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Asymmetric Supercapacitors with Metal-Like Ternary Selenides and Porous Graphene Electrodes

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Abstract

Asymmetric supercapacitors provide a promising approach to fabricate capacitive energy storage devices with high energy and power densities. In this work, asymmetric supercapacitors with excellent performance have been fabricated using ternary $(\text{Ni}, \text{Co})_{0.85}\text{Se}$ on carbon fabric as bind-free positive electrode and porous free-standing graphene films as negative electrode. Owing to their metal-like conductivity ($\sim 1.67 \times 10^6 \text{ S m}^{-1}$), significant electrochemical activity, and superhydrophilic nature, our nanostructured ternary nickel cobalt selenides result in a much higher areal capacitance (2.33 F cm^{-2} at 4 mA cm^{-2}), better rate performance and cycling stability than their binary selenide equivalents, and other ternary oxides and chalcogenides. Those hybrid supercapacitors can afford impressive areal capacitance and stack capacitance of 529.3 mF cm^{-2} and 6330 mF cm^{-3} at 1 mA cm^{-2} , respectively. More impressively, our optimized asymmetric device operating at 1.8 V delivers a very high stack energy density of 2.85 mWh cm^{-3} at a stack power density of 10.76 mW cm^{-3} , as well as 85% capacitance retention after 10,000 continuous

charge-discharge cycles. Even at a high stack power density of 1173 mW cm^{-3} , this device still delivers a stack energy density of 1.19 mWh cm^{-3} , superior to most of the reported supercapacitors.

Introduction

While batteries keep our portable devices working throughout the day, they take hours to recharge. For rapid power delivery and recharging, supercapacitors, also called as electrochemical capacitors, hold great promise.[1] In spite of their fast rate of charge and discharge, supercapacitors also demonstrate excellent reusability, safe operation and low maintenance cost. Hence, they have been widely used independently as back-up power devices or coupled with batteries in hybrid electronic vehicles.[2] However, supercapacitors have low energy density which greatly hinders their practical applications in various electronic smart devices. Hence there is an urgent need to increase the energy density of supercapacitors without compromising their power density. There are two key parameters which can be used to improve the energy density of supercapacitors: increasing the capacitance of the electrode material, C , or the operation voltage window, V , or both, since the energy stored is proportional to CV^2 .[3]

Very recently, it has been realized that asymmetric supercapacitors (ASCs) can be an alternative and efficient pathway (compared with symmetric supercapacitors), to extend the output voltage of supercapacitors beyond the thermodynamic limit of $\sim 1.23\text{V}$ in aqueous solutions. This increase in operating voltage led to significant enhancement of energy density of ASCs. These ASCs typically consist of a Faradic positive electrode as the energy source, and a capacitor-type negative electrode as the power source.[4, 5] For ASCs, using different negative

and positive electrode materials with well-separated potential windows widens the usable cell voltage, while simultaneously offering advantages of both supercapacitors (power density, rate, lifespan) and batteries (energy density).[4, 6] For example, Gao et al. fabricated an asymmetric supercapacitor using graphene hydrogel and MnO_2 , which possessed a wide potential window of 2.0 V and exhibited an energy density of 23.2 Wh kg^{-1} with a power density of 1.0 kW kg^{-1} . [7] Zhou et al. showed that the NiMoO_4 /activated carbon hybrid supercapacitor could deliver an energy density of 45.6 Wh kg^{-1} at 674 W kg^{-1} with a voltage of 1.62V.[8] However, to measure the energy density of supercapacitors in a more practical way, it has recently been suggested that the stack energy density (in units of mWh cm^{-3}) involving the entire supercapacitor components should be reported instead of the gravimetric one (which only considers the mass-loading of active materials in units of Wh kg^{-1}) to realistically evaluate supercapacitor devices.[3, 9, 10] Replacing aqueous electrolytes with organic electrolytes or ionic liquids is another strategy commonly investigated for the design of high-voltage supercapacitors. However, non-aqueous electrolytes always suffer from limited ionic conductivity, more cost, and environmental risks in case of leakage.[7] Therefore, the above-mentioned disadvantages make such an approach practically undesirable.

On the other hand, in order to improve the cell capacitance (another key parameter to enhance the capability), it's highly desirable to explore novel electrode materials with high specific capacitance and promising conductivity. In this regard, pseudocapacitive or Faradic MnO_2 , [11] Co_3O_4 , [12] Ni(OH)_2 [13] and some conducting polymers [14, 15] have been developed for advanced supercapacitor positive electrode materials. Yet, their low electrical conductivity and/or poor cycling stability make their electrochemical performance mostly inferior. Tremendous efforts have been exerted to overcome these limitations, including preparation of

