In-situ electrodeposition of bimetal Ni-Co selenides for high performance asymmetric supercapacitor

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Abstract: Transition-metal selenides have recently attracted increasing interest in supercapacitors (SCs) owning to their fascinating electrochemical properties. Here, binary metal selenides (NiCoSe2, NiCo2Se4, NiCo2Se4) are designed as novel electrode materials according to the reported NiSe and CoSe via a one-step electrodeposition process. The effects of different Ni/Co ratio on pseudo-capacitive properties of the binary metal selenides are investigated accordingly. Obviously, the designed binary metal selenides can combine the advantages of both metal selenides. As a result, the NiCoSe2 sample exhibits an optimized performance with a high specific capacity (334.2 mAh g\textsuperscript{-1}, 1 A g\textsuperscript{-1}), good rate capability, and excellent durability (90.7%, 5000 cycles). Most notably, the NiCoSe2//AC asymmetric SC (ASC) exhibits an excellent energy density of 41.7 Wh kg\textsuperscript{-1} at 800 W kg\textsuperscript{-1}. Hence, a variety of ions with complementary advantages can be combined by electrodeposition, which provides an efficient way to synthesize excellent materials with various properties.

1. Introduction
Rising environmental pollution and energy crisis let the development of new clean energy become an inevitable choice for the sustainable development of human society [1]. The so-called new clean energy mainly includes renewable energy such as nuclear energy, wind energy, solar energy. However, due to the uneven distribution of the above-mentioned new energy in the region or time, it is necessary to convert it into electric energy first, and then use it for different energy demand occasions. Supercapacitor (SC) is a type of electrochemical energy storage power supply with high power density, which is expected to become a new type of green power widely used in this century [1–3]. However, the low energy density still greatly hindered the large-scale application of SCs. Among the reported electro-active materials for SCs, metal selenides exhibit higher specific capacitance than carbon materials as well as better stability than conducting polymer materials, which are one of the most potential electrode materials for next generation supercapacitor with high energy density [4,5]. Especially, bimetallic Ni/Co based selenides which offer a rich set of physiochemical properties are highly intriguing for fundamental and technological research [6]. Plenty of studies have proved the synergy and complementary advantages of nickel and cobalt can greatly improvement the electrochemical performances of electrode [7–9]. Since the electrochemical performance of bimetallic
selenides is determinate to its composition, the reasonable adjusting the proportion of two metal elements in bimetallic compounds is becoming extremely important in development high performance SCs [10,11–13].

Herein, in this investigation, bimetallic selenides (NiCoSe$_2$, Ni$_2$CoSe$_4$, and NiCo$_2$Se$_4$) nanostructures are successfully deposited on skeleton of nickel foam (NF) through one-step electrodeposition strategy and directly serve as positive electrode in battery-type SCs. In-situ growth of Ni-Co binary selenides on NF can make the full utilization of materials and enhance the electric conductivity of the electrode. Results show that the Ni/Co ratio have a considerable influence on electrochemical performance of Ni-Co bimetallic selenides. In brief, Ni$_2$CoSe$_4$ delivers the highest specific capacity at 1 A g$^{-1}$, but suffers with inferior durability. While the NiCo$_2$Se$_4$ shows a totally different performance with a relatively low specific capacity but an excellent durability. Remarkably, the NiCoSe$_2$ electrode shows significantly improved performance with high specific capacity and superior rate capacity contrast with Ni$_2$CoSe$_4$ and NiCo$_2$Se$_4$ electrode. Moreover, all the Ni-Co bimetallic selenides are assembled into ASCs to investigate the practical application of our materials. This one-step electrodeposition strategy offers a highly efficient route to fabricate a wide variety of materials which have a combination of diversified complementary advantageous ions.

2. Experimental section

2.1 Materials
All of the chemical reagents were directly used without any further purification. Nickel (II) chloride hexahydrate puratrem (NiCl$_2$ 6H$_2$O), cobaltous chloride hexahydrate (CoCl$_2$ 6H$_2$O) and lithium chloride hydrate (LiCl H$_2$O) were purchased form Sinopharm Chemical Reagent Co. Ltd.. Selenium dioxide was from Shanghai Macklin Biochemical Co., Ltd..

2.2 Synthesis of nickel-cobalt selenide
The pre-treatment of NF was followed by our previous study [14]. The bimetallic Ni-Co selenides were deposited on NF through a three-electrode system in a CV rate of 5 mV s$^{-1}$ between –1.6 and 0 V for 2 cycles at room temperature in a solution containing NiCl$_2$ 6H$_2$O, CoCl$_2$ 6H$_2$O and SeO$_2$ with various molar ratio of 1:1:2, 2:1:4, and 1:2:4 respectively. 200 mg LiCl H$_2$O was dissolved in above solution as support electrolyte. NF, Pt foil and saturated calomel electrode were used as working, counter and reference electrode respectively. The achieved Ni-Co selenides were carefully washed with DI water and dried at 60 °C overnight. The mass loadings of NiCoSe$_2$, Ni$_2$CoSe$_4$, and NiCo$_2$Se$_4$ on NF were estimated to be 0.7, 1, and 2.5 mg cm$^{-2}$, respectively.

