Electronic Supplementary Information

FeSe\textsubscript{2}/carbon nanotubes hybrid lithium-ion battery for harvesting energy from triboelectric nanogenerators

Yang Tian,\textsuperscript{a} Zhaoying Wang,\textsuperscript{b} Jiangming Fu,\textsuperscript{c} Kequan Xia,\textsuperscript{c} Jianguo Lu,*\textsuperscript{a,}\textsuperscript{b} Haichao Tang,\textsuperscript{a} Rabia Khatoon,\textsuperscript{a} Hongwen Chen,\textsuperscript{a} Zhiyuan Zhu,*\textsuperscript{c} Qinghua Zhang,\textsuperscript{b,}\textsuperscript{d} Yu-Jia Zeng,\textsuperscript{e} Zhizhen Ye*\textsuperscript{a}

\textsuperscript{a} State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: lujianqiao@zju.edu.cn, yezz@zju.edu.cn

\textsuperscript{b} Ningbo Research Institute, Zhejiang University, Ningbo 315100, China

\textsuperscript{c} Ocean College, Zhejiang University, Zhoushan 316021, China. zyzhu@zju.edu.cn

\textsuperscript{d} College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

\textsuperscript{e} Shenzhen Key Laboratory of Laser Engineering, College of Optoelectronic Engineering, Shenzhen University, Shenzhen, 518060, China
**Experimental Section**

**Oxidation of carbon nanotubes**

The purchased multi-walled carbon nanotubes (MWCNTs) are 20–40 nm in diameter and 30–100 μm in length. The MWCNTs are hydrothermally oxidized by concentrated nitric acid. Typically, 1.5 g MWCNTs are added into a Teflon-lined stainless autoclave, then 50 mL HNO₃ is added. The mixture is sonicated at 50 °C for about 2 h. After that, the Teflon-lined stainless autoclave is heated at 100 °C for 6 h. Then, the oxidized MWCNTs are naturally cooled down to room temperature, centrifuged and washed with deionized water several times until the pH of suspension liquid reaches around 7. The oxidized MWCNTs are dried at 120 °C for 12 h.

**Synthesis of FeSe₂−CNTs hybrid microspheres**

In a typical procedure, 2 mmol Fe(NH₄)₂(SO₄)₂·6H₂O is added to 60 mL distilled water. After stirring for 10 minutes, 4 mmol SeO₂ is added into the above solution and continuously stirred for 10 minutes. Then, 4.0 g citric acid monohydrate is added to the resulting mixture under continuous stirring for 10 minutes, followed by addition of 12 mL NH₄·H₂O (85 wt.%) under continuous stirring. After that, 0.02 g MWCNTs are added into the resulting solution. After sonication, the suspension is transferred into a 100 mL Teflon-lined stainless steel autoclave and heated to 180 °C for 12 h. After the reaction, the obtained FeSe₂−CNTs hybrid are collected by centrifugation and successively washed with deionized water and absolute ethanol for 3 times, respectively. After drying in vacuum at 60 °C for 12 h, the as-synthesized FeSe₂−CNTs are obtained.

The synthetic procedure of FeSe₂ microspheres is the same as that of FeSe₂−CNTs hybrid microspheres, except that no MWCNTs are added in the reaction system.

**Materials Characterizations**

The crystal structures of the samples were investigated through X-ray diffraction (XRD, Rigaku, Japan, the scan rate of 10 °C min⁻¹) using Cu Kα radiation (λ = 1.540589
Å) at the Bede D1 system. In addition, field-emission scanning electron microscopy (FESEM; Hitachi S-4800) and energy-dispersive X-ray analysis spectroscopy (EDS) were used to analyze the morphology and element distribution of the samples. Besides, the microstructure was examined by the transmission electron microscopy (TEM, TF20, Joel 2100F) and high-resolution TEM (HRTEM). To elucidate elements chemical states, the element analysis of the samples was performed using X-ray Photoelectron Spectroscopy (AXIS Supra. Kratos). Finally, thermogravimetric analysis (TGA) was performed using a Pyris 1 TGA in the air at a heating rate of 20°C·min⁻¹.