hybrid carbon/oxide electrodes[16], deposition nanostructured electroactive materials into a conductive network[8, 14], and so on. As previously demonstrated by our group[17-19] and other researchers[20-24], one main direction to improve the performance of electrode materials is the rational design of three-dimensional (3D) nanostructured ternary transition metal chalcogenides such as metallic NiCo_2S_4 [25]. Due to their superior electrical conductivity, richer electrochemical redox reactions, better chemical stability and shorter diffusion path for both electrons and electrolyte ions, 3D ternary metal chalcogenides show promising performance for supercapacitor positive electrodes. In particular, nickel/cobalt-based chalcogenides are considered as ideal candidates due to their low cost, abundance, and environmental friendliness. While the high-performance ternary chalcogenide electrode has been studied, most studies have used low mass-loading for positive electrode materials (typically $0.5\sim 1\text{ mg cm}^{-2}$), which makes it hard to predict how these materials will perform in real applications. On the negative side of supercapacitors, graphene has been explored extensively because of its large theoretical surface area, excellent conductivity and chemical stability. Various pioneering studies point out that the porous and yet densely packed graphene electrodes with large ion-accessible surface areas, and low ion transport resistance are crucial to the realization of graphene-based high-energy supercapacitors.[9, 26] Hence, we believe that graphene film with in-plane and out-of-plane pores, and carefully controlled packing density would be very suitable negative electrode material for ASCs.

Although considerable work has been done on ASCs, one remaining challenge is to combine appropriate electrode materials working in well-separated potential windows in the same electrolyte to achieve high operating voltage and consequently high energy density. In this article, we report a simple approach to achieve high-performance 3D ternary nickel cobalt

selenide ((Ni,Co)_{0.85}Se) supercapacitor positive electrode with high mass loading ($\sim 5.63 \text{ mg cm}^{-2}$). On the negative side, we use porous graphene films prepared by chemical activation. The fabricated (Ni,Co)_{0.85}Se//porous graphene planar ASCs exhibit outstanding electrochemical performance with total mass-loading of $\sim 10 \text{ mg cm}^{-2}$. Specifically, the optimized ASCs showed an areal capacitance of 530 mF cm^{-2} at 1 mA cm^{-2} and a maximum stack energy density (calculated based on entire device thickness) of $2.85 \text{ mW h cm}^{-3}$ at the power density of 10.8 mW cm^{-3} . Furthermore, such an asymmetric supercapacitor displayed impressive cycling stability (85% retention after 10,000 cycles at 20 mA cm^{-2}) at a voltage of 1.8V.

Experimental section

Preparation of (Ni, Co)_{0.85}Se.

The self-sacrificial template of Ni-Co-precursor nanoarrays were firstly fabricated using a hydrothermal method. Typically, 8 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 15 mmol of urea were dissolved in 80 ml deionized water to form a clear pink solution. This solution was subsequently transferred into a Teflon-lined autoclave with a piece of carbon fabric (CFC) immersed into the solution and kept at 120°C for 6 h. After cooling down to the room temperature, the precursor coated carbon fabric was obtained and washed with deionized water and ethanol. Afterwards, the Ni-Co-precursors were chemically converted in situ into (Ni, Co)_{0.85}Se by 1.0 M fresh NaHSe selenization. In a typical procedure, one piece of as-prepared NiCo-precursor, 38 mL Argon saturated deionized water and 2 mL of fresh prepared 1 M NaHSe solution were loaded into a Teflon lined stainless steel autoclave. The autoclave was heated at 160°C for 24 h, and then cooled to room temperature naturally. The final product was washed

and dried in vacuum at 60 °C. Note that 1.0 M fresh NaHSe was prepared by mixing ~0.16 g NaBH₄, ~0.16 g Se powder and 2 mL Argon saturated deionized water under inert gas protection according to the following equation: $4\text{NaBH}_4 + 2\text{Se} + 7\text{H}_2\text{O} = 2\text{NaHSe} + \text{Na}_2\text{B}_4\text{O}_7 + 14\text{H}_2$.

Preparation of porous graphene film.

The in-plane porous graphene oxide was prepared according to previous report.[27] Afterwards, the highly porous graphene film was obtained by vacuum filtration as described elsewhere.[9, 26, 27]

Fabrication of (Ni, Co)_{0.85}Se//porous graphene film asymmetric supercapacitors.

The as-synthesized (Ni, Co)_{0.85}Se was directly used as positive electrode. Thicker graphene films were made through stacking a certain number of graphene films together in a face-to-face manner in order to reach a charge balance in negative and positive electrode. The thicker graphene film was then attached to the carbon cloth and used as a negative electrode. Note that that carbon cloth in negative electrode also acted as the current collector. A 1.0 M KOH solution was used as electrolyte and a porous polymer membrane was used as the separator (Celgard 3501). The asymmetric devices were assembled in pouch cells by sealing them into plastic bags to avoid evaporation of the aqueous electrolyte during long-time measurement. For a typical asymmetric device, the total mass loading of the active material is ~10 mg cm⁻² with a stack thickness of ~0.84 mm.

Characterization.

X-ray diffraction (XRD) spectra were collected by a Bruker diffractometer (D8 Advance) with Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$. The morphology and microstructure of the samples were characterized by SEM (Nova Nano 630, FEI) and HRTEM (Titan 80; 300 kV for selenides and

80 kV for graphene). Energy-dispersive spectroscopy (EDS) elemental line scans were performed on the same instrument in scanning TEM (STEM) mode. The contact angle was imaged using Theta/Attension optical tensiometer. XPS spectra were recorded on Kratos AXIS Ultra DLD.

