Construction of hierarchical core-shell structured CoSe\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}@Fe\textsubscript{2}O\textsubscript{3} composite as advanced anodes for sodium ion batteries

Shi Luo\textsuperscript{a,1}, Chenghao Chen\textsuperscript{a,1}, Ruojin Feng\textsuperscript{a}, Xuanjia Chen\textsuperscript{a}, Wenlin Chen\textsuperscript{a}, Zhangjie Wu\textsuperscript{b}, Xiangzhong Kong\textsuperscript{a,b,c,13}

\textsuperscript{a} S. Luo, C. Chen, R. Feng, X. Chen, W. Chen, Z. Wu, X. Kong College of Mechanical Engineering Hunan Institute of Science and Technology Yue yang, 414006, China
\textsuperscript{b} X. Kong Institute of New Energy Hunan Institute of Science and Technology Yue yang, 414006, China
\textsuperscript{1} These authors contributed equally to this work.

* Corresponding authors: xzhkong@hotmail.com

Abstract. Transition metal selenides/oxides have received extensive attention, due to there suitable voltage plateaus and abundant reserves. However, intrinsic low electrons conductivity and huge volume change during sodiation/desodiation process limit its wide application. To address these issues, CoSe\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}@Fe\textsubscript{2}O\textsubscript{3} with heterogeneous structure was successfully synthesized. As a SIBs anodes, the CoSe\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}@Fe\textsubscript{2}O\textsubscript{3} composite presents high electrochemical reversibility with a capacity of 360 mA h g\textsuperscript{-1} after 100 cycles at 100 mA g\textsuperscript{-1}.

Keywords: CoSe\textsubscript{2}, Fe\textsubscript{3}O\textsubscript{4}, heterogeneous structure, anode, sodium ion batteries

1. Introduction

With the gradual depletion of fossil fuels, people's demand for safe, green, and economical rechargeable batteries is becoming more and more urgent. In recent years, lithium-ion batteries (LIBs) has been widely focused. However, due to limited lithium resources, the development prospects of LIBs are limited [1-3]. The sodium element has the advantages of abundant reserves, uniform resource distribution, and low price, thus sodium ion batteries (SIBs) have been extensively studied. [4-7]. To date, researchers have developed various anode materials for SIBs, such as metal sulfides, metal oxides, metal selenides, and carbon-based materials, which have demonstrated excellent electrochemical performance [8-9]. However, the radius of sodium ions is larger, which makes it more difficult to insertion/extraction, and the volume changes more drastically, which makes it difficult for sodium ion batteries to meet actual needs [10-13].

Till now, in order to solve the above problems, several solutions have been proposed based on the foregoing, such as ion doping, composite formation, and dimension reduction. At present, the application of heterostructures to electrochemical-related technologies has received extensive attention. For example, Fang et al. reported a selenide heterostructure (CoSe\textsubscript{2}/ZnSe), where charge transfer and electron mobility generally increase at the heterogeneous interface [9]. Heterogeneous structure has excellent performance in improving electronic conductivity and cycling performance. Its unique structure and versatility have great potential in improving electrochemistry [14-16].

In this work, we synthesized the heterostructured CoSe\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}@Fe\textsubscript{2}O\textsubscript{3} by a hydrothermal process combined with a simple selenization process. The final products own nano flower-like structure. The unique heterostructure improves the conductivity, promotes the transmission of electrons of CoSe\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}@Fe\textsubscript{2}O\textsubscript{3} nanocrystals. The CoSe\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}@Fe\textsubscript{2}O\textsubscript{3} exhibits excellent electrochemical performance during the electrochemical reaction.
2. Experimental

Preparation of CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$:

Typically, 81ml C$_2$H$_6$O$_2$, 24ml NH$_3$·H$_2$O, 4.2ml Si((OC$_2$H$_5$)$_4$, were mixed and dissolved and stirred at for 1h. The resulting product was then centrifuged to obtain a template (SiO$_2$). Then, 10ml 0.1M Fe$_6$(HNO$_3$)$_3$, 10ml 0.1M C$_2$H$_6$CoO$_2$, 0.27g SiO$_2$ and 20g CH$_3$N$_2$O were mixed with 360 mL deionized water, sonicate for 30 minutes. After that, the obtained solution was hydrothermal treated at 105°C for 12 hours. After the supernatant of the reaction is poured out, the after washing six times using deionized water and ethanol to obtain the precursor (Fe-Co@SiO$_2$). Finally, put 1g Fe-Co-N and 2g Se powder into a tube furnace respectively, and carry out selenization treatment under the protection of N$_2$ at 600 °C for 6 h. Finally get the sample CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$. The CoSe$_2$, Fe$_3$O$_4$@Fe$_2$O$_3$ was prepared as the control sample with the same process excepting the addition of Fe$_3$(HNO$_3$)$_3$ or C$_2$H$_6$CoO$_2$.

2.1. Materials characterizations

Surface morphology of the prepared materials was characterized by scanning electron microscope (SEM JSM-7600F), X-ray diffraction (XRD D/Max 2700 X-ray diffractometer with Cu- Kα radiation), the Brunauer-Emmett-Teller (BET, Quantachrome AutosorbiQ2-XR).

2.2. Electrochemical measurements

Sodium storage performances were characterized using CR2012 coin cells. The active material was mixed with Super-p and CMC in a mass ratio of 8:1:1 to prepare an active electrode. The active material is evenly casted onto the aluminum foil dried overnight at 60 °C under vacuum to make a working electrode. The electrolyte comes from a mixture of 1, 2-Dimethoxyethane (DME) and 1 M KPF$_6$. Charge/discharge measurements, rate performance and cycling stability were tested on a Land tester.

3. Results and Discussion

The heterostructure of CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$ was synthesized by a hydrothermal process combined with a simple selenization process Figure 1 shows the detailed synthesized process of it. The iron salt and cobalt salt are uniformly coated on the SiO$_2$ sphere by one-step hydrothermal method to form a precursor (Fe-Co@SiO$_2$). Then, CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$ is obtained by simple selenization of the precursor in an Ar atmosphere at 600 °C.

![Figure 1](image)

Figure 1. The schematic fabrication process of CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$.

The structure and morphology of the Co@SiO$_2$, Fe@SiO$_2$, Fe-Co@SiO$_2$ precursor and the as-obtained CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$ composite are investigated by the SEM measurements. Figure 1a and b displays the SEM image of Co@SiO$_2$, showing an urchin-like structure with a diameter of about 500nm assembled with numerous burrs. Figure 1c-f shows that the SEM image of Fe@SiO$_2$, Fe-Co@SiO$_2$ respectively. The Fe@SiO$_2$, Fe-Co@SiO$_2$ is composed of many uniform nanospheres with the diameter of 500nm. As shown in Figure 1g-i, the CoSe$_2$, Fe$_3$O$_4$, Fe$_2$O$_3$ nanoparticles are uniformly coated outside the SiO$_2$ sphere to form a double-layer structure, which shortens the diffusion of Na$^+$ and effectively increases the transmission rate, and promotes the reaction kinetics.

Figure 3a-e shows the XRD typical peaks of the CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$, CoSe$_2$, Fe$_3$O$_4$, Fe$_2$O$_3$. All peaks of CoSe$_2$, Fe$_3$O$_4$, Fe$_2$O$_3$ are well indexed to the orthorhombic CoSe$_2$ (JCPDS card no. 88-1712),
\[ \text{Fe}_2\text{O}_3 \ (86-0050), \ \text{Fe}_3\text{O}_4 \ (88-0866). \] There were no additional peaks found, indicating the samples was successfully synthesized.

**Figure 2.** SEM of the Co@SiO\(_2\) (a, b), Fe@SiO\(_2\) (c, d), Fe-Co@SiO\(_2\) (e, f) and CoSe\(_2\)@Fe\(_3\)O\(_4\)@Fe\(_2\)O\(_3\) (g-i).