**Assembly of lithium-ion batteries**

The electrochemical properties of the obtained FeSe₂ and FeSe₂–CNTs hybrid microspheres were analyzed using 2032-type coin cells. The lithium metal and microporous polypropylene film (Celgard 2500) were used as the counter electrode and separator, respectively. The anode was prepared by mixing the active materials, super p, and polyvinylidene fluoride (PVDF) binder in the solvent of N-methyl-pyrrolidinone in a weight ratio of 7:2:1. After grinding, the slurry was blade-coated onto the copper foil and then dried at 60 °C for 24 h. Then the dried copper foil with coating was punched into disks with a diameter of 16 mm. The mass loading of active materials was approximately 1 mg·cm⁻². The electrolyte was 1 M LiPF₆ in the mixture of ethylene carbonate and dimethyl carbonate with a volume ratio of 1:1.

**Electrochemical measurements**

The charge/discharge profiles of the obtained electrodes were investigated by cycling the half cells in a potential range of 0.01–2.7 V and 0.01-3.0V at different current destinies on CT2001A LAND battery test system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured on CHI760E electrochemical workstation (CH Instruments, Inc.). CV curves were measured at various scan rates from 0.2 mV s⁻¹ to 1 mV s⁻¹. The EIS test was carried out in a frequency range of 0.01 Hz to 100 kHz at certain potential.

**Triboelectric nanogenerator (TENG) for charging**
The triboelectric pairs of TENG consists of the Teflon film (5 cm × 5 cm) and Nylon film (5 cm × 5 cm), and the conductive copper serves as the conductive electrode. A mechanical exciter was used to provide external force to activate TENG. The separate distance is controlled at 7 cm. The contact frequency is between 2 Hz and 18 Hz. The fabricated TENG was used to charge FeSe$_2$-CNTs based LIB via a power management circuit. The energy storage system was illustrated in Fig.3a in manuscript. A digital oscilloscope (DXOS6004A) with a 100 MΩ probe was used to measure the current and voltage of this system.
The HRTEM image of the FeSe$_2$ microspheres (Fig. S1a) shows some clear lattice fringes with two d-spacings values of 0.37 and 0.28 nm, which correspond to the (110) and (101) planes of cubic orthorhombic FeSe$_2$, respectively. It can be further found from the selected area electron diffraction (SAED) ring patterns (Fig. S1b) that there are some diffraction spots, matching (110) and (101) crystal planes. The HRTEM image of oxidized MWCNT (Fig. S1c) reveals lattice fringes with an inter-planer spacing of 0.34 nm, which can be indexed as the (002) planes of MWCNTs. The diffraction ring of the (002) crystal plane is shown in the SAED ring pattern (Fig. S1d). These results demonstrate that FeSe$_2$ and CNTs are polycrystalline.
**Fig. S2** a) Element mapping and b) EDX spectrum of FeSe$_2$. 
Fig. S3 XRD patterns of FeSe$_2$ and FeSe$_2$-CNT hybrid.
Fig. S4  a) XPS spectra of FeSe$_2$-CNTs and high-resolution XPS profiles b) C1s; c) Fe 2p; d) Se 3d.

X-ray photoelectron spectroscopy (XPS) spectra and high-resolution XPS profiles of FeSe$_2$-CNTs are shown in Fig. S4. The XPS spectra in Fig. S4a confirms the presence of Fe, Se, and C elements. The high-resolution XPS spectrum of Fe 2p (Fig. S4b) features two sharp peaks located at 707.1 and 720.0 eV, corresponding to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ of FeSe$_2$, respectively. Furthermore, the deconvolution result of Fe 2p XPS spectrum verifies the coexistence of Fe$^{2+}$ and Fe$^{3+}$ in the iron oxide forms. The presence of iron oxides was caused by the partial oxidation of the FeSe$_2$ surface.\textsuperscript{51}

The Se 3d spectrum (Fig. S4c) can be deconvoluted into two peaks at 54.8 and 55.7 eV, corresponding to Se 3d$_{5/2}$ and Se 3d$_{3/2}$ in FeSe$_2$, respectively. The broad peak located at 59.3 eV corresponds to the Se-O bond, which is ascribed to the surface
oxidation of FeSe₂ microspheres. These results are in good agreement with the previous investigation of iron selenides.²,³

The high-resolution XPS spectrum of C 1s (Fig. S4d) shows four different carbon bonding states, with C=C (sp²), C-C (sp³), C-O and C=O peaks located at 284.8, 285.5, 286.5, and 289.0 eV, respectively. The existence of C-O and C=O bonds indicates the successful oxidation of MWCNTs.⁴
Fig. S5 a) XPS spectra of FeSe$_2$ and high-resolution XPS profiles for b) Fe 2p; c) Se 3d.