Electrochemical measurements.

The electrochemical tests were conducted at room temperature in a VMP3 electrochemical workstation (Bio-Logic) by the techniques of electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge-discharge (CD). 1.0 M KOH was used as the electrolyte for all supercapacitor devices. In 3-electrode measurements, selenide-covered CFC or graphene film directly used as working electrode with a Pt counter electrode and a saturated Ag/AgCl reference electrode. Electrical impedance spectroscopy was recorded under the following conditions: ac voltage amplitude 5 mV, frequency ranges 10^5 to 0.1 Hz and open circuit.

The energy density was calculated from the galvanostatic discharge (CD) curves :

$$E_{\text{areal}} = \frac{I \int_{t(U_{\text{max}})}^{t(U_{\text{min}})} U(t) dt}{A}$$

$$E_{\text{stack}} = \frac{I \int_{t(U_{\text{max}})}^{t(U_{\text{min}})} U(t) dt}{T}$$

Where I is the constant current for charge-discharge and $t(U_{\text{max}})$ and $t(U_{\text{min}})$ are the times at the maximum and minimum voltage during a discharge process. A is the area of the entire electrode and T is the entire volume of our as-prepared ASCs.

Power density:

$$P = \frac{E}{t}$$

While capacitance can be calculated from the following equation:

$$C = \frac{2E}{U_{\max}^2}$$

Where $U_{\max}$ is the voltage window (1.8 V) applied during the charge-discharge measurements.

Results and Discussion

Nanostructured ternary nickel cobalt selenides were directly grown on carbon fabric (CFC) substrate in order to avoid the addition of polymer binders and conductive agents which are non-desirable for high-performance supercapacitors. In addition, direct growth on CFC results in lower contact resistance between the electroactive materials and the CFC current collector which facilitates the electron transfer from electrochemical reaction sites to the collector.[8] As a result, we believe that such a direct fabrication method is superior to the conventional slurry process that is often used to prepare supercapacitor electrodes. Typical X-ray diffraction (XRD) pattern (Figure 1A) and energy-dispersive spectroscopy (EDS) analysis (Figure S1A) support the formation of hexagonal Ni doped $\text{Co}_{0.85}\text{Se}$ (JCPDS 52-1008). Moreover, our XPS survey spectrum analysis confirms the successful introduction of Ni into $\text{Co}_{0.85}\text{Se}$ lattice (Figure S1B). It is well known that the cations in cobalt based oxides and chalcogenides can be easily substituted by nickel ions without significantly distorting their

crystal structures.[28] Additionally, the introduction of nickel ions into cobalt compounds might cause a significant enhancement of electrical conductivity (conductivity of NiCo_2O_4 is at least 100 times higher than Co_3O_4)[23]. To show this conductivity enhancement effect, we directly measured the electrical transport properties of the as-prepared $\text{Co}_{0.85}\text{Se}$ and $(\text{Ni}, \text{Co})_{0.85}\text{Se}$ from the temperature dependence of resistivity using pellets compressed from chemically prepared nanopowders, along with NiCo_2O_4 as control. The data in Fig.S2 clearly shows that the electrical conductivity of $(\text{Ni}, \text{Co})_{0.85}\text{Se}$ is about 2 times higher than that of pure $\text{Co}_{0.85}\text{Se}$ at room temperature. Furthermore, unlike the typical semiconductor NiCo_2O_4 , the resistivity of the selenides actually increases linearly with temperature from 2 to 300 K, indicating their metallic nature.[25] Such an excellent conductivity ($1.67 \times 10^6 \text{ S m}^{-1}$ compared with $9.1 \times 10^6 \text{ S m}^{-1}$ for Pt) can facilitate the charge transfer process and minimize the voltage drop in the electrode, which are highly desired features for high-rate supercapacitor electrodes. Furthermore, our previous study has clearly demonstrated that the $(\text{Ni}, \text{Co})_{0.85}\text{Se}$ nanostructure offers much higher electrochemical active surface area and electrochemical activity than $\text{Co}_{0.85}\text{Se}$.[29] Thus, this ternary $(\text{Ni}, \text{Co})_{0.85}\text{Se}$ shows clear advantages over binary $\text{Co}_{0.85}\text{Se}$ as supercapacitor electrode.

