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## ARTICLE

# Electrodeposition of ultrathin nickel-cobalt double hydroxide nanosheets on nickel foam as high-performance supercapacitor electrodes

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The present work demonstrates a facile, one-step electrodeposition approach for the preparation of ultrathin Ni-Co double hydroxide (DH) nanosheets on Ni foam as supercapacitor electrodes. The as-prepared Ni-Co DH electrodes in the electrolyte with Ni/Co ratio of 4/1 deliver an ultrahigh specific capacitance of 3028 F g<sup>-1</sup> at 2 A g<sup>-1</sup> as well as very good cyclic stability probably due to their robust and well-defined nanoporous structure and amorphous nature. The Ni-Co DH nanosheets also present an impressive energy density of 127.22 Wh kg<sup>-1</sup> at 0.605 kW kg<sup>-1</sup>, and the value still remains 93.48 Wh kg<sup>-1</sup> at a high power density of 15.125 kW kg<sup>-1</sup>, indicating the excellent rate capability of these materials. In addition, the simple electrodeposition method involved in this study can potentially be scaled up for economic production of high performance supercapacitors.

## Introduction

Supercapacitors, which possess higher power density and longer cycling life than batteries, and also larger energy density than traditional capacitors, have been regarded as advanced energy storage systems as they fill the gap between batteries and capacitors.<sup>1</sup> Generally, supercapacitors can be divided into electrical double layer capacitors and pseudocapacitors. Electric double layer capacitors contain very limited specific capacitance since the electric energy is stored in the electrode/electrolyte interface.<sup>2</sup> Pseudocapacitors, in which the capacitance arises from interfacial reversible Faradic reactions, exhibit much higher energy density as compared to electric double layer capacitors.<sup>3, 4</sup> Transition metal oxides or hydroxides, like RuO<sub>2</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, NiO, Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, are commonly studied pseudocapacitive materials.<sup>5, 6</sup> For instance, RuO<sub>2</sub> is reported to exhibit very high capacitance and cyclic stability while suffering from high cost and limited availability.<sup>1</sup> By contrast, Ni(OH)<sub>2</sub> possesses low cost, high theoretical capacitance (up to 2358 F g<sup>-1</sup>) and low toxicity. It has been extensively studied recently as an emerging pseudocapacitive material.<sup>7, 8</sup> Nevertheless, the high capacitance of the Ni(OH)<sub>2</sub> is difficult to realize due to its poor electric conductivity which means that the redox reactions can only take place on the surface.<sup>9, 10</sup>

Recently, a family of layered 2D materials, metallic

double hydroxide (DH) nanosheets, have drawn increasing interest as promising electrode materials for supercapacitors because of their abundant slabs and electrochemically active sites, tunable composition, high redox activity, and environmentally friendly nature.<sup>5, 11, 12</sup> For example, by partly replacing Ni with other cations, the obtained Ni-X DHs (X could be Co<sup>13</sup>, Al<sup>14, 15</sup>, Fe<sup>16</sup>, Mn<sup>17</sup> or Ti<sup>18</sup>) usually present increased capacitance and enhanced cycle stability as compared with pristine Ni(OH)<sub>2</sub>. However, the practical application of metallic DHs is limited by their relative low mass diffusion and electron transfer rate which could bring drawbacks such as low rate capability and poor durability.<sup>19</sup> Therefore, some efforts have been done to improve the electrochemical performances of metallic DHs. First, by introducing highly conductive carbon materials, such as activated carbon, graphene and carbon nanotubes, the prepared metallic DHs-carbon hybrid materials are shown to have better performance than pure DHs.<sup>20</sup> Second, strategies also have been attempted to fabricate ultrathin metallic DH nanosheets with large specific surface area which can provide more active sites.<sup>21, 22</sup> Third, the 3D nanoporous structures with enlarged specific surface area and suitable mesopore distribution have been designed to improve the Faradic redox reaction and promote the mass transfer of electrolytes.<sup>23</sup> In addition, binder-free methods by directly depositing active materials on conductive substrates also have been mentioned.<sup>5, 24</sup> In spite of these advances, the metallic DH materials obtained with the above methods still find the limitations of either complex preparation process, unstable structure, poor rate capability or short cycle life.

