# Scalable CNTs/NiCoSe<sub>2</sub> Hybrid Films for Flexible All-Solid-State Asymmetric Supercapacitors

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Cite This: https://doi.org/10.1021/acsami.1c15392 ACCESS | Ind Metrics & More I Article Recommendations Supporting Information ABSTRACT: The rapidly developing wearable flexible electronics makes the development of high-performance flexible energy storage devices, such as all-solid-state

ment of high-performance flexible energy storage devices, such as all-solid-state supercapacitors (SCs), particularly important. Herein, we report the fabrication of CNTs/NiCoSe<sub>2</sub> hybrid films on carbon cloth (CC) through a facile co-electrodeposition method based on flexible electrodes for all-solid-state SCs. The NiCoSe<sub>2</sub> sheets grown on CNTs uniformly with a diameter of 50–100 nm act as the active materials. The CNTs in the hybrid films act as the scaffold to offer more deposition sites for NiCoSe<sub>2</sub> and provide a conductive network to facilitate the transfer of electrons. Moreover, the one-step electrodeposition process avoids the usage of any organic binders. Benefiting from the high intrinsic reactivity and unique 3D architecture, the obtained CNTs/NiCoSe<sub>2</sub> electrode delivers high specific capacity (218.1 mA h g<sup>-1</sup>) and satisfactory durability (over 5000



cycles). Remarkably, the CNTs/NiCoSe<sub>2</sub>//AC flexible all-solid-state (FASS) ASC provides remarkable energy density (112.2 W h kg<sup>-1</sup>) within 0–1.7 V and maintains 98.1% of its initial capacity after 10,000 cycles. In addition, this flexible ASC device could be fabricated at a large scale ( $5 \times 6 \text{ cm}^2$ ), and the LED arrays (>3.7 V) can be easily lighted up by three ASCs in series, showing its potential practical application.

KEYWORDS: CNTs/NiCoSe<sub>2</sub>, hybrid electrode, synergistic effect, electrodeposition, all-solid-state, asymmetric supercapacitor

## 1. INTRODUCTION

The booming market of smart wearable and integrated electronics, such as electronic skins, smart textiles, flexible displays, and personal health monitoring, has stimulated the demand for flexible energy storage devices.<sup>1-3</sup> SCs, as one of the commercial power sources, play an increasing significant role in wearable and integrated devices due to their exceptional power density and high cycle efficiency up to a million cycles.<sup>4-6</sup> It is well known that Faraday pseudocapacitors can provide much higher energy density than electric double-layer capacitors (EDLCs) due to different energy storage mechanisms.<sup>7-9</sup> In the past decades, lots of transition metal compounds have been widely exploited as pseudocapacitor materials to achieve high capacitive performance. However, poor electrical conductivity and low rate performance limit the full play of their theoretical capacitance.<sup>10</sup> Recent experimental and theoretical investigations reveal that the performance of SCs depends to a large extent on the structures and properties of electrode materials. Herein, choosing proper active materials and designing rational electrode structure are the two feasible strategies to acquire peak performance for SCs.<sup>11</sup>

As one group of emerging multifunctional materials, metallic selenides have been extensively studied and applied in various electrochemical reactions such as SCs,<sup>12–15</sup> water electrolysis,<sup>16</sup> and rechargeable batteries,<sup>17,18</sup> owing to their high theoretical capacity, ease of chemical bonding, and superior metallic characteristics. For example, three-dimensional hier-

archical nanostructured GeSe2 was fabricated by Shen and coworkers via a simple thermal evaporation method delivering a high specific capacitance of 300 F g<sup>-1</sup> at 1 A g<sup>-1</sup>.<sup>12</sup> As high as 933  $Fg^{-1}$  at 1 Å  $g^{-1}$  is achieved for nickel selenide spheres.<sup>19</sup> Bamboo-like CoSe<sub>2</sub> arrays exhibit a high specific capacitance of 544.6 F  $g^{-1}$  at 1 mA cm<sup>-2</sup>.<sup>20</sup> Compared with monometallic selenides, the introduction of the second metal atoms endows bimetallic selenides a higher electrochemical performance.<sup>21</sup> Until now, a series of bimetallic selenides have been reported as the cathode for SCs.<sup>14,22,23</sup> Among them, Ni/Co bimetallic selenides attracted tremendous attention and were studied extensively for advanced SCs due to their multifarious valences, satisfied electrochemical activities, attractive electrical conductivity, and high theoretical specific capacity.<sup>24,25</sup> For example, NiCoSe<sub>2</sub> nanorods on Ni foam show a high areal capacity of 1.4 mA h cm<sup>-2</sup> at 3 mA cm<sup>-2</sup>. NiCoSe<sub>2</sub> nanoflakes on Ni form via electrodeposition that was reported by us can reach 485 mA h g<sup>-1</sup> at 2 A g<sup>-1.26</sup> In Ni–Co bimetallic selenides, multiple redox-active sites will be formed by the coexistence of both Ni and Co atoms. Specially, a higher