2.3 Characterization
Powder X-ray diffraction (XRD, D8 Advance, Bruker), energy dispersive spectral analysis (EDS) and X-ray photoelectron spectroscopy (XPS, AXIS Supra, KRATOS) tests were used to determine the crystal structure, quantitative distribution and electronic state of major elements in the fabricated NiCoSe$_2$, Ni$_2$CoSe$_4$ and NiCo$_2$Se$_4$ samples. Scanning electron microscopy (SEM, Phenom Pharos) was used to characterize the surface morphologies of the above samples.

2.4 Electrochemical Characterizations
The electrochemical performances of the NiCoSe$_2$, Ni$_2$CoSe$_4$ and NiCo$_2$Se$_4$ samples were investigated by CV, galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) and cycling performance in a three-electrode system with as-prepared electrodes as working electrode, Pt wire and Hg/HgO as counter electrode and reference electrode, respectively. Besides, a two-electrode configuration was carried out to determine the electrochemical performances of ASCs. All electrochemical measurements were conducted in a 3 M KOH electrolyte.
3. Results and discussion

Figure 1. (a) XRD patterns of NiCoSe2, Ni2CoSe4 and NiCo2Se4, (b-d) EDS patterns of NiCoSe2, Ni2CoSe4 and NiCo2Se4.

The crystal structures of the as-prepared samples were characterized by XRD measurements, as illustrated in Figure 1a. Notably, all samples for XRD test were collected from the powder peeled off from NF through ultrasonic. The XRD patterns of the Ni-Co bimetallic selenides can be respectively indexed to the hexagonal phase of NiCoSe2 (JCPDS No. 70-2851) [15], Ni2CoSe4 (JCPDS No. 04-006-5239) [16] and NiCo2Se4 (JCPDS No. 81-4821) [17]. To confirm the elemental ratio of each sample, EDS pattern of NiCoSe2, Ni2CoSe4 and NiCo2Se4 samples are performed in Figure 1b to c. The molar ratio of Ni:Co in the NiCoSe2, Ni2CoSe4, and NiCo2Se4 sample is 15.77:11.62, 20.25:13.26, and 10.16:22.04, which is very close to the stoichiometric ratio of 1:1, 2:1, and 1:2. All those results indicate that NiCoSe2, Ni2CoSe4, and NiCo2Se4 are confirmed on NF respectively.

Figure 2. XPS spectra of NiCoSe2, Ni2CoSe4, and NiCo2Se4: (a, d, and g) Ni 2p, (b, e, and h) Co 2p, (c, f, and i) Se 3d.
XPS was also carried out to gather information on the element compositions of NiCoSe$_2$ (Figure 2a–c), Ni$_2$CoSe$_4$ (Figure 2d–f), and NiCo$_2$Se$_4$ (Figure 2g–i) sample. For Ni 2p spectrum of NiCoSe$_2$ (Figure 2a), the peaks sitting at the binding energy (BE) of 856.9 and 874.0 eV can be attributed to Ni$^{2+}$ (Figure 2a) [18]. The peaks centering at BE of 797.9 and 782.1 eV in Co 2p spectrum (Figure 2b) are spin-orbit characteristic of Co$^{2+}$ [18]. The Se 3d of NiCoSe$_2$ deconvoluted into the pair of 3d$_{3/2}$ and 3d$_{5/2}$ peaks are the typical feature of metal-selenium bonds [18,19]. The additional peak in Se 3d spectrum was observed due to the oxidized selenium species (Se-O). The Ni 2p spectrum of Ni$_2$CoSe$_4$ is similar to that of NiCo$_2$Se$_4$, which shows that the Ni 2p$_{3/2}$ (~856.3 eV) and Ni 2p$_{1/2}$ (~874.1 eV) with two shakeup satellites at ~863.3 and ~880 eV, suggesting the existence of Ni$^{2+}$ (Figure 2d and g) [19]. The peaks at ~858.9 and ~876.4 eV is exclusively characteristic of Ni$^{3+}$. In the Co 2p spectrum (Figure 2e and h), the peaks at 776.9/797.4 eV and 782.1/800.5 eV demonstrate the coexistence of Co$^{3+}$ and Co$^{2+}$ states in Ni$_2$CoSe$_4$ and NiCo$_2$Se$_4$ [20]. Obviously, the Se 3d spectrum of Ni$_2$CoSe$_4$ and NiCo$_2$Se$_4$ is similar to that of NiCoSe$_2$ sample.