In the present work, ultrathin Ni-Co DH nanosheets are prepared via a facile one-step electrodeposition method and then employed as supercapacitor electrodes. In contrast to most formerly reported methods for the fabrication of metallic DH

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nanosheets, this method requires neither special additives to produce hydroxide ions or trivalent cations, nor high temperature treatment processes. With a relatively low current density of  $-1 \text{ mA cm}^{-2}$  and a short time of only 5 min, Ni-Co DH nanosheets are uniformly deposited on Ni foam substrates in an aqueous solution containing Ni and Co cations. In comparison with previously reported metallic DHs, the materials produced in the current study have at least three advantages: (1) ultrathin Ni-Co DH nanosheets are vertically aligned on 3D porous Ni foam substrates forming a well-defined hierarchical nanostructure, which may provide a very high specific surface area and be beneficial for the mass diffusion and electron transport; (2) the Ni-Co DHs prepared here are amorphous, which has been reported to possess a comparable capacitance to crystalline ones but with much higher power density as well as better cycling stability;<sup>25</sup> and (3) no binder is needed since the active materials are directly grown on Ni substrate, therefore avoiding the electric conductivity decay caused by the resistance of binder.<sup>24</sup> As a result, the fabricated Ni-Co DH nanosheets as supercapacitor electrodes present very high specific capacitance, excellent rate capability, and long cycle life, which are superior to those of most formerly reported electrodes of Ni-based metallic oxides/hydroxides.

## Experimental

### Fabrication of Ni-Co DH nanosheets

Prior to electrodeposition, Ni foam, with a size of  $20 \times 12 \text{ mm}$ , was ultrasonically cleaned with ethanol and DI water and then dried in vacuum oven for 24 h. The electrodeposition of Ni-Co DHs was performed in a traditional 3-electrode electrochemical cell with Ni foam, Pt foil and Ag/AgCl as the working, counter and reference electrode, respectively. The electrolyte, prepared with DI water,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , contained 0.01 M metal ions with varied Ni/Co molar ratios. After immersing the clean Ni foam into the solution for 600 s, the electrodeposition was carried out with a constant current density of  $-1 \text{ mA cm}^{-2}$  for 300 s. The samples were then dried in vacuum oven for 24 h. The mass of the loaded active materials on Ni foam was obtained by the weight difference of the samples before and after deposition. Typically, the amount of the electrodeposited Ni-Co DHs on Ni foam in solution of Ni/Co (1/1) was about  $0.12 \pm 0.1 \text{ mg cm}^{-2}$ .

### Characterization

The X-ray photoelectron spectroscopy (XPS) spectra were detected by a Kratos Axis Ultra DLD spectrometry. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed with a TESCAN GAIA instrument. Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns were recorded with a JEOL JEM-2010 microscope. The X-ray diffraction (XRD) patterns were obtained by a Rigaku SmartLab X-ray diffractometer.

### Electrochemical measurement

The cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) measurements were carried out in 1 M KOH solution with a GAMRY Reference 3000 electrochemical workstation. The as-prepared Ni foam supported Ni-Co DHs was directly used as the working electrode, a Pt plate was employed as the auxiliary electrode, and Hg/HgO was selected as the reference electrode.

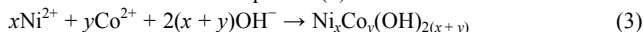
## Results and discussion

### Synthesis of Ni-Co DH nanosheets

In the aqueous solution of 1 mM nickel (II) and cobalt (II) nitrates, an electrochemical co-deposition of nickel and cobalt hydroxides is involved for the growth of Ni-Co DHs on Ni foam. As has been mentioned elsewhere, hydroxide ions are first produced at the electrode surface possibly through the reduction of  $\text{NO}_3^-$  (equation (1)) or  $\text{H}_2\text{O}$  (equation (2)).<sup>26, 27</sup>