Received: August 12, 2021 Accepted: October 21, 2021





Figure 1. Schematic illustration for the growth of CNTs/NiCoSe<sub>2</sub> hybrid films on CC.

electronic conductivity will be realized due to the covalent interaction between the orbital overlapping of Ni 2d, Co 2d, and Se 3p. It is mainly due to the different valence electrons with different spin configurations in both Ni and Co atoms, which make the valance interaction between the above two transition metal atoms possible.<sup>27,28</sup> However, the inefficient surface contact between bimetallic selenides and conductive substrate always leads to only partial bimetallic selenides participating in the energy storage process and thus inevitably dwarf the capacitive and rate capability of the electrode. To further improve the electronic conductivity and utilization of active materials, samples with various morphologies, especially grown on the conductivity scaffold, have been synthesized and reported.<sup>13,23,29</sup> Especially, carbon nanotubes (CNTs) can be used as both current collectors and supporters for the construction of a high-performance electrode because of their intrinsic properties of high specific surface area, outstanding stability, and superior conductivity.<sup>30,31</sup> For example, powder NiSe2@CNTs deliver a high rate performance with 92% capacitance retention when the current density increased from 1 to 10 A  $g^{-1}$ .<sup>13</sup> NiCoSe<sub>2</sub> lamella arrays on N-CNTs were also reported with a specific capacitance of 1308 F  $g^{-1}$  at 1 A  $g^{-1}$ .<sup>32</sup> Despite these exciting advances, fabrication of transition metal selenide-based electrodes that integrate superb electronic conductivity and high utilization rate of the whole materials by a sample process remains an enormous challenge.

Consequently, we reported a co-electrodeposition process to generate self-supported CNTs/NiCoSe<sub>2</sub> hybrid films on carbon cloth (CC). The CNTs/NiCoSe<sub>2</sub> hybrid films were directly grown on CC, which could form a strong combination between active materials and the substrate and induce efficient electron transport.<sup>33</sup> "Dead surface" of active materials caused by using the polymer binders was also addressed effectively. As a result, the CNTs/NiCoSe<sub>2</sub> electrode with rich active sites and high conductivity delivers enhanced reversibility, improved stability, and excellent bifunctional activity. The CNTs/ NiCoSe<sub>2</sub>//AC FASS ASC achieves a high power density of 8.5 kW kg<sup>-1</sup> and an excellent energy density of 112.2 W h kg<sup>-1</sup> and reserves a superior durability of 98.1% after 10,000 cycles. Notably, this ASC can be scaled up into  $5 \times 6$  cm<sup>2</sup>, which further illustrated the practical applications of this hybrid electrode material.

### 2. EXPERIMENTAL SECTION

**2.1. Materials.** CNTs (5-15 nm) were obtained from TANFENG Tech. Inc. Lithium chloride monohydrate (LiCl·H<sub>2</sub>O),

cobalt(II) chloride hexahydrate (CoCl<sub>2</sub>· $6H_2O$ ), and nickel(II) chloride hexahydrate (NiCl<sub>2</sub>· $6H_2O$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd. Selenium dioxide (SeO<sub>2</sub>) was bought from Alfa Aesar (China) Chemical Co. Ltd. Polyethylene glycol 10,000 (PEG, H(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH, MW: 8500–11,500) came from Shanghai Macklin Biochemical Co., Ltd. All the reagents were used as received.