XPS spectra and high-resolution XPS profiles of FeSe$_2$ microspheres are shown in Fig. S5. Similar analyses can be carried out on this sample, as those in Fig. S4. As for FeSe$_2$, the chemical state of Fe and Se is almost the same as that of FeSe$_2$-CNTs.
**Fig. S6** \( \text{N}_2 \) adsorption / desorption isotherm curves and BJH pore size distribution of a) FeSe\(_2\) and b) FeSe\(_2\)-CNTs.
According to the reaction between FeSe$_2$ and O$_2$ described in Equation S1, the theoretical weight loss of pure FeSe$_2$ is 62.64 wt. % above 700 °C (See Equation S2 for details). The weight loss of FeSe$_2$-CNTs hybrid is consistent with that of pure FeSe$_2$ and CNTs, which can be described as Equation S3,

$$4\text{FeSe}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + 8\text{SeO}_2 \uparrow$$ \hspace{2cm} (S1)

$$1 - \frac{M_{\text{Fe}_3\text{O}_4}}{2M_{\text{FeSe}_2}} = 1 - \frac{159.68}{2 \times 213.76} = 62.64\%$$ \hspace{2cm} (S2)

$$M_{\text{FeSe}_2} \times 62.62\% + M_{\text{CNTs}} = M_{\text{loss}}$$ \hspace{2cm} (S3)

The CNTs content of the hybrids and the enthalpy change with the increasing temperature was performed by TG-DTA analysis (Fig. S7). The results showed that the weight loss is around 65.4% in the temperature range 200–700 °C. The increase in weight percentage can be detected between 200 and 400 °C and a sharp peak appeared in DTA curve, on account of the generation of iron oxide and selenium dioxide, which may originate from the oxidation of FeSe$_2$. The decrease in mass above 400 °C with a sharp peak in DTA curves corresponds to the sublimation of selenium dioxide and the flaming of carbon. The mass loss of the pure FeSe$_2$ is 62.6%, which is consistent with
the theoretical calculation. Therefore, the accurate loading of FeSe$_2$ and CNTs in the FeSe$_2$-CNTs was determined to be 92.5 and 6.5%.
Fig. S8 Cycling performance of (a) FeSe\textsubscript{2} and (b) FeSe\textsubscript{2}-CNTs in the voltage window of 0.01-2.7 V and 0.01-3 V.