Subsequently, the deposition of Ni-Co DHs on a Ni foam surface is carried out via equation (3):



The surface composition of the as-deposited materials on Ni foam was detected by XPS. From the typical survey XPS spectrum, it can be found that the formed materials are mainly composed of Ni, Co and O (Fig. 1a). The O 1s XPS spectrum can be divided into two small peaks, in which the main peak at around 531.1 eV is attributed to hydroxide groups ( $\text{OH}^-$ ),<sup>25, 28</sup> revealing the formation of metallic hydroxides (Fig. 1b). For the Ni 2p spectrum, the peaks at 873.5 eV in  $2\text{p}_{1/2}$  and 855.9 eV in  $2\text{p}_{3/2}$  is correspond to  $\text{Ni}^{2+}$  in Ni hydroxides (Fig. 1c).<sup>11, 25</sup> Similarly, the Co 2p XPS spectrum also has two peaks, which are both assigned to  $\text{Co}^{2+}$  (Fig. 1d).<sup>11, 25</sup> In short, the XPS measurements clearly show that the as-prepared materials on Ni foam are Ni-Co DHs.

**Figure 1**

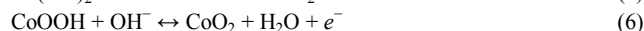
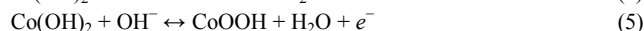
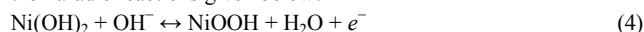
Fig. 2 shows the structure and surface features of the Ni-Co DHs formed with the Ni/Co feeding ratio of 1/1. The low magnification SEM image shows that the Ni-Co DHs are uniformly loaded onto Ni foam scaffold (Fig. 2a). Fig. 2b presents an enlarged image of the yellow square area marked in Fig. 2a. It can be found that ultrathin Ni-Co DH nanosheets, with the thickness only around 10 nm, are vertically aligned and inter-connected together on the substrate, forming nanoporous Ni-Co structures, with the pore size of about 100–200 nm. Similar surface features also can be found from the TEM images (Fig. 2c), in which these nanosheets are quite transparent, implying their ultrathin features. It is worth noting that similar rippled nanosheet structures can be also found for the Ni monometallic hydroxides formed in the solution containing only Ni ions (see Fig. S1a). The difference is that the nanosheets are much smaller for the Ni hydroxides, with the inter-pore size of only around 100 nm. With the increasing Co ratios in the solution, the fabricated nanosheets grow larger and larger (see Fig. 2b and Fig. S1b and c). In particular, Co monometallic hydroxides own the largest inter-pore size of about 500 nm (see Fig. S1d).

**Figure 2**

Fig. S2 presents the EDS mapping images of the Ni foam supported Ni-Co DH nanosheets. It can be found that both Ni and Co elements are uniformly distributed throughout the whole tested area, implying the homogeneous deposition of Ni-Co DHs over the Ni foam scaffold. The selected area electron diffraction pattern implies that the as-prepared Ni-Co DHs are amorphous (Fig. 2c). This can also be proved by the high resolution TEM images (Fig. 2d) in which no typical lattice fringes can be detected. Moreover, the XRD patterns exhibit only three diffraction peaks from the Ni foam substrate (Fig. S3),<sup>16</sup> further confirming the amorphous nature of the as-prepared Ni-Co DHs. Although most studies about the design of supercapacitor electrodes are based on crystalline metallic hydroxides, Li and co-workers, in recently published works, reported that amorphous mixed/mono-metallic hydroxides displayed enhanced capacitance and cycle stability as compared to the crystalline phases.<sup>29</sup> They proposed that the charge changing of metallic ions during charging/discharging would result in anisotropic electrostatic interactions, thereby reducing the structural stability of the crystalline metallic hydroxides. By contrast, for the amorphous phases, this kind of electrostatic force could be fully relaxed or released due to their disorderly nature. Therefore, the amorphous metallic hydroxides exhibited more stable electrochemical properties during long-term cycling.<sup>25, 29</sup>