2.2. Synthesis of the CNTs/NiCoSe<sub>2</sub> Composite. Before the synthesis of the CNTs/NiCoSe<sub>2</sub> composite, pure CC  $(1 \times 3 \text{ cm}^2)$  was activated through the hydrothermal process to enhance its hydrophilicity.<sup>34</sup> At room temperature, the CNTs/NiCoSe<sub>2</sub> composite was fabricated through the cyclic voltammetry (CV) method at 5 mV s<sup>-1</sup> for two cycles from -1.6 to 0 V with CC, Pt foil, and Ag/AgCl as the working, counter, and reference electrodes, respectively. CVs for the deposition of CNTs, NiCoSe2, and CNTs/NiCoSe2 on ACC are illustrated in Figure S1. In a typical procedure, 25 mg of PEG (as surfactant) was soluble in 25 mL of DI water, followed by adding 200 mg of LiCl (as a support electrolyte) and 0.022 g of concentrated  $H_2SO_4$  to adjust the bath pH (~1). After stirring evenly, 3 mg of CNTs was added in the above solution under ultrasonic condition. Finally, NiCl<sub>2</sub>·6H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, and SeO<sub>2</sub> with a molar ratio of 1:1:2 were added successively to form a uniformly dispersed solution. The CNTs and NiCoSe<sub>2</sub> samples were prepared thorough the same method with the synthesis of CNTs/NiCoSe<sub>2</sub>. The electrolyte for the deposition of CNTs was the absence of NiCl<sub>2</sub>·6H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, and SeO2, while for NiCoSe2 was the absence of CNTs. Samples obtained after electrodeposition were carefully washed by DI water and dried at 60 °C for 12 h. The mass loading of CNTs, NiCoSe2, and CNTs/NiCoSe<sub>2</sub> on CC was about 0.2, 0.7, and 1.3 mg cm<sup>-2</sup>, respectively.

**2.3. Characterization.** The crystalline structure, phase, and chemical state of  $CNTs/NiCoSe_2$  were identified by X-ray diffraction (XRD, Rigaku MiniFlex600) and X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi), respectively. The morphologies and micro–nanostructures of samples were characterized by transmission electron microscopy (TEM, FEI Tecnai G2 F20) and scanning electron microscopy (SEM, Phenom Pharos). The Brunauer–Emmett–Teller (BET) specific surface area (SSA) and pore size distribution were characterized by N<sub>2</sub> adsorption/desorption isotherms (BET, Kubo X1000). Raman spectra were obtained by an iHR550 spectrometer (HORIBA Scientific) to further determine the structural characteristics of the as-fabricated samples.

**2.4. Electrochemical Tests.** The electrochemical performance tests including CV, galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed on a CHI 660E workstation (Chenhua Shanghai) with CNTs/NiCoSe<sub>2</sub>, Pt foil, and Hg/HgO as the working, counter, and reference electrodes, respectively. All the electrochemical tests under the three-electrode system were carried out with 3 M KOH as the electrolyte. The FASS CNTs/NiCoSe<sub>2</sub>//AC ASC device with a PVA/KOH gel electrolyte<sup>35</sup> was constructed to evaluate the practical

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Figure 2. Spectroscopic characterization of CNTs/NiCoSe<sub>2</sub>: (a) XRD pattern; (b) full XPS survey spectrum; and XPS elemental spectra of (c) C 1s, (d) Ni 2p, (e) Co 2p, and (f) Se 3d.



Figure 3. SEM images of (a) CNTs, (b) NiCoSe<sub>2</sub>, and (c) CNTs/NiCoSe<sub>2</sub> samples and (d-f) TEM images and (g-k) elemental mapping images of the CNTs/NiCoSe<sub>2</sub> sample.

application of this ASC. Briefly, the  $CNTs/NiCoSe_2$  electrode and the AC electrode were fully infiltrated with the PVA/KOH gel electrolyte and then moisture was volatilized in the electrolyte at room temperature overnight. Finally, the  $CNTs/NiCoSe_2$  electrode and the AC electrode were assembled face to face to form a FASS ASC. A plastic film was used for further packaging of the device.