The morphology and microstructure of as-obtained $(\text{Ni}, \text{Co})_{0.85}\text{Se}$ was examined by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The panoramic and close-up FESEM images (Figure 1B, C) show that the $(\text{Ni}, \text{Co})_{0.85}\text{Se}$ consists of closely packed and vertically aligned nanotube arrays on CFC. The formation of the hollow interior is related to the diffusion process of the cations, known as the Kirkendal effect.[30] Further, the corresponding TEM and high-angle annular dark-field scanning TEM (HAADF-STEM) images (Figure 1D and S3) reveal that the surface of $(\text{Ni}, \text{Co})_{0.85}\text{Se}$ nanotube is very

rough and highly porous. As we know, the woven conductive CFCs demonstrate macroporous nature themselves (Figure S4) which can serve as an excellent scaffold for the deposition of electroactive materials. As a result, the ternary (Ni, Co)_{0.85}Se electrodes offer a combination of macroporosity (from the carbon fiber) and mesoporosity from the nanostructure of the ternary chalcogenide nanowires. This combination is believed to facilitate the electrolyte ion trapping and access to electrochemical active sites, which reduces the electrolyte ion diffusion distance during the charge-discharge process. Similar design of nanoporous materials on macroporous substrate have previously shown as promising integrated electrode for supercapacitor devices.[17, 31] The high-resolution TEM in Figure 1E shows clear well-defined lattice fringes for (Ni, Co)_{0.85}Se, indicating a high degree of crystallinity. The crystal lattice with a spacing of ~0.2 nm and ~0.18 nm corresponds to the (102) and (110) planes of Co_{0.85}Se, respectively. Further, the selected area electron diffraction (SAED) of as-prepared (Ni, Co)_{0.85}Se (Figure 1F) shows its polycrystalline nature, in agreement with the XRD result.

Cycling voltammetry (CV) is generally used to characterize the capacitive behavior of an electrode material. Figure 2A shows the CV curves of as-prepared (Ni, Co)_{0.85}Se at different scan rate in 1.0 M KOH electrolyte. All the CV plots here exhibit a pair of pronounced redox peaks, which correspond to the typical faradic reaction among transformation of Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺/Co⁴⁺ in alkaline solution.[17, 18, 23] The symmetric characteristic of the anodic and cathodic peaks indicates the excellent reversibility of selenide electrodes. Additionally, Figure 2B shows that a linear relationship exists between the potential of the anodic and cathodic peaks and the square root of scan rate. This linear behavior indicates the dominance of diffusion-controlled electrode reactions, which reveals that the energy storage in our selenide electrode is mainly based on the faradic reactions rather than electric double-layer physisorption. Likewise,

the voltage plateaus observed in the galvanostatic charge-discharge (CD) profiles also confirm the faradic process (Figure 2C), which is consistent with the electrochemical behavior of the CV curves. The negligible voltage (IR) drop observed in the CD curves is attributed to the excellent conductivity of (Ni, Co)_{0.85}Se ($1.67 \times 10^6 \text{ S m}^{-1}$) which result in prominent rate capability. The CD curves of as-synthesized (Ni, Co)_{0.85}Se nanotube arrays are nearly symmetric in nature, which reveals the highly reversible nature of our electrodes.[30] As summarized in Figure 2D, the areal capacitance of (Ni, Co)_{0.85}Se electrode was calculated to be 2.33 F cm^{-2} and 1.86 F cm^{-2} at current density of 4 mA cm^{-2} and 20 mA cm^{-2} , respectively. Impressively, the areal capacitance of our ternary electrode is ~2.5-folds higher than previously reported binary Co_{0.85}Se supercapacitor electrode at same current density of 4 mA cm^{-2} . [30] Besides, our ternary electrode showed an enhanced rate capability when compared to binary Co_{0.85}Se. Specifically, 80% of the capacitance retention takes place when the current density increase from 4 mA cm^{-2} from 20 mA cm^{-2} whereas that of Co_{0.85}Se is only ~64%. [30] As we mentioned above, such an improvement is probably related to their remarkable electrical conductivity and nanostructure. What's more, it's worthwhile to note that the areal capacitance reported here is higher than the values reported so far for pseudocapacitive oxides/hydroxides/chalcogenides, such as NiCo₂O₄ nanoneedles ($\sim 1.44 \text{ F cm}^{-2}$ at 2.78 mA cm^{-2}), [32] Co_xNi_{1-x}(OH)₂/NiCo₂O₄ ($\sim 2.3 \text{ F cm}^{-2}$ at 2 mA cm^{-2}), [33] CoNi₂S₄ nanosheets arrays ($\sim 1.12 \text{ F cm}^{-2}$ at 4 mA cm^{-2}), [17] and MnO₂/NiCo₂O₄ ($\sim 2.01 \text{ F cm}^{-2}$ at 2 mA cm^{-2}). [34] The excellent electrochemical capacitive performance of our ternary selenide electrode can be attributed to the following facts: 1) the fabrication process of our integrated electrodes prevents the addition of “dead volume” from binder and conductive agent, which provides a superb highways for fast electron transportation and electrolyte ion diffusion; 2) the metallic nature of (Ni, Co)_{0.85}Se reduces the equivalent series resistance (ESR)

and insures fast electron transport to the current collector, thereby enhancing the rate capability; 3) the superhydrophilic nature of (Ni, Co)_{0.85}Se-covered CFC (supporting videos) means the aqueous solution easily spreads on the entire surface (external and internal) of our integrated electrode, hence boosting the electrolyte ion trapping and access to the active sites; 4) the 3D nanostructured porous morphology shortens the diffusion path for mass transport and enhances the concentration of active sites. Overall, because of the promising performance of our ternary positive electrode material, we decided to fabricate asymmetric supercapacitor devices with a suitable negative electrode material with well-separated operating voltage window compared to (Ni, Co)_{0.85}Se positive electrode.