#### Electrochemical performance of Ni-Co DH nanosheets

The electrochemical properties of the fabricated Ni-Co DHs as supercapacitor electrodes were measured by CV, galvanostatic charge/discharge and EIS. Fig. 3 presents the typical CV curves and galvanostatic charge/discharge curves of Ni foam supported Ni-Co DHs. A pair of redox peaks can be clearly found for the deposited Ni-Co DHs (Fig. 3a), indicating their strong pseudocapacitive behavior. As mentioned before, the redox peaks can be attributed to the Faradic reactions given below:



The obvious charge/discharge plateaus shown in Fig. 3b further demonstrates the pseudocapacitive nature of the electrodes. Also, the galvanostatic charge/discharge curves are symmetric, implying that the formed Ni-Co DH nanosheets have good electrochemical capacitive features. As can be found in the insert of Fig. 3b, the charge/discharge curve is still symmetric with clear plateaus even at a high current density of 50 A g<sup>-1</sup>, indicating the high stability of these materials.

**Figure 3**

Fig. 4 displays the comparison of electrochemical performances of Ni-Co DHs formed in the solution of different Ni/Co ratios, in which the effect of the Ni/Co feeding mole ratios on the properties of Ni-Co DHs can be investigated. As shown in Fig. 4a, the pure Ni hydroxides display a pair of high, narrow and well defined redox peaks in the potential range from 0.3 to 0.5 V. By adding a small amount of Co cations in the electrolyte, the redox peaks of the deposited materials turn lower but broader, which may mean an improved capacitance. Subsequently, with the increasing Co ratios in the solution, the anodic peaks of the formed metallic DHs clearly shift to more negative potentials, which is in agreement with previous studies.<sup>30</sup> In particular, the Co hydroxides present a couple

of small redox peaks at the potential range of 0.05 to 0.25 V. Moreover, the pristine Ni foam substrate also gives rise to a pair of redox peaks, but the peaks are very small and narrow, indicating that the substrate contributes little to the total capacitance of the hybrid electrodes. However, if the Ni foam was pretreated by hydrochloric acid before deposition as described elsewhere,<sup>16</sup> the induced CV peaks would be much higher and broader probably due to an activation process during the acidic pretreatment (Fig. S4a).<sup>30</sup> Thus the contribution of the substrate on the electrochemical performances of the Ni-Co DHs/Ni foam electrodes could not be ignored (Fig. S4b). In other words, if the purpose of the study is to evaluate the performances of only Ni-Co DHs, employing the HCl pretreated Ni foam substrates will bring exaggerated results.

Fig. S5 shows the galvanostatic charge/discharge curves at different current densities of Ni-Co DHs formed in solution with different Ni/Co ratios. The specific capacitance ( $C_s$ ) of the Ni-Co DHs can be obtained by the discharge curves using the following equation:<sup>31</sup>

$$C_s = I\Delta t/m\Delta V \quad (7)$$

where  $I$  represents the discharge current,  $\Delta t$  is the total discharge time,  $m$  is the mass of active material, and  $\Delta V$  represents the discharge potential range. The evolution of  $C_s$  with current density of Ni-Co DH nanosheets formed with different Ni/Co feeding molar ratios is displayed in Fig. 4b. The pure Ni hydroxides deliver a high  $C_s$  of 2540 F g<sup>-1</sup> at 2 A g<sup>-1</sup>, which is close to the results reported by Yang and co-workers.<sup>32</sup> The  $C_s$  values decrease fast as the current density increases, with only 1530 F g<sup>-1</sup> at 50 A g<sup>-1</sup>, implying poor stability of these materials. By adding a small amount of Co cations in the solution (with the Ni/Co ratios of 9/1), the  $C_s$  of the deposited DHs is clearly enhanced, but still decreases fast with increasing current density. The Ni-Co DH nanosheets formed in the solution of Ni/Co (4/1) present a very high  $C_s$  of 3028 F g<sup>-1</sup> at 2 A g<sup>-1</sup>. Moreover, the electrode is relatively stable as the employed current increases. At a high current density of 50 A g<sup>-1</sup>, it still presents a high  $C_s$  of 2225 F g<sup>-1</sup>, which is significantly higher than those of most previous studies (see Table S1), indicating excellent rate capability of these materials.<sup>12</sup> As the Co ratios in the solution continues to increase, the  $C_s$  values of the formed Ni-Co DHs decreases gradually. The Co hydroxides display the lowest  $C_s$  of only 1250 F g<sup>-1</sup> at 2 A g<sup>-1</sup>, but this capacitance decreases slowly as the current increases. It should be noted that the final compositions of the electrode material may not be as same as Ni/Co feeding ratios, however, the effects of Ni/Co ratio are clearly observed.