**Figure 3d** shows that the surface and pore features of CoSe\(_2\)@Fe\(_3\)O\(_4\)@Fe\(_2\)O\(_3\), CoSe\(_2\), Fe\(_3\)O\(_4\)@Fe\(_2\)O\(_3\) by N\(_2\) adsorption-desorption isotherms. The specific surface area of CoSe\(_2\)@Fe\(_3\)O\(_4\)@Fe\(_2\)O\(_3\), CoSe\(_2\), Fe\(_3\)O\(_4\)@Fe\(_2\)O\(_3\) are calculated to be as high as 200, 160, 80 m\(^2\) g\(^{-1}\), respectively. And it can be found that the pore size is mainly distributed at about 75, 240, 260 nm. The composite of CoSe\(_2\)@Fe\(_3\)O\(_4\)@Fe\(_2\)O\(_3\) has a higher specific surface area due to the unique thorn-like heterostructure structure effectively increases its surface area. The high surface area is beneficial to promote electrolyte infiltration and can provide abundant active sites, thereby improve the electrochemical performance of the CoSe\(_2\)@Fe\(_3\)O\(_4\)@Fe\(_2\)O\(_3\) composite.
Figure 3. (a-c) XRD patterns and (d) Porosity characterization of CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$, CoSe$_2$, Fe$_3$O$_4$@Fe$_2$O$_3$.

Figure 4a shows that the representative discharge/charge voltage curves of CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$ cycling at 100 mA g$^{-1}$. The discharge capacity can reach a value of 475 mAh g$^{-1}$. While the discharge capacity can reach a value of the second and third cycles are 325 mA h g$^{-1}$ and 323 mA h g$^{-1}$, respectively. The coulomb efficiency also reached 96% and 94% respectively, which indicates the rapid improvement of reversibility. Cycle performances of CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$, CoSe$_2$, Fe$_3$O$_4$@Fe$_2$O$_3$ at 0.1 A g$^{-1}$ are displayed in Figure 4b. After 100 cycles, CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$ electrode maintains excellent reversible capacity of 360.5 mAh g$^{-1}$. The capacities of CoSe$_2$ and Fe$_3$O$_4$@Fe$_2$O$_3$ are 281.6 and 202.4 mAh g$^{-1}$, respectively. The higher capacities of CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$ than those of CoSe$_2$ and Fe$_3$O$_4$@Fe$_2$O$_3$ demonstrate that the heterostructure can effectively improve electrochemical performance of the composites. To further demonstrate the excellent electrochemical performance of CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$, Figure 4c displays the rate capabilities of the CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$, CoSe$_2$, Fe$_3$O$_4$@Fe$_2$O$_3$. The CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$ electrode exhibits the best rate capability with capacities of 416, 350, 337, 295.3 and 260 mAh g$^{-1}$, respectively. Compared with CoSe$_2$ (314, 286.9, 268.5, 236.4, 202, 182.1 mAh g$^{-1}$), Fe$_3$O$_4$@Fe$_2$O$_3$ (261.3, 241.6, 222.4, 194.6, 163.7, 139 mAh g$^{-1}$), the rate of CoSe$_2$@Fe$_3$O$_4$@Fe$_2$O$_3$ electrode has obvious advantage. The Fe$_3$O$_4$@Fe$_2$O$_3$ electrode has an excellent rate performance because of unique heterostructure.
Figure 4. Na\(^+\) storage performances of the obtained samples. (a) Charge–discharge curves (0.1 A g\(^{-1}\)) of CoSe\(_2@\)Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\). (b) Cycling stability of CoSe\(_2@\)Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\), CoSe\(_2\), Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\) at at 100 mA g\(^{-1}\). (c) Rate capabilities of CoSe\(_2@\)Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\), CoSe\(_2\), Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\) electrode from 0.05 to 2 A g\(^{-1}\). (d) Nyquist plots of CoSe\(_2@\)Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\), CoSe\(_2\), Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\) electrodes.

Figure 4d shows the Nyquist plots of CoSe\(_2@\)Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\), CoSe\(_2\), Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\) and the corresponding equivalent circuit model. The Ohmic resistance of the cell (Rs) is reflected by the high frequency region intercept, is mainly related to electrolytes. Compared with Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\) (280 Ω) and CoSe\(_2\) (240 Ω), CoSe\(_2@\)Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\) (195Ω) has the smallest charge transfer impedance, which shows the best electrochemical kinetics.