As a well-known member of carbon family, graphene has emerged as a promising negative electrode material for supercapacitors because of its extraordinary conductivity, large theoretical surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) and excellent chemical stability. However, the exploitation of graphene-based bulk material faces a key scientific and technical challenge. Apart from other carbonaceous materials, the performance of graphene-based materials is strongly affected by the way the individual sheets are arranged. The strong π - π interaction between the graphene layers is conducive to restacking of the sheets, resulting in significantly compromised graphene electrodes. Previous reports have shown that water, the very “soft” matter, can serve as an effective “spacer” to prevent the restacking of chemically converted graphene (CCG) sheets.[9, 26] The CCG film-like electrodes have shown outstanding performance in energy storage applications, where large-scale application of graphene in bulk film form appears to be close to the market.[17, 26] Further studies showed that the in-plane pores in individual graphene sheet can efficiently boost the mass transportation and expanded electrode/electrolyte contact areas in such a graphene film electrode, which are favorable for high-performance supercapacitor electrode.[4, 27] In this respect, self-

supported porous graphene film would be very suitable negative electrode for construction of an advanced asymmetric supercapacitors.

The porous graphene was prepared according to previous reports.[26, 27] FESEM image (Figure 3A and Figure S5A) of the as-obtained graphene reveals that numerous wrinkled and folded regions are exhibited on the sheets. Such a rough surface produces higher surface area which is particularly favorable for carbonaceous materials. We can see from Figure 3A and Figure S5B, C that considerable mesopores are randomly distributed on the individual graphene sheets with a thickness of few atomic layers. Moreover, the typical FESEM image (Figure 3B) of our porous graphene film demonstrates the presence of abundant out-of-plane pores inside this bulk electrode, which was prepared by vacuum filtration.[26] The large out-of-plane macropores originate from graphene sheets where the aqueous electrolyte serves as the “spacer”. As we mentioned above, such a nanoarchitecture with both mesopores and macropores present, is highly desirable for energy storage devices. When evaluated as supercapacitor negative electrode, as displayed in Figure 3C, the porous graphene film shows typical rectangular CV curves. It can be clearly seen that all the CV curves retained perfect rectangular shapes as the scan rate was increased from 50 to 1000 mV s^{-1} , implying the improved mass transport, efficient electron transfer, and small ESR. It is very important to notice that even when the scan rate goes up to 10,000 mV s^{-1} (Figure 3D), such a porous electrode still could keep a quasi-rectangular shape. This result clearly indicates the high rate performance of our porous graphene film which is very important for practical supercapacitor applications.[30] The capacitive performances of these graphene negative electrodes were studied by galvanostatic charge-discharge measurements, as shown in Figure 3E. The symmetrical triangle feature and negligible IR drop at any current densities re-confirms its low internal resistance and typical capacitor behavior. As summarized in

Figure 3F, in a prolonged voltage window of 1.2 V, the porous graphene film electrode not only offers a high areal capacitance (249.1 mF cm^{-2} at 2 mA cm^{-2}) but also maintains superior rate performance. In spite of the increase in the current density by a factor of 100, ~53% retention (131 mF cm^{-2} at 200 mA cm^{-2}) of initial capacitance is observed. Notably, all the measurements indicate that this graphene film is ideal as a negative electrode for advanced asymmetric supercapacitors.

Our hybrid supercapacitors are constructed with ternary $(\text{Ni,Co})_{0.85}\text{Se}$ as positive electrode, porous graphene film as negative electrode, and 1.0 M KOH as electrolyte which is schematically illustrated in Figure 4. To optimize the performance of the ASCs, the mass loading of the two electrode was balanced before making the full cell using the following equation:[17]

$$\frac{m_+}{m_-} = \frac{C_{s-} \cdot \Delta V_-}{C_{s+} \cdot \Delta V_+}$$

where m is the mass, C_s is the specific capacitance and ΔV is the voltage range for positive electrode (+) and negative electrode (-) electrodes, respectively. According to their respective potential windows, the operating potential window of the full cell was determined to 1.8 V (Figure S6). CV was first used to estimate the electrochemical behavior of balanced $(\text{Ni,Co})_{0.85}\text{Se}$ /porous graphene film ASC. As shown in Figure 5A, a pair of distinct peaks under different scan rates could be observed, corresponding to the redox reactions of selenide electrode in basic electrolyte. Taking advantages of their porous nature and intrinsically high conductivity of both positive and negative electrodes, the shifting of redox peaks at high scan rate of the ASC is small, indicating superior rate performance. Moreover, CD measurements were also performed using different current densities in a potential window of 0-1.8 V (Figure 5B). The nearly symmetric CD profiles with a coulombic efficiency of >98% and very small voltage drops also