![Figure 3. (a to c) SEM images of NiCoSe$_2$, Ni$_2$CoSe$_4$ and NiCo$_2$Se$_4$ (the insets are the SEM images at low magnification).](image)

Interestingly, the synthesized NiCoSe$_2$, Ni$_2$CoSe$_4$ and NiCo$_2$Se$_4$ samples reveal a totally distinct morphology. SEM image of the deposited NiCoSe$_2$ sample showed that they were a granular, rough film with nanoflake-like morphology. Besides, both of the Ni$_2$CoSe$_4$ and NiCo$_2$Se$_4$ samples exhibit spheres-like structures. However, the sphere size of Ni$_2$CoSe$_4$ and NiCo$_2$Se$_4$ is quite different. Clearly, the sphere size of the former one is larger than that of the latter. It is suggested that high specific surface area and good porosity play an important role in formation massive electroactive sites and simplifying ion transportation for electrochemical reactions [21]. Therefore, the NiCoSe$_2$ sample is expected to illustrate an exceptional electrochemical performance.
Figure 4. Comparison electrochemical performance of NiCoSe\(_2\), Ni\(_2\)CoSe\(_4\) and NiCo\(_2\)Se\(_4\): (a) CV curves at 50 mV s\(^{-1}\), (b-d) the corresponding linear calibration plot between redox current vs. square root of scan rate, (e) contribution ratio of capacitive process to cathode capacity, (f) GCD curves at 5 A g\(^{-1}\), (g) Rate capacity, (h) Nyquist plots, and (i) cycling performance at 5 A g\(^{-1}\).

Figure 4 show the comparative electrochemical performances of as-deposited NiCoSe\(_2\), Ni\(_2\)CoSe\(_4\) and NiCo\(_2\)Se\(_4\) electrodes. All CVs in Figure 4a deliver a pair of redox peaks during anodic and cathodic sweeps, demonstrating the Faradaic redox reactions dominate the capacity characteristics of these materials [22]. The anodic peak of Ni\(_2\)CoSe\(_4\) however, shift to higher potentials unlike that of NiCo\(_2\)Se\(_4\). This may be due to the high Ni concentration in Ni\(_2\)CoSe\(_4\) electrode, which contributes to the inherent electrochemical response to the electrolyte [23,24]. The linear relationships between square root of scan rate and redox peak current in Figure 4b to d are clearly demonstrated that the kinetic process of our Ni-Co selenide electrodes followed the diffusion-controlled process [25]. However, the higher contribution by capacitive process well explains NiCoSe\(_2\) electrode’s superior rate capability (Figure 4e) [26]. Figure 4f exhibits the comparative GCDs of as-synthesized electrodes at 1 A g\(^{-1}\). A pair of obvious voltage plateaus in each GCD curve can be observed, which originate in the adsorption/desorption of OH\(^-\) between the electrode and electrolyte interface. A high specific capacity of 337.8 mAh g\(^{-1}\) is derived from the Ni\(_2\)CoSe\(_4\) electrode at 1 A g\(^{-1}\). This value is higher than that of the NiCoSe\(_2\) (334.2 mAh g\(^{-1}\)) and NiCo\(_2\)Se\(_4\) (266.7 mAh g\(^{-1}\)) electrode, respectively. However, a significance specific capacity decrease of Ni\(_2\)CoSe\(_4\) electrode can be found when the current density is up to 5 A g\(^{-1}\) (Figure 4g). Instead, the NiCoSe\(_2\) and NiCo\(_2\)Se\(_4\) electrode shows a satisfied rate capacity with 94.7% and 91.2% capacity retention from 1 to 5 A g\(^{-1}\) respectively, indicating that the Ni/Co ratio has a significant influence on the rate performance of the Ni-Co selenides.