# 3. RESULTS AND DISCUSSION

Figure 1 illustrates the preparation processes of the  $CNTs/NiCoSe_2$  electrode. With the combined advantages of CNTs and  $NiCoSe_2$ , the derived composite exposes unique micro–nanostructures with abundant large pores and rich conductive

networks. The powder XRD pattern of the CNTs/NiCoSe<sub>2</sub> composite is shown in Figure 2a. Note that, before the XRD test, the as-fabricated CNTs/NiCoSe<sub>2</sub> sample was scraped from the CC to eliminate the influence of the substrate. The peak around 26.04° is assigned to the (002) diffraction of CNTs.<sup>36</sup> Except the peak of CNTs, the other four diffraction peaks are well indexed to NiCoSe<sub>2</sub> (JCPDS card no. 70-2851), and no obvious impurity peaks are found.

The chemical state of the  $CNTs/NiCoSe_2$  sample was detected by XPS. Figure 2b shows the full XPS survey spectrum of the sample, which demonstrates the co-existence of C, O, Se, Ni, and Co elements in this sample. The peaks

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Figure 4. Comparison of (a) CVs, (b) GCDs, and (c) Nyquist plots of CNTs, NiCoSe<sub>2</sub>, and CNTs/NiCoSe<sub>2</sub> electrodes; (d–g) electrochemical performance of the CNTs/NiCoSe<sub>2</sub> electrode; and (h,i) comparison of specific capacity and cycling performance of NiCoSe<sub>2</sub> and CNTs/NiCoSe<sub>2</sub>.

located at 284.8 and 286.3 eV in the C 1s spectrum (Figure 2c) can be identified as C–C and C–O, respectively.<sup>37,38</sup> The Ni 2p spectrum is fitted well with one major spin–orbit doublet, located at 856.4 and 874.6 eV, which indicated the existence of Ni<sup>2+</sup> (Figure 2d).<sup>39</sup> The fitting peaks at binding energies of 781.1 and 797.3 eV in Co 2p spectra can be assigned to Co<sup>2+</sup> (Figure 2e).<sup>40</sup> Interestingly, there exist a small amount of Ni<sup>0</sup> and Co<sup>0</sup> in the Ni 2p and Co 2p spectrum, which may be derived from the reduction of divalent Ni/Co ions during the electrodeposition process. This can enhance the conductivity of the electrode to a certain extent. Figure 2f presents the Se 3d spectra. The binding energies at 53.7 and 54.6 eV can be traceable in metal selenide bonds and also similar to other transition metal selenides.<sup>13</sup> The peak at 58.8 eV comes from the oxidized Se.

The SEM image indicates that pure CNTs (Figure 3a) are interacting together and self-assembled into a 3D loose structure, which can be used to increase the electrical and ionic conductivity to provide a connected electron/ion pathway, thus ensuring fast electro/ion transport, while pure NiCoSe<sub>2</sub> without CNTs (Figure 3b) shows a densely stacked structure on the surface of the CC substrate. After the coelectrodeposition process, CNTs/NiCoSe<sub>2</sub> composites were successfully decorated on the surface of CC with a porous 3D interconnected structure. Such morphology has been believed to be beneficial for the penetration of electrolyte ions into electrode materials. Meanwhile, the numerous micropores exist in the composite can shorten the ion transport pathways and supply rich electro-active sites for energy storage.

TEM was used to further investigate the detailed information of the CNTs/NiCoSe<sub>2</sub> sample. As depicted in Figure 3d-f, after treating with the co-electrodeposition process, some fluffy unorganized slices are well covered on CNTs. The uniform interlacing of the composite results in a 3D architecture with much fatter volume and higher porosity, which greatly increase the SSA and provide abundant reaction/ adsorption sites for electrolyte ions, indicating that this hybrid electrode would have good electrochemical property. Raman spectroscopy was used to study the disorder degree of the prepared samples (Figure S2). Obviously, the Raman spectra of each sample exhibit two strong peaks at ~1345 and 1590 cm<sup>-1</sup>, which belong to D and G bands, respectively. The bands at about 2700 and 2960 cm<sup>-1</sup> verify the existence of defective graphite carbon in these samples. It can be noted that the stepped increase of the relative intensity of D and G peaks ( $I_{\rm D}/$ I<sub>G</sub>) of raw-CC (0.99), ACC (1.02), CNT/ACC (1.05), NiCoSe<sub>2</sub>/ACC (1.04), and CNTs/NiCoSe<sub>2</sub>/ACC (1.10). The multiple defect sites and edges can be introduced on the surface of CC due to the increased structural distortion, resulting in the generation of a tremendous amount of capacitive sites and ultimately enhancing the performance of the device. These results manifest that each treatment step increases the BET SSA of the sample,<sup>41</sup> which can be verified by the  $N_{\rm 2}$  adsorption/desorption measurement. The SSA of the composite calculated from the BET plots is  $\sim 117.4 \text{ m}^2 \text{ g}^{-1}$ almost 3 times larger than that of pristine NiCoSe<sub>2</sub> (42.9 m<sup>2</sup>  $g^{-1}$ ) (Figure S3). Meanwhile, the average pore size of the CNTs/NiCoSe<sub>2</sub> sample is 8.96 nm, which is also bigger than

