High Performance Flexible All-Solid-State Asymmetric
Supercapacitors Based on Vertically-aligned CuSe@Co(OH)2
Nanosheet Arrays

Jiangfeng Gong\textsuperscript{a,*}, Yazhou Tian\textsuperscript{a}, Ziyuan Yang\textsuperscript{a}, Qianjin wang\textsuperscript{b}, Xihao Hong\textsuperscript{b}, Qingping Ding\textsuperscript{c}

\textsuperscript{a} College of Science, Hohai University, Nanjing 210098, P. R. China
\textsuperscript{b} Nanjing National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, P. R. China
\textsuperscript{c} Ames Laboratory, US DOE, Ames, Iowa 50011, United States

* To whom correspondence should be addressed. E-mail: jfgong@hhu.edu.cn

Abstract: The developments of electrode active materials provide the opportunities for next-generation energy storage devices. The arrangement of electrode materials on the substrate has recently emerged as a promising strategy for preparing high performance supercapacitors. Herein, we demonstrate a novel vertically-aligned CuSe@Co(OH)\textsubscript{2} nanosheet arrays electrode for supercapacitor application. The materials are thoroughly characterized by structural and spectroscopic techniques. Electrochemical performance of CuSe@Co(OH)\textsubscript{2} nanosheet arrays are investigated in detail, which exhibit a specific capacitance as much as 1180 F g\textsuperscript{-1} at a current density of 1 A g\textsuperscript{-1}. A flexible asymmetric all-solid-state supercapacitor is fabricated using CuSe@Co(OH)\textsubscript{2} nanosheet arrays as positive electrode and activated carbon as negative electrode. The device delivers a volumetric capacitance of 441.4 mF cm\textsuperscript{-3} with maximum energy density and maximum power density are 0.17 mWh cm\textsuperscript{-3} and 62.1
mW cm$^{-3}$, as well as robust cycling stability (~80.4% capacitance retention after 10000 cycles), excellent flexibility and mechanical stability. The excellent electrochemical performance can be attributed to its unique vertically-aligned configuration.

**Keywords:** CuSe@Co(OH)$_2$, vertically-aligned, nanosheet arrays, all-solid-state, asymmetric supercapacitor
1 Introduction

With the progress of the relevant science and technique, portable or wearable electronics, as a new and fast growing technology, has been greatly developed in recent years.\textsuperscript{1-2} The demand for energy storage is expected to grow substantially well into the foreseeable future. Supercapacitors (SCs) act as an emerging class of energy storage devices, have attracted great attentions due to their high power density, fast charge-discharge rate and long cycling life. For conventional SCs, two solid electrodes are directly immersed into the electrolyte containing Na\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{4}, KOH, et.al, which inherently have the risk of liquid leakage and integrity problems. As a result, all-solid-state (ASS) SCs are excellent alternatives because the gel electrolyte used in ASS-SCs is not as mobile as liquid solution and can be easily separated and encapsulated. Moreover, the fabricated ASS-SCs can be easily bended or to be twisted to meet the growing demands for thin, flexible, lightweight and even roll-up portable electronic devices, which is the focus of the present and future researches.\textsuperscript{3-4}

Electrode active materials are key component to constructing high performance ASS-SCs. Based on the energy storage mechanism, two types of materials have been widely studied. One kind is carbon-based materials, they store electrical energy by electrostatic accumulation of charges in the electric double layer (EDL) near the electrode/electrolyte interfaces.\textsuperscript{5-8} They are very stable during the charge/discharge (CD) process, but suffer from relatively low specific capacitances. The other kind is transition metal oxides/hydroxides, such as MnO\textsubscript{2},\textsuperscript{9-15} RuO\textsubscript{2},\textsuperscript{16-19} Co(OH)\textsubscript{2}\textsuperscript{20-23} et.al., the energy stored by reversible Faradic reactions occurring at the electrode surface. They have high theoretical capacitance, whereas their electrical conductivity and mechanical properties are poor. Great achievements had been achieved by designing singular electrode material or even their composited materials.\textsuperscript{24-30} In recent years, it was found that the arrangement of the electrode materials on the substrate is a cognitive
factor for high performance ASS-SCs. In the ASS-SCs, polymer gels were used as solid electrolyte, which is not as mobile as liquid electrolyte. It is difficult to ensure that the gel absorbed on entire surfaces of the electrode materials, this will lower the utilization levels of the electrode materials and thus reduce their energy storage capacity. The best solution is assembling the active materials on the well-arranged backbone with large open channels. For examples, Yang and co-authors fabricated single-crystal ZnO@amorphous MnO2 core-shell nanocable arrays based ASS-SCs, the device show achieved very high total areal capacitance of 26 mF cm\(^{-2}\). The method provides new strategy to enhance electrochemical performance of ASS-SCs.