Fig. 4c shows the EIS Nyquist plots of Ni-Co DHs obtained with different Ni/Co feeding molar ratios in the frequency range of 200 kHz to 0.01 Hz obtained at the charging potentials of the electrodes. All the electrodes have similar EIS performances, with a semicircle at the high-middle frequency and a linear Warburg slope at the lower frequency. The former is related to charge-transfer processes of Faradic reactions and the latter reflects the ion diffusion resistance. It can be found that the charge-transfer resistance of the Ni-Co DHs is close to that of the Co hydroxides and much smaller than that of the Ni hydroxides, implying that the Co substitution favors fast electron transport.<sup>9, 10</sup> In addition, the Warburg curve of the Ni-Co DHs is more close to a vertical spike than pristine Ni hydroxides, which indicates that the introduction of Co can also improve the capacitive performance of the electrodes.<sup>13</sup>



The cycle stability of the Ni-Co DH nanosheets prepared with different Ni/Co feeding molar ratios is shown in Fig. 4d. It can be generally found that the pure Ni hydroxides present a poor cycle performance, while the Co hydroxides and Ni-Co DHs exhibit good stability. For the pure Ni hydroxides, although they show high capacitance, the  $C_s$  decreases fast after repetitive charge/discharge cycles, with only about 50 % capacitance left after 200 cycles. By contrast, the Ni-Co DHs electrode formed with the Ni/Co ratio of 4/1 exhibits the best capacitive performance among the different samples (Fig. 4b). It has a slowly decreasing  $C_s$  during charge/discharge cycling, with a retention of about 94 % after 2000 cycles. The cycle stabilities of the Co hydroxides and the Ni-Co DHs formed with Ni/Co ratio of 1/1 are even better, as the  $C_s$  values have practically no change after 2000 charge/discharge cycles.

The cycle performances of these electrodes can be partly explained by their surface morphology change (see Figs. S1 and S6). For the cycled Ni hydroxides, it can be seen that the nanosheets structures have been significantly destroyed, which may be the main reason for the observed poor cycling life (Fig. S6a). By contrast, after 2000 charge/discharge cycles, the Ni-Co DHs formed with Ni/Co of 4/1 still present a clear nanosheets structure (Fig. S6b). As for the cycled Ni/Co DHs grown with 1/1 Ni/Co molar ratios, the electrode shows clear and robust nanosheets structures (Fig. S6c) and has almost no change compared to the as-prepared materials (see Fig. 2b). The cycled Co hydroxides display a similar phenomenon (Fig. S6d), which is in good agreement with their high cycle stability.

In brief, the repetitive galvanostatic charge/discharge tests as well as the SEM images clearly show that the pristine Ni hydroxides have high capacitance while poor stability, and the doping of Co can effectively enhance its structural stability and thus cycle stability. To the best of our knowledge, this improvement can be attributed to two main reasons: (1) the introduction of Co can significantly improve the poor conductivity of pure Ni hydroxides (Fig. 4c),<sup>33</sup> and (2) the well-defined and robust nanosheet structures for the Ni-Co DHs are beneficial for the electron migration and mass diffusion during charging/discharging (see Fig. 2b).<sup>5</sup> It is worth noting that to prepare a stable Ni-Co DH electrode, immersing the Ni foam in the electrolyte for some time before electrodeposition is necessary. As shown in Fig. S7, the  $C_s$  of the Ni-Co DHs formed in Ni/Co (1/1) solution without an immersing process decreases gradually with the charge/discharge repeating, with only about 85 % remain after 2000 cycles, which is obviously not as stable as the electrode formed in the same condition but with a 10 min pre-immersing process (see Fig. 4d). SEM images also display that the nanosheet structures of the Ni-Co DHs formed without immersing are not as robust as that of the materials obtained with pre-soaking (see Fig. 2b, Fig. S6c, and Fig. S8). This may be because during the pre-immersing process, the sample surface can be fully wetted by the solution, making it ready for the growth of stable metallic hydroxide nanosheets.