indicate nearly ideal supercapacitor performance with a rapid I-V response. Further, the areal capacitances of the (Ni,Co)_{0.85}Se//porous graphene film ASCs were calculated and summarized in Figure 5C. To be specific, this ASC shows impressive areal capacitance and stack capacitance of 529.3 mF cm⁻² and 6330 mF cm⁻³ at 1 mA cm⁻², respectively. This value is significantly better than previously report binary cobalt selenide//activated carbon ASCs (330 mF cm⁻² at 1 mA cm⁻²).[30] And impressively, these devices could reaches 297 mF cm⁻² and 3550 mF cm⁻³ at a very high current density of 50 mA cm⁻², meaning ~56.1% capacitance retention in spite of the increase in current density by a factor of 50. Note that such a high areal capacitance of our ASCs demonstrates their good capability to store enough energy in a confined area. Electrochemical impedance spectroscopy (EIS) was further employed to investigate the ASC. The ESR of the asymmetric device is mere ~1.1 Ω as shown in the Nyquist plot (Figure 5D), which also shows negligible charge transfer resistance (R_{ct}). This is due to the hydrated surface and highly porous nanoarchitecture of both negative and positive electrode materials, which minimizes the contact resistance between electrodes and electrolyte.

In view of the fact that cycling stability has always been regarded as a crucial role in ASC applications, the long-term cycling test was carried out for 10,000 CD cycles at a high current density of 20 mA cm⁻² (Figure 5E). Notably, our ASC is capable of retaining ~85% of the initial discharge capacitance after 10,000 cycles, showing an impressive lifespan. In addition, such cycling performance is highly competitive with those of some other ASCs, such as Ni(OH)₂//activated carbon (82% retention after 1000 cycles),[35] MnO₂@graphene//graphene (79% retention after 1000 cycles),[36] Ni(OH)-CNT//activated carbon (83% retention after 3000 cycles),[37] Ni_xCo_{3-x}O₄//activated carbon (82.8% retention after 3000 cycles),[38] and Ni-Co sulfide//activated carbon (73.1% retention after 3000 cycles).[39] To further illustrate the

electrochemical performance of our asymmetric cells, Ragone curve is plotted in Figure 5F based on the stack energy density and stack power density. In order to fairly and accurately reveal their energy storage performances, the values of high-energy lithium thin-film battery (4V/500 μ Ah) [40] and high-power aluminum electrolytic capacitor (3V/300 μ F) [41] are also included as control. The ASC cell shows a high stack energy density of 2.85 mWh cm^{-3} at a power density of 10.76 mW cm^{-3} . Even at a high power density of 1173 mW cm^{-3} , this device still delivers a stack energy density of 1.19 mWh cm^{-3} , superior to most of the reported supercapacitors including VOx//VN (0.6 mWh cm^{-3} at 80 mW cm^{-3}), [42] H-TiO₂@MnO₂//H-TiO₂@C (0.30 mWh cm^{-3} at 200 mW cm^{-3}), [43] ZnO@MnO₂//graphene (0.234 mWh cm^{-3} at 133 mW cm^{-3}), [44] TiN//TiN (0.05 mWh cm^{-3} at 120 mW cm^{-3}), [45] and TiO₂@C//TiO₂@C (0.01 mWh cm^{-3} at 19 mW cm^{-3}). [46] Such high energy and power density of our cells show great potential for practical energy storage applications.

Conclusions

To sum up, a facile synthetic approach has been developed here to directly assemble ternary (Ni,Co)_{0.85}Se nanotubes on CFC for supercapacitor application. Its unique structure, superhydrophilic nature, and excellent conductivity enable a high areal capacitance of 2.33 F cm^{-2} at 4 mA cm^{-2} , showing clear advantages over the conventional supercapacitor electrodes (Supporting table 1). Furthermore, an advanced asymmetric supercapacitor using metallic ternary (Ni,Co)_{0.85}Se as positive electrode and porous graphene film as negative electrode has been successfully developed. Thanks to the highly porous nature, ideal electron and electrolyte transportation path, and considerable electrochemical activity of both positive and negative

electrodes, our optimized (Ni,Co)_{0.85}Se//porous graphene film ASCs delivered a very high stack energy and power density, as well as robust stability.

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Supporting Information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org>.