Since the selenide anodes store lithium ions in a conversion reaction mechanism, the large volume changes in the charge / discharge process require an appropriate upper voltage limit to ensure high reversibility of lithium storage reactions. The cycling stability of the FeSe\textsubscript{2} and FeSe\textsubscript{2}-CNTs electrode was evaluated over different potential windows at the current density of 2.5 A g\textsuperscript{-1}, as shown in Fig. S8. As for FeSe\textsubscript{2} electrode
(Fig. S8a), when the cut-off voltage is 3.0 V, the specific capacity decreased significantly at the first 70 cycles and there is little remaining capacity at 300th cycle. When the cut-off voltage is 2.7 V, the capacity decrease rapidly after around 20 cycles and gradually increased to 96 mA h g⁻¹ at 1000th cycle. As for FeSe₂-CNTs electrode (Fig. S8b), this phenomenon is similar to that of FeSe₂. The battery shows better stability in voltage window of 0.01-2.7 V, with a remaining capacity of 158 mA h g⁻¹ after 1000 loops. However, the remaining capacity is less than 20 mA h g⁻¹ after 300 cycles in the voltage window of 0.01-3.0 V. The results show that the FeSe₂ and FeSe₂-CNTs electrode has a better cycle life in voltage window of 0.01-2.7 V compared with 0.01–3.0V. Therefore, a voltage window of 0.01-2.7 V was selected to give an excellent reversible lithium storage reaction.
Fig. S9 Long cycling performance of FeSe$_2$ and FeSe$_2$-CNTs at 0.5 A g$^{-1}$. The discharge capacity of FeSe$_2$-CNTs electrode slightly decreases at first and stabilizes at 571.2 mA h g$^{-1}$ in the 3rd cycle, which keeps stable in the main till 50 cycles with the capacity retention of 93.5% (74.0% for FeSe$_2$) at 50$^{th}$ cycle. The irreversible capacity loss may be due to the formation of solid electrolyte interface (SEI) membrane, and decomposition of electrolyte. After $\sim$ 50 cycles, the capacity quickly decreases arriving at the minimum value of 201.4 mA h g$^{-1}$ at 115$^{th}$ cycle. After 115 cycles, the capacity gradually increases with cycles, arriving at 272.5 mA h g$^{-1}$ at the 200$^{th}$ cycle, which is higher than that of FeSe$_2$ (172.9 mA h g$^{-1}$). Above all, the FeSe$_2$-CNTs electrode shows better electrochemical performance than FeSe$_2$. 
Fig. S10 Discharge / charge profiles of (a) FeSe$_2$ and (b) FeSe$_2$-CNTs in the 1$^{\text{st}}$, 2$^{\text{nd}}$, 10$^{\text{th}}$, and 50$^{\text{th}}$ cycles at 0.5 A g$^{-1}$. 
The discharge / charge profiles of FeSe\textsubscript{2} and FeSe\textsubscript{2}-CNTs electrodes at different number of cycles were studied at a current density of 0.5 A g\textsuperscript{-1}, as shown in Fig. S10. For both samples, there are two charge plateaus at \(~1.9\) V and 2.3 V and one discharge plateau at \(~1.5\) V in the first discharge process, which splits into two discharge plateaus at \(~2.0\) V and \(~1.55\) V after 2\textsuperscript{nd} cycle. The discharge voltage plateaus gradually shift downward and charge voltage plateaus shift upward as the number of cycles increases. The discharge plateau of FeSe\textsubscript{2}-CNTs electrodes is still obvious in the 50\textsuperscript{th} cycle, which is almost disappeared of FeSe\textsubscript{2}. It is obvious that the plateaus of FeSe\textsubscript{2} change more than that of FeSe\textsubscript{2}-CNTs, indicating the FeSe\textsubscript{2}-CNTs hybrid microsphere structure is more stable and less degree of polarization than that of FeSe\textsubscript{2}.
Fig. S11 Discharge / charge profiles of FeSe$_2$-CNTs at different current densities.
Long-term cycling performance of FeSe₂ and FeSe₂-CNTs at a current density of 2.5 A g⁻¹.

The long-term cycling performance of fabricated samples at high current density of 2.5 A g⁻¹ for 2000 cycles was investigated to ensure the superior performance of FeSe₂-CNTs microsphere hybrids (Fig. S12). The cycling performance of FeSe₂-CNTs hybrid electrode exhibits similar variation trend to that at 0.5A g⁻¹ in Fig S9. The capacity keeps stable in the main till ~20 cycles and quickly decreases after ~ 20th cycle, arriving at the minimum value of 68.7 mA h g⁻¹ at ~ 160th cycle and then the capacity gradually increases with cycles, arriving at 182.6 mA h g⁻¹ at the 2000th cycle with a Coulombic efficiency of nearly 100 %. The FeSe₂ electrode displays similar capacity changing trend to the FeSe₂-CNTs electrode, with the specific capacity of 89 mA h g⁻¹ at the 2000th cycle. Above all, the cycling tests showed that the electrochemical performance of FeSe₂-CNTs microsphere hybrids is also significantly superior to FeSe₂ microspheres at high current destiny long-term cycling.