**Figure 4**

Energy density ( $E$ ) and power density ( $P$ ) are another two important factors to evaluate the electrochemical performances of supercapacitor electrodes, in which  $E = (C_s U_0^2/2)$  and  $P = (E/\Delta t)$ , where  $U_0$  represents the potential at the end of charging.<sup>29</sup> Fig. 5 displays the specific energy and power density of Ni hydroxides, Co hydroxides, and Ni-Co DHs. It is obvious that the energy density of Ni-Co DHs is higher than that of the unitary Ni hydroxides and Co

hydroxides at a given power density. The Ni-Co DHs electrode presents a maximum energy density of 127.22 Wh kg<sup>-1</sup> at a power density of 0.605 kW kg<sup>-1</sup>, and the energy density remains a high value of 93.48 Wh kg<sup>-1</sup> with a high power density of 15.125 kW kg<sup>-1</sup>. Both of the results are higher than those of most previously reported Ni-based oxides/hydroxides (see Table S1).

**Figure 5**

## Conclusions

In summary, Ni foam supported Ni-Co DH nanosheets have been successfully prepared via a facile electrodeposition approach. The as-deposited Ni-Co DH nanosheets are ultrathin, vertically aligned and interconnected together on the substrate, giving rise to nanoporous structures. Subsequently, the as-prepared materials are employed as supercapacitor electrodes and tested by electrochemical methods, and the results reveal that the Ni-Co DHs present much better electrochemical performances than pristine Ni hydroxides or Co hydroxides. The Ni-Co DH electrodes obtained with the Ni/Co feeding molar ratio of 4/1 exhibit an ultrahigh specific capacitance of 3028 F g<sup>-1</sup> at 2 A g<sup>-1</sup> and an impressive energy density of 127.22 Wh kg<sup>-1</sup> at 0.605 kW kg<sup>-1</sup>, as well as very high rate capability and cycle stability. These results are significantly higher than other reported electrodes of Ni-based hydroxides/oxides. The high electrochemical performance of Ni-Co DHs electrodes could be attributed to their well-defined nanoporous structure and amorphous nature. The introduction of Co element also plays an important role. Moreover, for the reason that only a simple, versatile electrodeposition approach is involved, our study can potentially be employed for industrial scale preparation of high-performance supercapacitors.