References

- [1] P. Simon, Y. Gogotsi, B. Dunn, *Science*, 343 (2014) 1210-1211.
- [2] J. Yan, Q. Wang, T. Wei, Z.J. Fan, *Adv Energy Mater*, 4 (2014).
- [3] Y. Gogotsi, P. Simon, *Science Magazine*, 334 (2011) 917-918.
- [4] J. Yan, Z. Fan, W. Sun, G. Ning, T. Wei, Q. Zhang, R. Zhang, L. Zhi, F. Wei, *Adv Funct Mater*, 22 (2012) 2632-2641.
- [5] X.F. Lu, X.Y. Chen, W. Zhou, Y.X. Tong, G.R. Li, *Acs Appl Mater Inter*, 7 (2015) 14843-14850.
- [6] H. Xia, C. Hong, B. Li, B. Zhao, Z. Lin, M. Zheng, S.V. Savilov, S.M. Aldoshin, *Adv Funct Mater*, 25 (2015) 627-635.
- [7] H. Gao, F. Xiao, C.B. Ching, H. Duan, *Acs Appl Mater Inter*, 4 (2012) 2801-2810.
- [8] C.X. Zhou, W. Yang, G.F. Zeng, Y. Lei, L. Gu, X.H. Xi, D. Xiao, *Chem-Asian J*, 10 (2015) 1745-1752.
- [9] X. Yang, C. Cheng, Y. Wang, L. Qiu, D. Li, *Science*, 341 (2013) 534-537.
- [10] W. Chen, C. Xia, H. Alshareef, *Nano Energy*, 15 (2015) 1-8.
- [11] T. Brousse, M. Toupin, R. Dugas, L. Athouël, O. Crosnier, D. Bélanger, *J Electrochem Soc*, 153 (2006) A2171-A2180.
- [12] X.H. Xia, J.P. Tu, Y.J. Mai, X.L. Wang, C.D. Gu, X.B. Zhao, *J Mater Chem*, 21 (2011) 9319-9325.
- [13] U. Patil, K. Gurav, V. Fulari, C. Lokhande, O.S. Joo, *J Power Sources*, 188 (2009) 338-342.
- [14] C. Xia, W. Chen, X.B. Wang, M.N. Hedhili, N.N. Wei, H.N. Alshareef, *Adv Energy Mater*, 5 (2015) 1401805.
- [15] E. Frackowiak, V. Khomenko, K. Jurewicz, K. Lota, F. Beguin, *J Power Sources*, 153 (2006) 413-418.
- [16] Q. Liao, N. Li, S. Jin, G. Yang, C. Wang, *Acs Nano*, 9 (2015) 5310-5317.
- [17] W. Chen, C. Xia, H.N. Alshareef, *Acs Nano*, 8 (2014) 9531-9541.

- [18] C. Xia, H.N. Alshareef, *Chem Mater*, 27 (2015) 4661-4668.
- [19] N. Kurra, C. Xia, M. Hedhili, H. Alshareef, *Chem. Commun.*, 51 (2015) 10494-10497.
- [20] L.F. Shen, J. Wang, G.Y. Xu, H.S. Li, H. Dou, X.G. Zhang, *Adv Energy Mater*, 5 (2015) 1400977.
- [21] J. Pu, T. Wang, H. Wang, Y. Tong, C. Lu, W. Kong, Z. Wang, *Chempluschem*, 79 (2014) 577-583.
- [22] L. Shen, L. Yu, H.B. Wu, X.Y. Yu, X. Zhang, X.W. Lou, *Nat Commun*, 6 (2015) 6694.
- [23] J.W. Xiao, L. Wan, S.H. Yang, F. Xiao, S. Wang, *Nano Lett*, 14 (2014) 831-838.
- [24] S.J. Peng, L.L. Li, C.C. Li, H.T. Tan, R. Cai, H. Yu, S. Mhaisalkar, M. Srinivasan, S. Ramakrishna, Q.Y. Yan, *Chem Commun*, 49 (2013) 10178-10180.
- [25] C. Xia, P. Li, A.N. Gandi, U. Schwingenschlögl, H.N. Alshareef, *Chem Mater*, 27 (2015) 6482-6485.
- [26] X. Yang, J. Zhu, L. Qiu, D. Li, *Adv Mater*, 23 (2011) 2833-2838.
- [27] S. Chen, S.-Z. Qiao, *Acs Nano*, 7 (2013) 10190-10196.
- [28] C. Yuan, H.B. Wu, Y. Xie, X.W.D. Lou, *Angewandte Chemie International Edition*, 53 (2014) 1488-1504.
- [29] C. Xia, Q. Jiang, C. Zhao, M.N. Hedhili, H.N. Alshareef, *Adv Mater*, 28 (2016) 77-85.
- [30] A. Banerjee, S. Bhatnagar, K.K. Upadhyay, P. Yadav, S. Ogale, *Acs Appl Mater Inter*, 6 (2014) 18844-18852.
- [31] X.Y. Yan, X.L. Tong, L. Ma, Y.M. Tian, Y.S. Cai, C.W. Gong, M.G. Zhang, L.P. Liang, *Mater Lett*, 124 (2014) 133-136.
- [32] G.Q. Zhang, H.B. Wu, H.E. Hoster, M.B. Chan-Park, X.W. Lou, *Energ Environ Sci*, 5 (2012) 9453-9456.
- [33] L. Huang, D. Chen, Y. Ding, S. Feng, Z.L. Wang, M. Liu, *Nano Lett*, 13 (2013) 3135-3139.
- [34] L. Yu, G. Zhang, C. Yuan, X.W.D. Lou, *Chem Commun*, 49 (2013) 137-139.
- [35] J.-W. Lang, L.-B. Kong, M. Liu, Y.-C. Luo, L. Kang, *J Solid State Electr*, 14 (2010) 1533-1539.
- [36] Z.-S. Wu, W. Ren, D.-W. Wang, F. Li, B. Liu, H.-M. Cheng, *Acs Nano*, 4 (2010) 5835-5842.
- [37] Z. Tang, C.h. Tang, H. Gong, *Adv Funct Mater*, 22 (2012) 1272-1278.
- [38] X. Wang, C. Yan, A. Sumboja, P.S. Lee, *Nano Energy*, 3 (2014) 119-126.
- [39] Y. Li, L. Cao, L. Qiao, M. Zhou, Y. Yang, P. Xiao, Y. Zhang, *J Mater Chem A*, 2 (2014) 6540-6548.
- [40] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna, P. Simon, *Nat Nanotechnol*, 5 (2010) 651-654.
- [41] M.F. El-Kady, V. Strong, S. Dubin, R.B. Kaner, *Science*, 335 (2012) 1326-1330.
- [42] X. Lu, M. Yu, T. Zhai, G. Wang, S. Xie, T. Liu, C. Liang, Y. Tong, Y. Li, *Nano Lett*, 13 (2013) 2628-2633.
- [43] X. Lu, M. Yu, G. Wang, T. Zhai, S. Xie, Y. Ling, Y. Tong, Y. Li, *Adv Mater*, 25 (2013) 267-272.
- [44] W. Zilong, Z. Zhu, J. Qiu, S. Yang, *J Mater Chem C*, 2 (2014) 1331-1336.
- [45] X. Lu, G. Wang, T. Zhai, M. Yu, S. Xie, Y. Ling, C. Liang, Y. Tong, Y. Li, *Nano Lett*, 12 (2012) 5376-5381.
- [46] H. Zheng, T. Zhai, M. Yu, S. Xie, C. Liang, W. Zhao, S.C.I. Wang, Z. Zhang, X. Lu, *J Mater Chem C*, 1 (2013) 225-229.