There is another hurdle has to be overcome for high performance SCs, they suffer from limited energy density compared with lithium ion battery and lead–acid battery. Working voltage is a key parameter related to its energy density according to energy density equation, \(E = \frac{1}{2} CV^2\), C is the device capacitance and V is the working voltage. This equation indicates that the enhancement of energy density can be achieved by improving the device capacitance and/or by widening the potential window. Based on theoretical capacity limit of active materials, increasing the operating voltage is an efficient way to improve energy density. The asymmetric design is an effective way to extend the operating voltage by making use of different potential window of the two electrodes. In which, one electrode consists of a battery-type active material as energy source, and the other electrode a capacitor-type electrode as power source. The configuration ensures high energy density without sacrificing cycle life and power density.

Based on the above consideration, we design and fabricate vertically-aligned CuSe@Co(OH)\(_2\) nanosheet arrays on Au coated polyethylene terephthalate (PET) substrate as a binder-free electrode to construct high performance flexible asymmetric ASS-SCs. The
hierarchical CuSe@Co(OH)$_2$ nanostructures composed of vertically-aligned CuSe nanosheet arrays severed as the backbone, and ultrathin Co(OH)$_2$ nanosheets used as the outer shell layer. The vertically-aligned electrode materials show great advantage: 1) The synthesized CuSe@Co(OH)$_2$ nanosheets cross each other, such configurations can inhibit the re-stacking of electrode materials and fully utilize their surfaces. 2) A lot of open channels were formed between the hybrid nanosheets, which benefit the diffusion of electrolyte ions and transfer of electrons, enable fast redox reaction and consequently enhance the specific capacitance of the electrode. 3) The CuSe shows good electrical conductivity and excellent electrical contact with the Au/PET substrate, which would serve as direct electrical pathways involving in electrochemical reactions. Benefit from the synergetic contribution from nanostructured Co(OH)$_2$ and electrically conductive CuSe, the composited CuSe@Co(OH)$_2$ nanosheet arrays exhibit a specific capacitance as much as 1180 F g$^{-1}$ at a current density of 1 A g$^{-1}$, which is much higher than those of reported results. Furthermore, asymmetric ASS-SCs with CuSe@Co(OH)$_2$ nanosheet arrays as the positive electrode and activated carbon (AC) as the negative electrode were fabricated. The device can deliver a high volumetric capacitance of 441.4 mF cm$^{-3}$ with the maximum energy density and the maximum power density are 0.17 mWh cm$^{-3}$ and 62.1 mW cm$^{-3}$, which is much higher than recent reported Cu(OH)$_2$ SSCs, Bi$_2$O(OH)$_2$SO$_4$ MSCs, TiN SSCs, Carbon nanotube (CNT) SSCs, Activated-Carbon SSCs, all carbon SSC, ZnO/MnO$_2$ SSCs, MnO$_2$ nanotube (NT) SSCs, or comparable to Amorphous NH$_3$NiPO$_4$ ASCs. In addition, the asymmetric ASS-SCs show robust cycling stability, excellent flexibility and mechanical stability.

2. Experimental

2.1 Reagents and Materials
All chemicals were analytic grade from commercial sources. Co(NO$_3$)$_2$ (97%) 0.1M KNO$_3$ (99%), CuCl$_2$·2H$_2$O (99%), SeO$_2$ (99%), KCl (99%), KOH(99%), and HCl (37%) were purchased from Alfa Aesar. Polyethylene terephthalate (PET) pieces and polyvinyl alcohol (PVA) were purchased from Zhuhai Kaivo Optoelectronic Technology Co. and Chengdu Kelong Chemical Reagent Co., respectively.