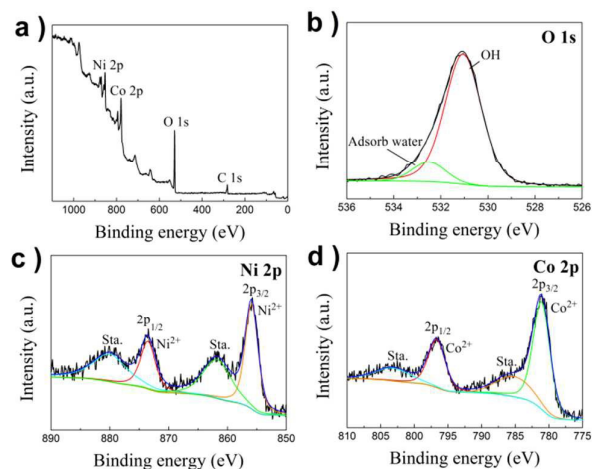
## Acknowledgements

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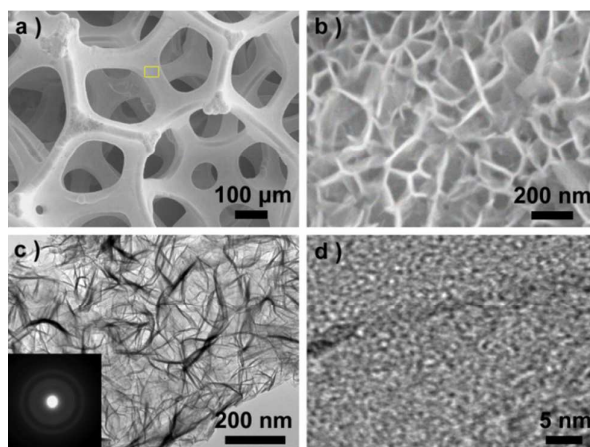
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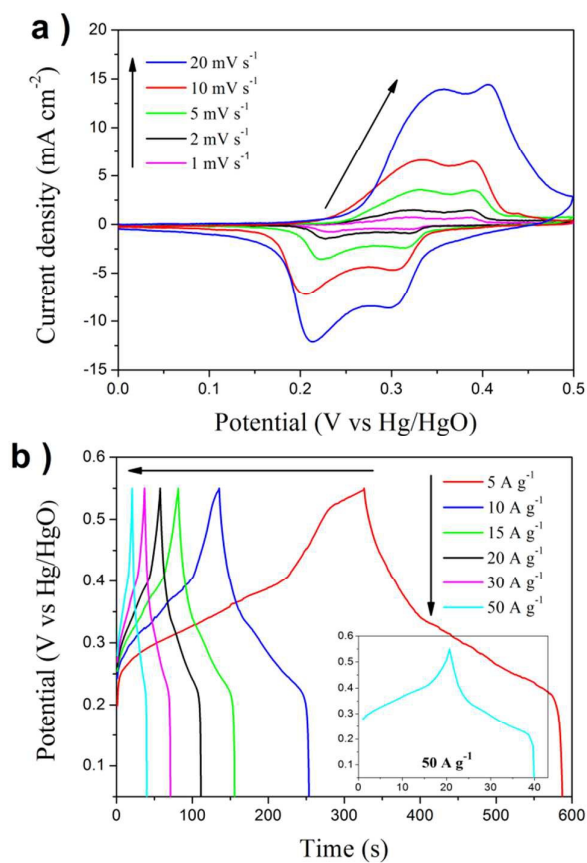