Figure 1. (A) The representative XRD pattern for as-prepared (Ni, Co)_{0.85}Se nanotube arrays on CFC. The typical (B, C) FESEM and (D, E) TEM images for as-prepared (Ni, Co)_{0.85}Se nanotubes as well as (F) corresponding SAED pattern.

Figure 2. (A) Cyclic voltammetry curves of $(\text{Ni, Co})_{0.85}\text{Se}$ at different scans; and (B) plots of anodic and corresponding cathodic peak densities presented in (A) versus the square root of scan rate. (C) galvanostatic charge-discharge profiles of $(\text{Ni, Co})_{0.85}\text{Se}$ with different current densities, and (D) corresponding discharge areal capacitance.

Figure 3. (A) FESEM and (inset) TEM images of as-obtained porous graphene. (B) Typical cross-section FESEM image of vacuum filtered porous graphene film. The inset of (B) shows the digital photo of porous graphene film. (C, D) Cyclic voltammetry plots of porous graphene film at different scans. (E) Plots of galvanostatic charge-discharge profiles of porous graphene film with different current densities, and (F) corresponding discharge areal capacitance.

Figure 4. Schematic of the design of asymmetric supercapacitors by applying nickel cobalt selenide arrays on carbon cloth as a positive electrode and porous graphene film as a negative electrode.

Figure 5. Electrochemical performance of the $(\text{Ni, Co})_{0.85}\text{Se}$ //porous graphene film ASC. (A) Cyclic voltammetry curves; (B) plots of galvanostatic charge-discharge profiles; (C) areal and stack capacitance; (D) Nyquist plot; (E) cycling stability performance and (F) Ragone plot.

Graphical abstract

Asymmetric supercapacitors with excellent performance have been fabricated using ternary $(\text{Ni, Co})_{0.85}\text{Se}$ on carbon fabric as binder-free positive electrodes and porous free-standing graphene films as negative electrodes. Our optimized asymmetric device operating at 1.8 V delivers a very high stack energy density of 2.85 mWh cm^{-3} at a stack power density of 10.76 mW cm^{-3} , as well as 85% capacitance retention after 10,000 continuous charge-discharge cycles. Even at a high stack power density of 1173 mW cm^{-3} , this device still delivers a stack energy density of 1.19 mWh cm^{-3} , superior to most of the reported supercapacitors.

Vitae

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Highlights

1. A highly conductive ternary nickel cobalt selenide electrode is fabricated for supercapacitor application for the first time.
2. The ternary chalcogenide electrodes show much higher areal capacitance and better rate performance than their binary counterparts.
3. Freestanding porous graphene film with excellent supercapacitor performance is successfully prepared.
4. Ultrahigh stack energy and power densities, and outstanding long term cycling stability can be achieved in optimized asymmetric supercapacitor using ternary chalcogenides and graphene films as positive electrode and negative electrode, respectively.

Video Captions:

Video 1(named as clean carbon fabric): The contact angle measurement of pristine carbon cloth.

Video 2(named as selenides covered carbon fabric): The contact angle measurement of ternary nickel cobalt selenide covered carbon fabric.