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Figure 5. (a) CVs and (b) GCDs of CNTs/NiCoSe<sub>2</sub>//AC ASC; (c) specific capacity of the CNTs/NiCoSe<sub>2</sub>//AC ASC from 1 to 10 A  $g^{-1}$ ; (d) Ragone plots; (e) cyclic stability of CNTs/NiCoSe<sub>2</sub>//AC ASC; and (f) Nyquist plots of CNTs/NiCoSe<sub>2</sub>//AC ASC before and after 10,000 cycling.

the pure NiCoSe<sub>2</sub> sample (6.62 nm). The increased SSA of the CNTs/NiCoSe<sub>2</sub> electrode with a 3D micro–nanostructure can offer multiple ion transport channels and more electrolyte accessible areas, which is in favor of the rapid transmission of electrons and ions, thus leading to an enhanced charge storage capability.<sup>42</sup> The EDS mapping images (Figure 3g–k) demonstrate that the signals of C, Ni, Co, and Se are evenly distributed in the whole observation region, which confirms the compositional homogeneity of the obtained product.

The electrochemical performances of the CNTs/NiCoSe<sub>2</sub> electrode were investigated to detect its possibility of high energy storage material for SCs. Pure CNTs and NiCoSe<sub>2</sub> electrodes were fabricated for comparison. It is worth noting that the CNTs/NiCoSe<sub>2</sub> electrode possesses a larger CV integrated area and higher redox peak intensity than the CNTs electrode and NiCoSe<sub>2</sub> electrode (Figure 4a), suggesting that a higher capacity value could be expected for the CNTs/ NiCoSe<sub>2</sub> electrode. Besides, the discharge time for the CNTs/ NiCoSe<sub>2</sub> electrode is much longer than those for the CNTs and NiCoSe<sub>2</sub> (Figure 4b), implying that the CNTs/NiCoSe<sub>2</sub> electrode delivers a higher specific capacity. The enhanced electrochemical activity indicates that the existence of CNTs with good electrical conductivity leads to a low internal resistance; particularly, CNTs offer rich charge transfer paths, resulting in rapid Faraday redox reactions.43 Meanwhile, the hybrid films with an abundant mesoporous structure can contribute to rapid electron transfer throughout the whole electrode. Consequently, the CNTs/NiCoSe<sub>2</sub> electrode exposes a higher specific capacity of 218.1 mA h g<sup>-1</sup> than the pure CNTs electrode (29.2 mA h  $g^{-1}$ ) and the NiCoSe<sub>2</sub> electrode (155.7 mA h  $g^{-1}$ ) at 5 A  $g^{-1}$ .

The charge-transfer kinetics of the electrodes were further estimated through EIS measurement. An equivalent circuit model (Figure S4) was used to fit the Nyquist plots (Figure 4c), and the corresponding results are depicted in Figure S5 and Table S1. Benefiting from the synergistic effects between CNTs and NiCoSe<sub>2</sub>, the CNTs/NiCoSe<sub>2</sub> electrode reveals a modified charge-transfer resistance ( $R_{ct}$ ) and equivalent series resistance ( $R_s$ ), suggesting that this electrode has an enhanced charge mobility and electrical conductivity. All those results further convincingly prove that the CNTs/NiCoSe<sub>2</sub> electrode can take full advantages of CNTs and NiCoSe<sub>2</sub>. In this case, the introduction of CNTs can effectively enhance the electron conductivity and facilitate the electron transport. Otherwise, the high porosity of the hybrid films minimizes the ions' diffusion distance and maximizes the contact area. Thus, the CNTs/NiCoSe<sub>2</sub> electrode shows outstanding electrochemical properties. Finally, the direct growth of NiCoSe<sub>2</sub>-decorated CNTs on CC results in less "dead area" of the electro-active materials and provides efficient paths for rapid ionic/electronic transport.