**Figure 1** XPS spectra of Ni-Co DHs formed in solution of Ni/Co (1/1): (a) survey, (b) O 1s, (c) Ni 2p, and (d) Co 2p.

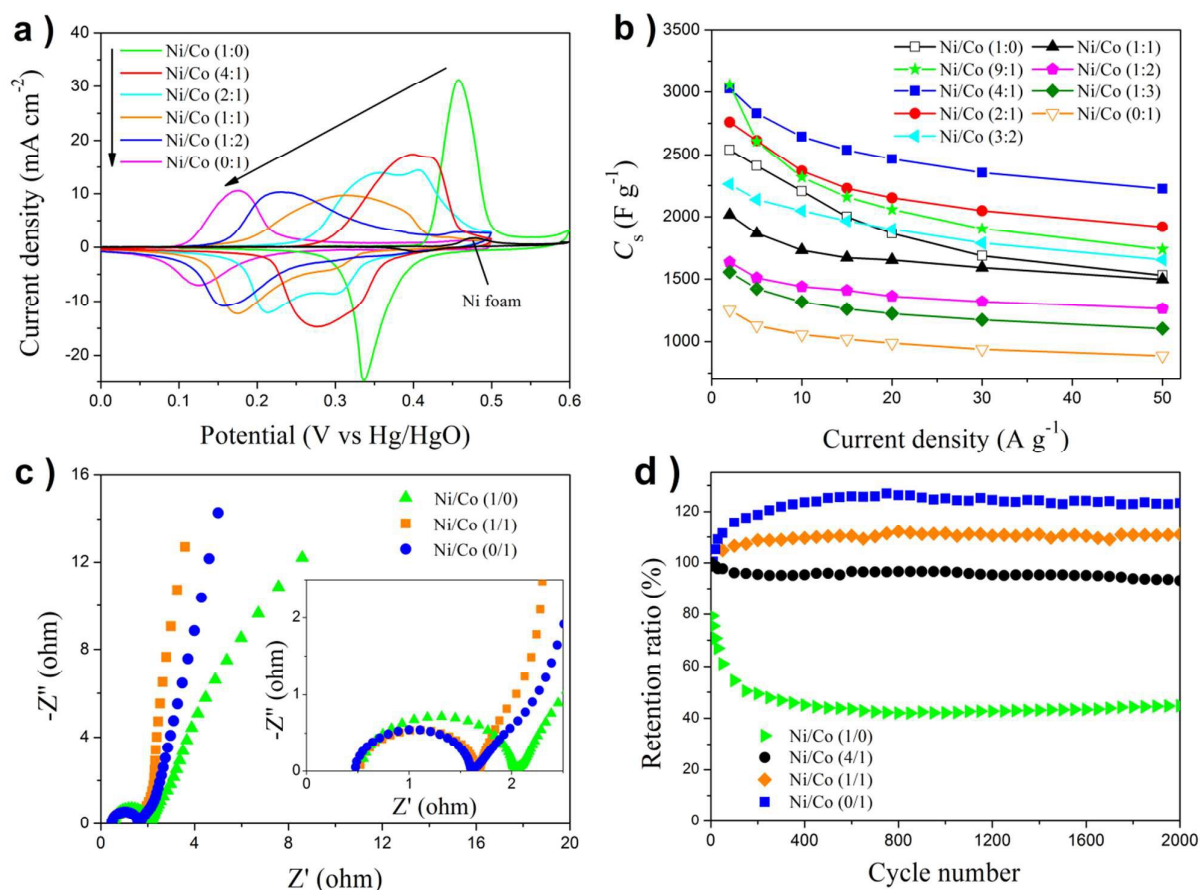


**Figure 2** Structure and morphology of Ni-Co DHs formed in Ni/Co (1/1) solution: (a) low and (b) high magnification SEM images of Ni-Co DH nanosheets supported on Ni foam, (c) low and (d) high resolution TEM images of Ni-Co DH nanosheets, the low-left inset in (c) represents the corresponding selected area diffraction pattern.

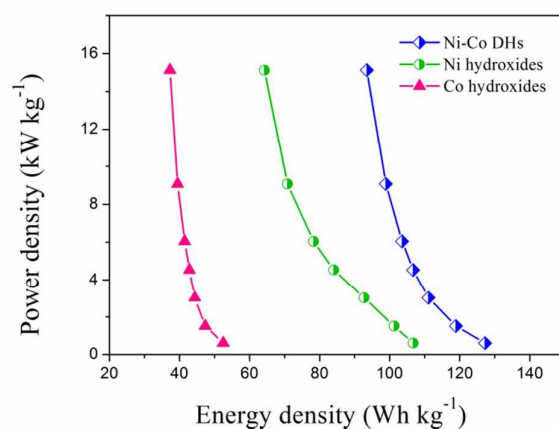




**Figure 3** (a) CV curves at different scanning rates and (b) galvanostatic charge/discharge curves at various current densities of Ni foam supported Ni-Co DHs fabrication in solution of Ni/Co (2/1).



**Figure 4** Electrochemical properties of Ni-Co DHs formed in solution with different Ni/Co ratios: (a) CV curves at scanning rate of  $20 \text{ mV s}^{-1}$ , (b) evolution of specific capacitance with discharge current density, (c) EIS Nyquist plots, and (d) galvanostatic cycling performance at current density of  $20 \text{ A g}^{-1}$ .



**Figure 5** Ragone chart of Ni hydroxides, Co hydroxides and Ni-Co DHs obtained from the galvanostatic charge/discharge tests, Ni-Co DHs are formed in solution with Ni/Co ratio of 4/1.