Figure 4h shows the Nyquist plots of the synthesized samples. Obviously, the EIS spectra are similar in form. It can be clearly seen from the enlarged view of Nyquist plots that the semicircle of Ni\(_2\)CoSe\(_4\) electrode is much smaller than that of NiCo\(_2\)Se\(_4\) electrode, which indicates that the charge transfer resistance (R\(_{ct}\)) can be greatly reduced by Ni ions. In the low-frequency range, the line slope of NiCo\(_2\)Se\(_4\) electrode is higher than that of Ni\(_2\)CoSe\(_4\) electrode, signifying that Co ions are helpful to accelerate the charge transfer and interface ion absorption/desorption rate. Long cycle ability is used to evaluate the practical application of as-prepared samples. As shown in Figure 4i, after 5000 cycles, the NiCoSe\(_2\) electrode still dominated much higher specific capacity than the Ni\(_2\)CoSe\(_4\) and NiCo\(_2\)Se\(_4\) electrode. Meanwhile, a superior cycling stability can find in NiCo\(_2\)Se\(_4\) electrode, which means a higher Co content in Ni/Co bimetallic selenides contribute to well durability. The difference in the effects Ni/Co ratio in binary metal selenides on their pseudocapacitance are probably due to the fact that Ni and Co possess different redox reaction mechanisms [27,28]. The single-metal-component (Ni-based) materials always display a high specific capacity, but their cycle stability and rate performance are relatively low, while the Co-based single-metal-component has a relatively better rate performance and cycle stability with a lower capacity. Meanwhile, Ni element in NiCo\(_2\)Se\(_4\) and Co element in Ni\(_2\)CoSe\(_4\) are often in a lower valence state and are more likely to have a strong direct contribution to the pseudocapacitance performance of the bimetallic selenides [29,30]. As a result, Ni\(_2\)CoSe\(_4\) electrode possess of a higher specific capacity than NiCo\(_2\)Se\(_4\) electrode, but its rate capacity and cycle stability are poor than the latter one. Compared with Ni\(_2\)CoSe\(_4\) and NiCo\(_2\)Se\(_4\) electrode,
NiCoSe₂ exhibits an optimized electrochemical performance with high specific/rate capacity and excellent durability due to both of the Ni and Co ions in NiCoSe₂ are in a lower valence state.

Based on above analysis, NiCoSe₂//AC, Ni₂CoSe₄//AC and NiCo₂Se₄//AC ASC were fabricated to further evaluate the electrochemical capability of the binary metal selenides. Owning to the impact of AC electrode in ASC, CV curves of the ASC exhibit both pseudocapacitive and double-layer behaviors with no obvious deformation at a high working voltage of 1.6 V (Figure 5a). At 50 mV s⁻¹, Ni₂CoSe₄//AC ASC exhibits a much larger integral area than NiCoSe₂//AC and NiCo₂Se₄//AC, which is in agreement with the results of three-electrode cell. The CVs and GCDs of the as-assembled NiCoSe₂//AC were measured in a series of test condition, as shown in Figure 5b and c. Obviously, with the increase of scan rates, the shape of the CVs is remained almost the same shape, manifesting wonderful rate performance of this ASC device [20]. Meanwhile, the GCDs collected at various current densities show good symmetry, indicating its satisfied rate performance. The comparison results of specific capacitance in Figure 5d demonstrate the NiCoSe₂//AC and NiCo₂Se₄//AC ASCs own a superior rate efficiency of about 82.7% and 81.4% respectively with the current density increased from 1 to 5 A g⁻¹ respectively, which are much higher than that of Ni₂CoSe₄//AC ASC (68.5%) at the same test condition. The Ragone plot of the ASCs in Figure 5e shows that the specific energy density of Ni₂CoSe₄//AC ASC up to 45.4 Wh kg⁻¹ at 800 W kg⁻¹. However, it decreased rapidly with 31.1 Wh kg⁻¹ at 4000 W kg⁻¹. Conversely, the NiCoSe₂//AC and NiCo₂Se₄//AC ASC also delivers a high energy density of 41.7 Wh kg⁻¹ and 34.8 Wh kg⁻¹ at 800 W kg⁻¹ respectively, and even maintaining 34.6 Wh kg⁻¹ and 28.3 Wh kg⁻¹ at 4000 W kg⁻¹, which means both of the NiCoSe₂//AC and NiCo₂Se₄//AC own good rate capability. Meanwhile, the trend of specific capacitance retention after 10000 cycles is: NiCo₂Se₄//AC > NiCoSe₂//AC > Ni₂CoSe₄//AC, which intuitively confirms the active materials with a high Co content is more conducive to durability.

4. Conclusion
In a word, based on the advantages and disadvantages of common nickel/cobalt selenide electrode materials, the bimetallic selenides (NiCoSe₂, Ni₂CoSe₄ and NiCo₂Se₄) were designed and fabricated by one-step electrodeposition process. Through the characterization and systematic study of the pseudocapacitance performance of the above materials, we found that the Ni/Co ratio can greatly impact Ni-Co bimetallic selenides’ electrochemical performance. Obviously, NiCoSe₂ with a Ni/Co ratio of 1:1 exhibits an optimized electrochemical performance in terms of a relatively high specific
capacity, superior rate capability and satisfied cyclic stability, illustrating the best synergistic effect between Ni and Co elements. This work shows that the electrodeposition process can be used as an effective way to fabricate electro-active materials with multi-components for high performance energy storage devices, and adjusting the component of electro-active materials is a practicable strategy to optimize the electrochemical properties of electro-active materials.

Acknowledgments
This work was financially supported by the National Key Research and Development Program of China (Grant No.2017YFA0701001).

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