2.2 Synthesis of CuSe@Co(OH)$_2$ Nanosheet Arrays

Vertically-aligned CuSe@Co(OH)$_2$ nanosheet arrays were synthesized by electrodeposited Co(OH)$_2$ on the pre-prepared CuSe nanosheets. The synthesized of CuSe nanosheets were described elsewhere in detail.$^{47}$ Electrodeposited Co(OH)$_2$ nanosheets were carried out in the traditional three-electrode system under a potentiostatic mode. CuSe nanosheets were used as working electrodes, the Pt plate and saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. The potentials were measured with respect to SCE. The distance between anode and cathode was 8 cm.

The electrolyte was prepared by dissolved 0.1M Co(NO$_3$)$_2$ and 0.1M KNO$_3$ in aqueous domain. The pH value of the electrolyte was adjusted to 5 by addition of H$_2$SO$_4$. To obtain high performance SCs device, various deposition parameters (deposition potential, deposition time and electrolyte temperature) were investigated through orthogonal test. After the reaction, the product was rinsed out with distilled water and dried at room temperature on standby.

2.3 Materials Characterizations

The morphologies of CuSe@Co(OH)$_2$ nanosheet arrays were characterized with scanning electron microscopy (SEM, Zeiss G500 and Quanta 200, FEI). The microstructures of the
products were detected by TEM and high-resolution TEM (Tecnai F20, FEI) were operated at an acceleration voltage of 200 kV. Energy dispersive X-ray spectrums (EDS) were collected by the EDS spectroscopy (EDAX Co.) equipped on TEM. XPS were performed on an XPS system (ESCALAB 250 Xi, Thermo Fisher Scientific). The binding energies were calibrated using C1s peak (BE = 284.6 eV) as a standard.

2.4 Assembly of Asymmetric ASS-SC Device

For preparation of the flexible asymmetric SC devices, vertically-aligned CuSe@Co(OH)2 nanosheet films and active carbon (AC) thin films were used as anodic and cathodic electrode respectively. The AC thin films were fabricated as previous work. AC (YP-50F, Kurary) (80%), conductive carbon black (10%) and polytetrafluoroethylene (PTFE) (10%) were added in N-Methy pyrrolidone(C5H9NO) under vigorous stirring. The suspension was coated on the Au/PET substrate and dried at 100 °C for 24 h. The PVA/KOH gel electrolyte was used as binder and hydrate cellulose was used as separator. The PVA/KOH gel was prepared as following: 6 g KOH of and 6 g PVA were dissolved in 60mL deionized water, the mixture was heated to 85°C under stirring until it became transparent.

2.5 Electrochemical Measurements

The electrochemical tests of the electrode active materials were carried out in the three-electrode measurements. In which, CuSe@Co(OH)2 nanosheet arrays and AC thin films were used as the working electrode, Pt network as the counter electrode, and SCE as the reference electrode. 1 M KOH solution was used as electrolyte for electrochemical measurements. The asymmetric ASS-SCs devices were tested in the two-electrode mode. The electrode loaded with CuSe@Co(OH)2 nanosheet arrays acting as positive electrode and AC thin film as
negative electrode. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and Electrochemical impedance spectroscopy (EIS) was carried out in frequency range of $10^{-2}$~$10^5$ Hz in an electrochemical workstation (CHI 660D, Chenghua Co. Shanghai).

3 Results and discussion

![Diagram](image)

**Fig. 1.** (a) Design of hybrid core/shell nanostructures based supercapacitors. (b) Schematic illustration of the formation process of vertically-aligned CuSe@Co(OH)$_2$ nanosheet arrays.

To achieve enhanced electrochemical properties, one of the effective ways is to construct vertically aligned core/shell nanostructures as illustrated in **Fig. 1a**. In which, the “core” materials have low electric resistance, they can serve as direct electrical pathway to the collection of electrons during charge-discharge process. However, the decorated “shell” materials should have large surface area and provide larger specific capacitance. Our strategy for preparing such hierarchical core-shell nanostructures through a two-step approach was shown in **Fig. 1b**. First, the interconnected CuSe nanosheet arrays was deposited on flexible Au/PET substrate. Due to its special configuration and high electric conductance (The hole mobility can reach 1.87 cm$^2$ V$^{-1}$ s$^{-1}$, reference 48), CuSe nanosheet arrays are much suitable to
be employed as an ideal backbone. The second step was to grow Co(OH)$_2$ nanostructures on surfaces of CuSe through simple electrodeposition method. The advantage of the treatment is that we can control nanosheets density and loading amount by adjusting the electrodeposition parameters. (The details of the experiment are shown in the experiment section). Finally, the vertically aligned CuSe@Co(OH)$_2$ nanosheet arrays were built on flexible Au/PET substrate.