Meanwhile, from 5 to 50 mV  $s^{-1}$ , a dramatic increase in the current density of all CVs can be seen clearly (Figure 4d), signifying the fast transfer of electrons and ions at the interface between CNTs/NiCoSe<sub>2</sub> and KOH. The capacitive contribution can be evaluated by eq S1. The CVs and GCDs of the NiCoSe<sub>2</sub> electrode are presented in Figure S6. As summarized in Figures 4e and S6b, the CNTs/NiCoSe<sub>2</sub> electrode possesses excellent reversibility than the NiCoSe<sub>2</sub> electrode. The linear correlation of the corresponding peak current also proves that the electrochemical reactions inside of the CNTs/NiCoSe<sub>2</sub> electrode and NiCoSe2 electrode are dominated by a diffusioncontrolled mechanism.<sup>44</sup> Meanwhile, eq S2 was used to characterize the total response current (i) at a scan rate of v. The fitting results are displayed in Figures 4f, S6c, and S7. Obviously, at 20 mV<sup>-1</sup>, the CNTs/NiCoSe<sub>2</sub> electrode possesses a much higher capacitive process contribution than the NiCoSe<sub>2</sub> electrode. At the same time, the CNTs/NiCoSe<sub>2</sub> electrode still retains a 57.6% capacitive contribution at 1 mV s<sup>-1</sup>. Since the capacitive process represents fast kinetics, the CNTs/NiCoSe<sub>2</sub> electrode with higher capacitive process contribution has superior rate capability. Figure 4g indicates the GCDs of the CNTs/NiCoSe<sub>2</sub> electrode at different current densities  $(1-20 \text{ A g}^{-1})$ . The GCDs with a nearly symmetry shape suggest that the hybrid electrode possesses a satisfactory Coulomb efficiency.<sup>45</sup> The discharge-specific capacity values at various current densities are plotted in Figure 4h (according eq S3). At 1 A  $g^{-1}$ , the CNTs/NiCoSe<sub>2</sub> electrode shows a specific



**Figure 6.** Practical application of the CNTs/NiCoSe<sub>2</sub> ASC device. (a) Charged flexible CNTs/NiCoSe<sub>2</sub>//AC ASC device and its open-circuit voltage (1.43 V); (b–d) CVs at different bending angles at 50 mV s<sup>-1</sup> and five red LEDs powered by two connected ASC devices with different bending angles and different times; (e,f) large-sized CNTs/NiCoSe<sub>2</sub>//AC ASC ( $5 \times 6$  cm<sup>2</sup>) and photograph of an LED array (>3.7 V) powered by three connected ASCs.

capacity of 251.8 mA h g<sup>-1</sup>, which is much higher than the NiCoSe<sub>2</sub> electrode and other transition metal-based selenides or a CNTs-based electrode (Table S2). When the current density increases from 1 to 20 A g<sup>-1</sup>, the retention of specific capacity can be reached 71.9%, which exceeds that of the NiCoSe<sub>2</sub> sample (67.7%). Furthermore, at 2 A g<sup>-1</sup>, the CNT/ NiCoSe<sub>2</sub> electrode shows an enhanced durability (Figure 4i), which arises from the high chemical stabile CNTs, and the unique 3D architecture of the composite can accommodate the volume changes of NiCoSe<sub>2</sub> during long-term cycling.<sup>46</sup> From all the above analyses, the self-standing CNTs/NiCoSe<sub>2</sub> electrode is beneficial to use in SCs since it possesses large SSA, abundant porous structures, high specific capacity, and excellent cycling stability.