As shown in Fig. S12, the capacity decreases rapidly after 20 cycles. This phenomenon can be commonly observed in LIBs, which is believed to be due to the large polarization, unstable SEI membrane, and poor infiltration of electrolyte and active materials during the electrochemical processes. Interesting, the steady increase in capacity during subsequent cycles is found in Fig. S12, which is also seen in other
transition metal selenides (e.g., MnSe and ZnSe) as anodes for lithium ion batteries. \textsuperscript{S6} This may be ascribed to the reactivation of active materials, current collector (Cu) involving in the reaction, structural restructuring, and the reversible growth of a polymer / gel-like film caused by the decomposition of the electrolyte at low potentials, as suggested in precious literatures \textsuperscript{S5-7} and partially confirmed in our research (see Fig. S13). The steady increase in capacity during the long-term cycles may be the merits of FeSe\textsubscript{2}-based LIBs for practical applications.
To deeply investigate the FeSe$_2$-CNTs electrodes, XRD and SEM data were measured before and after cycling. The XRD spectra of the FeSe$_2$-CNT electrode before cycling and after 1000 loops were shown in Fig. S13a. After 1000 loops, the characteristic peaks of FeSe$_2$ disappeared. The characteristic peak of Fe appears in 43.6°, meanwhile a characteristic peak of CuSe$_2$ appear at 32.8°, indicating that Cu is involved in the electrochemical reaction of the electrode during cycling, resulting in the formation of CuSe$_2$. The amorphization of FeSe$_2$ in electrode occurred during the cycling.

Based on the SEM images, the morphology changes can be clearly identified for the FeSe$_2$-CNT electrode before cycling (Fig. S13b) and after 1000 cycles (Fig. S13c). After 1000 cycles, the FeSe$_2$-CNT no longer contains microspheres composed of regular nano-octahedra. In contrast, the irregular spheres composed of irregular small particles appear, indicating that the anode materials went through the structure recombination during cycling and the nano-octahedra particles might be refined. In addition, the size of nanoparticles increases after 1000 cycles, further revealing the aggregation and reconfiguration of anode materials during electrochemical process.
Fig. S14 EIS of the as-prepared (a) FeSe$_2$ and (b) FeSe$_2$-CNTs after the 1$^{st}$, 50$^{th}$, 150$^{th}$, 500$^{th}$ and 1000$^{th}$ cycle; c) the equivalent circuit diagram.

To evaluate the electrochemical dynamical behaviors of samples at discharging process before and after cycling, EIS of FeSe$_2$ and FeSe$_2$-CNTs were measured, analyzed, and compared at discharging to 1.5V (Fig. S14). The equivalent circuit diagram was shown in Fig. S14c, which includes the resistances of the electrolyte and cell components ($R_e$), the resistance of the solid electrolyte interface ($R_{sei}$), the charge-transfer resistance ($R_{ct}$), Warburg impedance ($Z_w$), SEI film capacitance ($Q_1$) and
double-layer capacitance ($Q_2$). Before cycling at open circuit voltage, the $R_e$ of FeSe$_2$ (1.47 $\Omega$ cm$^{-2}$) is smaller than that of FeSe$_2$-CNTs (6.67 $\Omega$ cm$^{-2}$) because it is easier for the FeSe$_2$ nanoparticles to be wetted by electrolyte. In the 1$^{st}$ cycle, the SEI film is forming. The $R_{sei}$ of FeSe$_2$-CNTs (78.64 $\Omega$ cm$^{-2}$) is larger than that of FeSe$_2$ (45.52 $\Omega$ cm$^{-2}$) because the SEI formation process in FeSe$_2$ is easier than that of FeSe$_2$-CNTs. And more remarkable, the $R_{ct}$ of FeSe$_2$-CNTs (12.06 $\Omega$ cm$^{-2}$) is significantly smaller than that of FeSe$_2$ (34.31 $\Omega$ cm$^{-2}$). This suggests that the addition of CNTs in hybrids has improved the charge-transfer resistance through the high electronic conductivity of oxidized CNTs. With the cycling, we noted that the $R_{ct}$ of FeSe$_2$-CNTs electrodes gradually decreases from 202.9 to 11.65 $\Omega$·cm$^{-2}$ from the 50$^{th}$ to 1000$^{th}$ cycles, which might be ascribed to the surface reactivation and lattice expansion triggering better Li$^+$ transfer.$^{88}$ In addition, this phenomenon also may be due to the side reaction of the Cu-involved electrochemical reaction forming new substances (e.g. CuSe$_2$ and Fe) as active material, as confirmed in Fig. S13. Of course, further study is still needed to clarify the specific reasons for the gradual decrease of $R_{ct}$. The slope line of the EIS was related to the $Z_w$ of lithium ion diffusion. The slope of the EIS decreased after 150 cycles and increased in the following cycles, which is consistent with the cycle performance. After 1000 cycles, the electrode has been activated fully. The $R_e$ of FeSe$_2$-CNTs (11.23 $\Omega$ cm$^{-2}$) is smaller than that of FeSe$_2$ (16.7 $\Omega$ cm$^{-2}$) and the $R_{sei}$ of FeSe$_2$-CNTs (64.78 $\Omega$ cm$^{-2}$) is also smaller than that of FeSe$_2$ (100.6 $\Omega$ cm$^{-2}$). The FeSe$_2$-CNTs electrode shows lower $R_{sei}$, $R_e$ and $R_{ct}$ than that of FeSe$_2$ anode, which is consistent with the better cycle performance.
Fig. S15 CV curves of (a) FeSe\(_2\) and (b) FeSe\(_2\)-CNTs with pseudocapacitive contribution (blue shade) at a scan rate of 0.8 mV s\(^{-1}\).