![Image of CuSe@Co(OH)$_2$ nanosheet arrays](image)

**Fig. 2.** (a) Low magnification SEM image of the CuSe@Co(OH)$_2$ nanosheet arrays obtained at -0.68 V (vs SEC) for 10 minutes. The insert is naked CuSe nanosheet. (b) High resolution and (c) cross-section SEM image of the CuSe@Co(OH)$_2$ nanosheet arrays (d) TEM image of the typical CuSe@Co(OH)$_2$ nanosheets and the corresponding SAED image (e). (f) High resolution TEM image of the Co(OH)$_2$ nanostructures. (g) EDX mapping of the elements Cu, Se, Co, O.
The insert in Fig. 2a shows the scanning electron microscopy (SEM) images of naked CuSe nanosheet arrays, it is clearly that the CuSe nanosheets were uniformly aligned vertically on Au/PET substrate at a large scale and formed large open framework between its intersections (Fig. S1). The CuSe@Co(OH)$_2$ core/shell nanostructures were fabricated through the secondary growth of Co(OH)$_2$ on CuSe nanosheets using electrodeposition. The growth processes of the Co(OH)$_2$ “shell” is initiated by the reduction of NO$_3^-$, which generated OH$^-$ ions at the surfaces of CuSe nanosheets by sacrificed electrons (Eq. S1). Then the Co$^{2+}$ ion moved to the negative charged CuSe nanosheets and forming Co(OH)$_2$ directly on its surface (Eq. S2). In this process, CuSe delivered electrons to its surface for reduction reaction successfully, showing its great electronic transmission capacity, which indicated that the CuSe nanosheets not only serve as backbones but also work as a current collector to enhance the capacitive performance of Co(OH)$_2$. To optimize the capacitance performance of the active materials, various electrodeposition parameters were adjusted. Fig. S2 show the SEM images of CuSe@Co(OH)$_2$ core/shell nanostructures deposited under different deposition potential. When the deposition potential is -0.6 V (vs. SEC), the density of Co(OH)$_2$ nanosheets is very low and the edge length is relatively large. With increasing the deposition potential, the density of Co(OH)$_2$ nanosheets increased obviously. When the deposition potential is -0.75 V (vs. SEC) or more, Co(OH)$_2$ nanosheets completely covered the CuSe films. Furthermore, deposition durations were also studied systematically as shown in Fig. S3, which would influence the loading amount of Co(OH)$_2$. To obtain highly uniformed nanostructures, the Co(OH)$_2$ were deposited on CuSe nanosheets at -0.68 V (vs. SEC) as shown in Fig. 2a. Obviously, the Co(OH)$_2$ nanostructures were grown perpendicularly on the surface of CuSe nanosheets, forming a scales-like surface morphology. Micro-pores with the diameters about 3 micrometers still remained, which is beneficial for
gel electrolytes fully penetrate into the active materials when constructing SCs device, and thus improve its specific capacitance. **Fig. 2b** shows the high magnification SEM image of the Co(OH)$_2$ nanosheets, the measured thickness is about 3.72 nm. **Fig. 2c** exhibits the cross-section SEM image of CuSe@Co(OH)$_2$ nanosheet arrays, which reveals that Co(OH)$_2$ nanostructures were covered on inner surface of the CuSe nanosheets. The thickness of the hybrid films were about 5.5 µm. The loading amount was 0.152 mg cm$^{-2}$ estimated from Faraday’s law (**Eq. S3**).