To further assess the applicability of the CNTs/NiCoSe<sub>2</sub> electrode, a FASS CNTs/NiCoSe<sub>2</sub>//AC ASC was constructed. The mass of AC in the CNTs/NiCoSe2//AC ASC was determined by eqs S5 and S6 and Figure S8. The CNTs/ NiCoSe<sub>2</sub> mass on the surface of ACC is 1.3 mg. At 1 A  $g^{-1}$ , the mass specific capacity of CNTs/NiCoSe<sub>2</sub> and AC is 251.8 and 71.8 mA h  $g^{-1}$ , respectively. Therefore, the AC mass in CNTs/ NiCoSe<sub>2</sub>//AC is 3.2 mg. Figure S9 depicts the CV curves for the CNTs/NiCoSe<sub>2</sub> electrode and the AC electrode at 50 mV  $s^{-1}$  in the three-electrode system. Clearly, their voltage window is 0 to 0.7 and -1.0 to 0 V, respectively, demonstrating that the working voltage window of the ASC can be extended up to 1.7 V. To confirm the stable operation voltage window of the CNTs/NiCoSe<sub>2</sub>//AC ASC, the typical CV and GCD curves acquired in various voltage windows (1.1 to 1.9 V) are illustrated in Figure S10. Apparently, under 0-1.7 V or less, the ASC still displays good electrochemical stability, but when the voltage window up to 1.9 V, polarization phenomenon could produce in both CVs and GCDs. Therefore, the optimum voltage window of CNTs/NiCoSe<sub>2</sub>//AC ASC was

identified as 0-1.7 V. The NiCoSe<sub>2</sub>//AC ASC, meanwhile, was also fabricated for comparison (Figure S11).

The CVs of the CNTs/NiCoSe<sub>2</sub>//AC ASC (Figure 5a) show a capacitive feature from 5 to 50 mV  $s^{-1}$ , which are a large discrepancy with the rectangle-shaped CV curves of carbon-based symmetric SCs because the ASC device contain both battery-like reaction electric double-layer capacitive behavior. In addition, at a fixed potential window, GCD measurement was used to examine the electrochemical performance of the ASC through varying the current densities from 1 to 10 A  $g^{-1}$  (Figure 5b). The specific capacity values corresponding to each applied current density from GCD curves are graphically represented in Figure 5c. Obviously, the CNTs/NiCoSe<sub>2</sub>//AC ASC delivers a much higher specific capacity of 132.2 mA h  $g^{-1}$  at 1 A  $g^{-1}$  than NiCoSe<sub>2</sub>//AC ASC (64.8 mA h  $g^{-1}$  at 1 A  $g^{-1}$ ). Besides, the Ragone plots obtained based on eqs S7 and S8 and GCD data are depict in Figure 5d. Surprisingly, the CNTs/NiCoSe<sub>2</sub>//AC ASC offers an ultrahigh energy density of 112.2 W h kg<sup>-1</sup> at 850 W kg<sup>-1</sup> and remains 67.1 W h kg<sup>-1</sup> even at a high power density of 8.5 kW kg<sup>-1</sup>. These results are outperformed or comparable to the  $NiCoSe_2//AC ASC (55 W h kg^{-1} at 850 W kg^{-1})$  and other latest reported transition metal compounds based on ASCs.<sup>4,13,38,47,48</sup>

The durability of SCs is another vital parameter to assess their practicability. Figure 5e shows comparative capacity retention of NiCoSe<sub>2</sub>//AC and CNTs/NiCoSe<sub>2</sub>//AC ASC at 2 A g<sup>-1</sup> upon 10,000 cycles. It is satisfying that after 10,000 cycles, the capacity retention of CNTs/NiCoSe<sub>2</sub>//AC ASC can be maintained at about 98.1% of the initial value, which is superior than that of NiCoSe<sub>2</sub>//AC ASC (92.3%). This result is also verified by the EIS test results (Figure 5f). Obviously, at a low-frequency region, the slope of each straight line is close to 90°, and the nearly unchanged  $R_s$  and  $R_{ct}$  values of the  $CNTs/NiCoSe_2//AC$  ASC device after the cycling test (as listed in Table S3) demonstrate that the well-protected cross-lined hybrid structure of  $CNTs/NiCoSe_2$  effectively suppresses the structural changes caused by the long cycle process.

