the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{RGO}$ nanocomposites with their facile synthesis enabled by our bio-inspired approach represent an excellent candidate for the replacement of rare and expensive supercapacitor materials such as RuO_2 , portending their applications in hybrid electric vehicles.

Acknowledgements

This work was supported by the HK-RGC General Research Funds (GRF no. HKUST 604809 and 605710) and the NSFC/HK-RGC Joint Research Scheme (N_HKUST609/09).

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