TEM investigations were performed to study the morphology and microstructure of CuSe@Co(OH)$_2$ nanosheets. **Fig. 2d** shows the typical low magnification TEM image of the samples. We can see that the central “core” is covered with plenty of tiny nanosheets on its surface, forming typical hierarchical core/shell nanostructures. **Fig. 2e** is the selected area electron diffraction (SAED) pattern corresponding to the area labelled with circle in **Fig. 2d**. The concentric rings show its poly crystal nature. The measured d-spacings from inside to outside are 0.247 nm, 0.210 nm, 0.161nm, 0.128nm and 0.101nm, which can be indexed to the planes of (100), (102), (104), (106), and (108) of Co(OH)$_2$ respectively (JCPDS no. 26-1107). High resolution TEM were also performed to study its lattice information, the measured lattice fringe is 0.253 nm and can be indexed to the (100) of hexagonal Co(OH)$_2$, which is consistent well with the SAED results. We further employed energy dispersive X-ray spectroscopy (EDS) mapping to study the elemental distribution (the area marked with square in **Fig. 2d**) of CuSe@Co(OH)$_2$ core/shell nanostructure as shown in **Fig. 2g**. The EDS elemental mapping images correspond to the K-edge signals of Cu, Se, Co, and O, respectively. The distributions of the Cu and Se are almost the same and show a sharp edge, which corresponding to the CuSe nanosheet, the area of Co and O elements demonstrates the
uniform deposition of the Co(OH)$_2$ nanostructures, which further confirms the successful preparation of the CuSe@Co(OH)$_2$ core/shell hybrid nanostructures by electrodeposition.

![XRD pattern of CuSe@Co(OH)$_2$ nanosheet arrays.](image)

Fig. 3. (a) XRD pattern of CuSe@Co(OH)$_2$ nanosheet arrays. (b-d) High resolution XPS spectrum of Cu 2p, Se 3d, Co 3p and O 1s.

XRD were used to characterize the crystal phase of as-synthesized samples as shown in Fig 3a. Due to the vertically-aligned configuration of CuSe and little amount of Co(OH)$_2$, only (102) diffraction peak of CuSe (JCPDS no. 34-0171) and (100) diffraction peak of Co(OH)$_2$ (JCPDS no. 26-1107) were detected, peaks located at 25.94° and 38.24° were originate from the Au-coated PET substrate. The accurate composition and atomic oxidation state of the hybrid electrode materials were further studied by the X-ray photoelectron
spectroscopy (XPS) technique. The full XPS spectrum (Fig. S4a) and high-resolution XPS spectrum (Fig. 3b) indicate that the signals of Co and O were much higher than that of Cu and Se. According to is emission theory, the detection depth of XPS is only several nanometers, which further demonstrated its core/shell structure. The spectrum of Co 2p was shown in Fig. 3c, which exhibits two peaks located at 782.1 eV and 798.1 eV with satellite peaks due to Plasmon losses and final state effects. The peaks were assigned to the electronic states of Co 2p3/2 and Co 2p1/2, respectively. The multiplet splitting energy (ΔE=16 eV) indicated that Co is existed as a Co(OH)2 version.49-50 The O 1s spectrum and its fitted curves was shown in Fig. 3d, the main peak at binding energy of 531.3 eV corresponds to the Co-O-H bond, and the shoulder peak can be ascribed to structural water (532.8 eV). The shape and peak positions of the O 1s XPS spectrum are in good agreement with that of the previously reported Co(OH)2.50-51
Fig. 4. The electrochemical performance of the CuSe@Co(OH)$_2$ nanosheet arrays electrode measured in 1 M KOH solution. (a) CV curves of the sample at different scan rate. (b) Relationship of specific current peaks versus the square root of sweep rates. (c) GCD curves and (d) Specific capacitances of the sample at different current densities. (e) Electrochemical impedance spectrum of the CuSe and CuSe@Co(OH)$_2$. Insert are equivalent circuit of CuSe@Co(OH)$_2$. (f) Cyclic stability of CuSe@Co(OH)$_2$ at current density of 10 A g$^{-1}$. Insert are SEM image of CuSe@Co(OH)$_2$ nanosheet after 1000 cycles.
The electrochemical performance of CuSe@Co(OH)₂ nanosheet arrays were evaluated in 1 M KOH electrolyte. Fig. 4a shows the cyclic voltammetry (CV) curves of the electrode at different scan rate, all of the CV curves display a pair of redox peaks, which demonstrates the Faradic-capacity behaviour of the CuSe@Co(OH)₂ electrode. The redox peaks are shifted and more separated accompanied with an increase of the specific current with the sweep rates, these results reveal the quasi-reversible nature of the redox reactions, suggesting the good charge storage at high sweep rates. The presence of broad anodic peaks at approximately 0.17 V (100 mV S⁻¹) can be attributed to the redox reactions related to Co²⁺/Co³⁺/Co⁴⁺ involving OH⁻ as below:

\[
\text{Co(OH)}_2 + \text{OH}^- \leftrightarrow \text{CoOOH} + \text{H}_2\text{O} + e^- \quad (1)
\]

\[
\text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- \quad (2)
\]