The contribution of pseudocapacitive (\(k_1 v\)) and diffusion-controlled behaviour (\(k_2 v^{1/2}\)) is calculated by the formula \(i = k_1 v + k_2 v^{1/2}\). As the scan rate is 0.8 mV s\(^{-1}\), the pseudocapacitive contribution ratio of FeSe\(_2\)-CNT is 95.05%, which is larger than that of FeSe\(_2\) (88.68%). This larger contribution ratio of pseudocapacitance is beneficial to fast charge storage and fast redox kinetics, resulting in the excellent rate performance.

Further, the lithium ion diffusion coefficient (D) can be calculated by the Randles-Sevick equation as follow:

\[
I_p = 0.4462nFAC\left(\frac{nFvD}{RT}\right)^{1/2} = 29000An^{2/3}C^{1/2}D^{1/2}v^{1/2}
\]

where \(I_p\): peak current; \(n\): charge transfer number; \(F\): Faraday's constant; \(A\): electrode surface; \(C\): Li\(^+\) concentration; \(v\): scan rate; and \(D\): diffusion coefficient.

The calculated D of FeSe\(_2\)-CNTs is \(8.11 \times 10^{-14}\) cm\(^2\) s\(^{-1}\) at the voltage of 1.93V, which is greater than that of FeSe\(_2\) (\(6.43 \times 10^{-14}\) cm\(^2\) s\(^{-1}\)). Above all, the FeSe\(_2\)-CNTs showing the larger contribution ratio of pseudocapacitance and larger D than FeSe\(_2\), indicating the better electrochemical properties of FeSe\(_2\)-CNTs.
Fig. S16 a) Frequency - dependent short circuit current measurements and b) corresponding current waveform of TNEG at 15 Hz; c) Frequency-dependent open circuit voltage measurements and d) corresponding voltage waveform of TNEG at 15 Hz.

The corresponding output performances of TENG were measured, as shown in Fig. S16. when the contact frequency increased under the same condition, the approximate values of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) increased owing to the fast induction and transferring of charges under the high-frequency contact. The active current $I_{sc}$ and maximum $V_{oc}$ of TENG at frequency of 15 Hz is approximately 3 μA and 589 V. The electrochemical performance of the battery is likely to be damaged by this pulse high voltage and special pulse waveform.
Fig. S17 The circuit diagram of the energy storage system (a) without voltage regulator (VR) and (b) with the VR.

The energy storage system without VR is shown in Fig. S17a. This system includes a rectifier, which could convert output alternating current (AC) of the TENG into direct current (DC), and then connect directly to the batteries to store energy. Fig. S17b shows a system with a VR. The main function of VR is to output a stable voltage. Its working principle is as follows. The energy could be stored in input capacitor firstly, and then starts the voltage regulator circuit inside when the voltage is higher than the threshold voltage, finally, the output voltage through the VR is about 3 V, which is close to the working voltage of battery. Thus, the voltage regulator could reduce the damage of the high pulse voltage to the battery, but it also consumes considerable energy.
Reference