To explore the application of CNTs/NiCoSe<sub>2</sub>//AC ASCs as a power supply for flexible electronics, the flexibility and mechanical stability of such ASCs were further evaluated. As shown in Figure 6a, a charged flexible CNTs/NiCoSe<sub>2</sub>//AC ASC device delivers an open-circuit voltage of 1.432 V. The CNTs/NiCoSe<sub>2</sub>//AC ASC device is easily bent (Figure 6b,c). Compared to the CV curve without bending (red one), the CV curves at bending angles of 90° (green line) and 180° (blue line) remain almost unchanged. The robust mechanical property of our ASC device can also confirm by repeated bending of this device from 0 to 180° with 500 cycles. Clearly, the specific capacity of the ASC is still maintained about 95.5% after 500 bends (Figure S12). Notice that the brightness of five red LEDs powered by two connected ASCs do not change with different bending angles of ASCs (Figure 6c1-c3). The powered LEDs can also be lighted for more than 10 min (Figure 6d). Such experiments confirm the excellent flexibility and stability of the device. Meanwhile, the CNTs/NiCoSe<sub>2</sub>// AC ASC is scaled up into  $5 \times 6$  cm<sup>2</sup> (Figure 6e), and three of them connected in series can power an LED array (>3.7 V) easily, which proves that the CNTs/NiCoSe<sub>2</sub> materials are suitable for commercial size SCs.

## 4. CONCLUSIONS

In summary, the CNTs/NiCoSe<sub>2</sub> film was successfully deposited on the CC via the co-electrodeposition process and directly acted as SC's cathode. As expected, due to the accessible active sites, short ion transport paths, and beneficial synergistic properties, the specific capacity, rate capability, and durability of the CNTs/NiCoSe<sub>2</sub> electrode are concurrently improved. Meanwhile, the assembled flexible all-solid-state CNTs/NiCoSe<sub>2</sub>//AC ASC shows ultra-high energy density (112.2 W h kg<sup>-1</sup>), outstanding durability (98.1% capacity retention after 10,000 cycles), and exceptional flexibility. Therefore, this CNTs/NiCoSe<sub>2</sub> electrode is an up-and-coming candidate for use as a positive electrode for high-performance flexible and wearable electronics. Meanwhile, the proposed coelectrodeposition strategy is the possibility of designing and fabrication of different kinds of CNTs based on transition metal-based flexible electrodes for other energy storage devices.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c15392.

CVs of the samples during the electrodeposition process; Raman spectra of each treatment step; N<sub>2</sub> adsorption/desorption isotherms and pore size distribution of the NiCoSe<sub>2</sub> and CNTs/NiCoSe<sub>2</sub> sample; equivalent circuit models; raw and fit Nyquist plots of CNTs, NiCoSe<sub>2</sub>, and CNTs/NiCoSe<sub>2</sub> electrode; electrochemical performances of the NiCoSe<sub>2</sub> electrode; capacitive process contribution of the CNTs/NiCoSe<sub>2</sub> electrode at 1 mV s<sup>-1</sup>; GCD curve of the AC electrode at 1 A g<sup>-1</sup>; overlaps of the CV plots of AC and CNTs/NiCoSe<sub>2</sub> electrodes; CVs and GCDs of CNTs/NiCoSe<sub>2</sub>//AC at different potential windows; CVs and

GCDs of NiCoSe<sub>2</sub>//AC; normalized capacities of the flexible all-solid-state CNTs/NiCoSe<sub>2</sub>//AC ASC with bending angles of  $0-180^{\circ}$  tested for 500 bends; fitted impedance data of the CNTs/NiCoSe<sub>2</sub> electrode; comparison of energy storage behavior of other transition metal-based selenides or CNTs-based materials with this work; impedance data of CNTs/NiCoSe<sub>2</sub>// AC before and after cycling; formulas to calculate power law; contribution of capacitive process; specific capacity; specific capacitance; mass of AC used in the ASC device; energy density; and power density (PDF)

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#### **Author Contributions**

B.Y. designed and completed the experiments, processed the experimental data, drew the figures, and wrote the manuscript. J.Z. assisted in lighting experiments. X.C. did the revision work. Q.Z., Y.Z., and J.W. discussed the experimental plan and supervised the study.

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This work was financially supported by the Fundamental Research Funds for the Central Universities (grant no. ZYGX2019J024), the National Natural Science Foundation of China (grant no.52002052), and the National Key Research and Development Program of China (grant no.2017YFA0701001).

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