The charge storage mechanisms of the CuSe@Co(OH)₂ nanosheet arrays were further studied. Fig. 4b shows the cathodic peak current densities vs. the square root of the sweep rates, the linear dependence demonstrated that the capacitive behaviour is dominated by diffusion-controlled ion intercalation process. Notably, due to its porous morphologies, double layer storage mechanisms may also contribute to the total storage capacity of the hybrid electrodes, we used a kinetic model described in Fig. S5 to study the contribution of both charge storage mechanism, the results indicated that the contributions of the double layer capacity is only 16% to the total capacity of the CuSe@Co(OH)₂ films. This is attributed to characteristics of Co(OH)₂ layered structure, which favours proton or OH⁻ ions insert/extract reversible to its crystal lattice. To determine the specific capacitance values, galvanostatic charge/discharge (GCD) measurements were performed at different current densities as shown in Fig. 4c. The GCD curve is probably symmetric, indicating the
reversible charging and discharging process. The specific capacitance values were calculated according to Eqs. S4-6. The maximum specific capacitance of the CuSe@Co(OH)\textsubscript{2} nanosheet film is 1180 F g\textsuperscript{-1} at the current density of 1 A g\textsuperscript{-1} (Fig. 4d), which is higher than reported Co(OH)\textsubscript{2} electrode\textsuperscript{20-21} and much higher than those of other electrode\textsuperscript{17, 52-53}. The superior electrochemical properties of Co(OH)\textsubscript{2} are attributed to the porous Co(OH)\textsubscript{2} shell which could greatly increase the contact interface between electrode and electrolyte. In addition, numerous inter-spaces of the Co(OH)\textsubscript{2} nanoflakes also facilitate the electrolyte ion transport and thus enhanced the electrochemical properties. Electrochemical impedance spectroscopy (EIS) was also performed to investigate the electrochemical performance of the electrodes in the frequency range of 0.01~10\textsuperscript{5} Hz. The Nyquist plots of the CuSe, CuSe@Co(OH)\textsubscript{2} electrodes were presented in Fig. 4e. The EIS of CuSe exhibits a Warburg behavior, indicating fast ion transport with its porous micro-pores configuration. Additional with the low equivalent series resistance (5.5 ohm) further confirmed that the CuSe nanosheet arrays could act as a good substrate for Co(OH)\textsubscript{2} loading. The EIS of CuSe@Co(OH)\textsubscript{2} electrode shows a semicycle at high frequency region followed with a straight line at low frequency denoted excellent capacitive behavior. The fitted equivalent circuit were also presented in Fig. 4e, where R\textsubscript{s} represents the total ohmic resistance of electrolyte resistance, R\textsubscript{ct} is the charge-transfer resistance, and C\textsubscript{p} is the capacitive element due to the redox process of electrode. The result of R\textsubscript{ct} is 4.9 ohm, which revealed that the porous CuSe@Co(OH)\textsubscript{2} electrodes own high electronic conductivity and electrochemical reactivity, and were suitable to being electrode active materials. Fig. 4f presents the cycling retention of the CuSe@Co(OH)\textsubscript{2} nanosheet arrays at a current density of 10 A g\textsuperscript{-1}. It is clearly that the micropore structure still remained after 1000 cycles, which demonstrate that the CuSe@Co(OH)\textsubscript{2} core/shell nanostructures are very stable during the electrochemical test. The specific
capacitance maintains 98.8% of initial capacitance, suggesting its steady electrochemical performance.

**Fig. 5.** Evaluation of electrochemical performance of asymmetric SC with CuSe@Co(OH)₂ as positive electrode and porous AC as negative electrode: (a) CV curves for evaluating the operational window, (b) CV curves of the asymmetric SC.