4. Conclusions
In summary, CoSe\(_2@\)Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\) with heterogeneous structure was successfully synthesized by one-step hydrothermal method and a simple selenization process. The unique heterostructure improves the electronic conductivity and effectively alleviates the volume change of CoSe\(_2@\)Fe\(_3\)O\(_4@\)Fe\(_2\)O\(_3\) during the sodiumization/ desodification process. In addition, N-doping provides abundant defects and effectively improves electronic conductivity. The facile synthetic strategy here can be also expanded to other advanced electrode materials.

5. Acknowledgments
This work was supported by the Scientific Research Foundation of Hunan Provincial Education Department (No.19B232), and Innovation and Entrepreneurship Program for college students(S202010543037).
References

[1] Wang, G., et al., Sacrificial template synthesis of hollow C@MoS$_2$@PPy nanocomposites as anodes for enhanced sodium storage performance. Nano Energy, 2019. 60: p. 362-370.

[2] Pan, J., et al., Layered-Structure SbPO$_4$/Reduced Graphene Oxide: An Advanced Anode Material for Sodium Ion Batteries. ACS Nano, 2018. 12(12): p. 12869-12878.

[3] Luu, T., et al., Monodispersed SnS nanoparticles anchored on carbon nanotubes for high-retention sodium-ion batteries. Journal of Materials Chemistry A, 2020. 8(16): p. 7861-7869.

[4] Li, Y.J., et al., Mesoporous Cu$_2$-xSe nanocrystals as an ultrahigh-rate and long-lifespan anode material for sodium-ion batteries. Energy Storage Materials, 2019. 22: p. 275-283.

[5] Guo, H., et al., In-Situ Fabrication of Bone-Like CoSe$_2$ Nano-Thorn Loaded on Porous Carbon Cloth as a Flexible Electrode for Na-Ion Storage. Chemistry-an Asian Journal, 2020. 15(9): p. 1493-1499.

[6] Lv, X., et al., Ultrafine FeSe nanoparticles embedded into 3D carbon nanofiber aerogels with FeSe/Carbon interface for efficient and long-life sodium storage. Carbon, 2019. 143: p. 106-115.

[7] Fang, G., et al., Metal Organic Framework-Templated Synthesis of Bimetallic Selenides with Rich Phase Boundaries for Sodium-Ion Storage and Oxygen Evolution Reaction. Acs Nano, 2019. 13(5): p. 5635-5645.

[8] Zhang, K., et al., Urchin-Like CoSe$_2$ as a High-Performance Anode Material for Sodium-Ion Batteries. Advanced Functional Materials, 2016. 26(37): p. 6728-6735.

[9] Wang, X.F., et al., Nontopatotic Reaction in Highly Reversible Sodium Storage of Ultrathin Co$_9$Se$_8$/rGO Hybrid Nanosheets. Small, 2017. 13(24): p. 8.

[10] ang, J., et al., Atomic layer deposition of TiO$_2$ shells on CoSe$_2$ nanorods towards enhanced lithium storage performance. Journal of Alloys and Compounds, 2020. 829: p. 154537.

[11] Duan, J., et al., Bimetal - organic Framework - derived Co$_9$S$_8$/ZnS@ NC Heterostructures for Superior Lithium - ion Storage. Chemistry - An Asian Journal, 2020. 15(10): p. 1613-1620.

[12] Cuan, J., et al., Multiple Anionic Transition-Metal Oxycarbide for Better Lithium Storage and Facilitated Multielectron Reactions. ACS nano, 2019. 13(10): p. 11665-11675.

[13] Lu, X., et al., Three dimensional graphene encapsulated ZnO-ZnFe$_2$O$_4$ composite hollow microspheres with enhanced lithium storage performance. Electrochimica Acta, 2017. 249: p. 79-88.

[14] Xu, E., et al., Ultrafast kinetics net electrode assembled via MoSe$_2$/MXene heterojunction for high-performance sodium-ion batteries. Chemical Engineering Journal, 2020. 385: p. 10.

[15] Qiu, L.C., et al., NiCo$_2$Se$_4$ as an anode material for sodium-ion batteries. Electrochemistry Communications, 2020. 112: p. 6.

[16] Hong, J., J. Kim, and C. Yun, Sodium-ion storage performance of hierarchically structured (Co$_{0.3}$Fe$_{2.7}$)$_2$Se$_2$ nanofibers with fiber-in-tube nanostructures. Journal of Materials Chemistry A, 2016. 4(40).