The capacitances of porous AC were evaluated in a potential window of 0.0 V to -1.0 V as shown in **Fig. S6**. The porous AC exhibited capacitance 84.2, 69.7, 61.6, 57.1 and 49.5 F g⁻¹ at the current density of 0.5, 1, 2, 3, and 5 A g⁻¹. Based on its CV results, they store energy followed electron double layer mechanism, which makes porous AC an ideal negative electrode material, especially heavy load charge-discharge performance when building the asymmetric SC device. An asymmetric SC was assembled by using CuSe@Co(OH)₂ nanosheet arrays as positive electrode and porous AC as negative electrode. In order to obtain the high performance of CuSe@Co(OH)₂//AC device, the charge on positive and negative
electrode should be optimized based on the individual capacitive performance (Eq. S7). The electrochemical potential windows of the electrodes were estimated in 1 M KOH electrolyte. Because the porous AC was measured within a stable voltage window of –1.0 to 0.0 V, while that of the CuSe@Co(OH)$_2$ electrode was tested from 0.0 to 0.5 V (Fig. 5a), the asymmetric CuSe@Co(OH)$_2$/AC SC device can extend the operating voltage window in aqueous electrolyte up to 1.5 V by taking advantage of the maximum applied voltage as shown in Fig. 5b. The operating voltage of asymmetric SC is much higher than the conventional symmetric SCs. In this case, the anodic micro-porous CuSe@Co(OH)$_2$ nanostructures provide easy access channels for the ions to penetrate inside the porous nanosheets, while in the cathode, the AC suffer high electron density due to EDL storage mechanism, the synergistic effect of two electrode materials makes the asymmetric CuSe@Co(OH)$_2$/AC SC to conduct ions and electrons at higher rates. Fig. S7 shows the GCD curves and the calculated specific capacitance of the CuSe@Co(OH)$_2$/AC ASC at the current density from 10 A g$^{-1}$ to 50 A g$^{-1}$. The asymmetric SCs exhibited maximum capacitance of 386 F g$^{-1}$ at current density of 40 A g$^{-1}$ for single electrode, which is significantly higher than most of the reported asymmetric SCs.
Fig. 6. (a) Schematic illustrations of assembled asymmetric ASS-SC. (b) CV curves at different sweep rates. (c) GCD curves and (d) specific capacitance at different currents density. (e) long-life cycle stability of the ASS-SC device. (f) Ragone plot of energy density versus power density based on the CuSe@Co(OH)2//AC asymmetric ASS-SC.
The experimental results indicated that the fabricated CuSe@Co(OH)2//AC have excellent electrochemical properties in aqueous solution. To test the feasibility of CuSe@Co(OH)2//AC based all-solid-state SCs, the devices were assembled using CuSe@Co(OH)2 as positive electrodes and porous AC as negative electrodes with PVA/KOH gel as solid-gel electrolyte (named as CuSe@Co(OH)2//AC ASS-SCs). The schematic illustration was shown in Fig. 6 a. The assembled CuSe@Co(OH)2//AC asymmetric ASS-SCs were shown in Fig. S8a. The average thickness of the well-assembled ASS-ASCs device is 0.30 mm and the test area is 2 cm². The asymmetric ASS-SCs devices show excellent flexibility and mechanical properties, and can endure high-angular winding as shown in Fig. S8b. The CuSe@Co(OH)2//AC ASS-SCs were tested in a two electrode system to verify its electrochemical performance. The delicate CV curves of the ASS-SC device were shown in Fig. 6b scanned from 2mV/s to 200mV/s. The CV plots have distinct redox peaks, indicating the enhanced electrochemical performance and the ability to conduct ions and electrons at high rates. The GCD curves of the asymmetric ASS-SCs at various current densities were presented in Fig. 6c, a slight potential drop during the initial discharging result from the low resistance. Besides, there are two mild platforms at about 0.8 V and 0.3 V, demonstrating a Faradaic capacitance property. The calculated volumetric capacitance is shown in Fig. 6d. The capacitances have a regular decline with the increased current densities, which was attributed to the decreasing the electrolyte ion diffusion and migration of the electrode material under high current density. The Co(OH)2@CuSe//AC ASS-SCs exhibit the maximum volumetric capacitance reached 441.4 mF cm⁻³ at 0.3mA cm⁻². The long-term cycling stability of the ASS-ASCs was evaluated by galvanostatic charge–discharge at 1 mA cm⁻². As shown in Fig. 6e, the specific capacitance shows very slow increase during the first initial 2500 cycles at the normal state, which may be attributed to the
activation process of the electrode materials. Then, the device was tested continuously under 90°, 180° bending state and normal state in turn under equal intervals. After 10000 cycles, the Co(OH)$_2$@CuSe//AC ASS-SCs show 80.4% retention of the initial capacitance, indicating excellent cycling performance and flexibility. Fig. 6f shows the Ragone plot of the CuSe@Co(OH)$_2$//AC ASS-ASC device with some of the recently reported devices (Calculation details were shown in Eqs. S8-9). The as-fabricated device can achieve a maximum volumetric energy density of 0.17 mWh cm$^{-3}$ at a current density of at 0.3 mA cm$^{-2}$, further verifying the good electrochemical performance of the as-prepared device. Compared to other ASS-SCs, the obtained maximum volumetric energy density is much higher than recent reported ZnO/MnO$_2$ SSCs, Cu(OH)$_2$ SSCs, Bi$_2$O(OH)$_2$SO$_4$ MSCs, TiN SSCs, CNT SSCs, Activated-Carbon SSCs, all carbon SSC, MnO$_2$-NT SSCs, and comparable to Amorphous NH$_3$NiPO$_4$ ASCs. In addition, the as-prepared device can deliver a maximum power density of 62.1 mW cm$^{-3}$ at a current density of 3 mA cm$^{-2}$. These results again confirmed that the vertically-aligned CuSe@Co(OH)$_2$ core/shell configuration was very promising as an anode material for high energy-density devices.

Fig. 7. GCD curves for the CuSe@Co(OH)$_2$ ASS-SCs with different configuration. Single and tandem devices were measured at a current density of 1 mA cm$^{-2}$, and paralleled device
was detected at a current density of 2 mA cm\(^{-2}\). Inset: red LED was powered by the tandem devices.

In some practical situation, the SCs would be used in series or in parallel to meet the energy and power requirements. For this consideration, Fig. 7 shows the GCD curves of two CuSe@Co(OH)\(_2\)//AC ASS-SCs and their combinations in series and parallel. The CD curve of the tandem devices kept the same trend with the single ASS-SC, which indicates excellent capacitive properties with minimal internal resistance. More important, the voltage window was extended by a factor of 2 compared with a single SC. While in the parallel mode, the output current was two times as that of a single device. To demonstrate the potential application of the as-prepared device, the tandem devices were employed to power a red light-emitting-diode (LED 1.6 V) in the inset of Fig. 7 and Video S1. The device can power a red LED for about 130 seconds after being charged at 1 mA cm\(^{-2}\) for 40s.

4 Conclusion

In summary, vertically-aligned CuSe@Co(OH)\(_2\) nanosheet arrays were successfully synthesized on flexible Au-coated PET substrate, and used as active electrode materials in electrochemical supercapacitor. The CuSe@Co(OH)\(_2\) electrode exhibited the specific capacitance of 1180 F g\(^{-1}\) at the current density of 1 A g\(^{-1}\). Asymmetric ASS-SCs were fabricated by using CuSe@Co(OH)\(_2\) and porous AC as positive and negative electrodes respectively. The CuSe@Co(OH)\(_2\)//AC ASS-SC shows a volumetric specific capacitance 441.4 mF cm\(^{-3}\) at 0.3mA cm\(^{-2}\) with maximum energy density of 0.17 mWh cm\(^{-3}\) additional with good cycling stability (80% capacitance retention after 10000 cycles), excellent flexibility, and desirable mechanical stability. This work developed an efficient way to resolve the spacial orientation of active electrode materials. The remarkable performances
can be attributed to its micro-porous vertically-aligned configuration, which increase the contact interface area between electrode and electrolyte and facilitate the electrolyte ion transport. Further integrating other electroactive materials with the CuSe nanosheet array to fabricate advanced hybrid electrodes is under way in our laboratory.

**Supporting Information**

This information contains electrochemical reaction for the formation Co(OH)$_2$ nanostructures, calculation details of the capacitance, energy density and power density; SEM images and XPS spectra of the CuSe@Co(OH)$_2$ nanosheet arrays, electrochemical data of active carbon, additional electrochemical data for asymmetric supercapacitors and photos of CuSe@Co(OH)$_2$/AC ASS-SC at different bending state.

**Acknowledgement**

This work was supported by the Fundamental Research Funds for the Central Universities (Grant Nos. 2015B22314 and 2016B46014) and the Funds for Basic Energy Sciences of Ames Laboratory (Grant No. DE-AC02-07CH11358).

**Reference**


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TOC graphic