3D CoMoSe$_4$ Nanosheet Arrays Converted Directly from Hydrothermally Processed CoMoO$_4$ Nanosheet Arrays by Plasma-Assisted Selenization Process Toward Excellent Anode Material in Sodium-Ion Battery

Shan Zhang$^{1,2}$, Yuanfei Ai$^2$, Shu-Chi Wu$^2$, Hsiang-Ju Liao$^2$, Teng-Yu Su$^2$, Jyun-Hong Chen$^2$, Chuan-Hsun Wang$^2$, Ling Lee$^2$, Yu-Ze Chen$^2$, Binbin Xu$^2$, Shao-Shin Lee$^2$, Jun Yin$^1$, Jing Li$^1$$^*,$ Junyong Kang$^1$ and Yu-Lun Chueh$^{2,3,5}$$^*$

Abstract

In this work, three-dimensional (3D) CoMoSe$_4$ nanosheet arrays on network fibers of a carbon cloth denoted as CoMoSe$_4$@C converted directly from CoMoO$_4$ nanosheet arrays prepared by a hydrothermal process followed by the plasma-assisted selenization at a low temperature of 450 °C as an anode for sodium-ion battery (SIB) were demonstrated for the first time. With the plasma-assisted treatment on the selenization process, oxygen (O) atoms can be replaced by selenium (Se) atoms without the degradation on morphology at a low selenization temperature of 450 °C. Owing to the high specific surface area from the well-defined 3D structure, high electron conductivity, and bi-metal electrochemical activity, the superior performance with a large sodium-ion storage of 475 mA h g$^{-1}$ under 0.5–3 V potential range at 0.1 A g$^{-1}$ was accomplished by using this CoMoSe$_4$@C as the electrode. Additionally, the capacity retention was well maintained over 80 % from the second cycle, exhibiting a satisfied capacity of 301 mA h g$^{-1}$ even after 50 cycles. The work delivered a new approach to prepare a binary transition metallic selenide and definitely enriches the possibilities for promising anode materials in SIBs with high performances.

Keywords: CoMoSe$_4$ nanosheet arrays, CoMoO$_4$ nanosheet arrays, Plasma-assisted selenization, Sodium-ion battery
insertion processes, generally resulting in structural degradation and instability of the solid electrolyte interphase, is still a serious issue. Therefore, further strategies are still needed to accommodate or buffer the material structures for practical applications [16, 17]. Recently, bimetallic sulfides/selenides, e.g., NiCo$_2$S$_4$, Co$_2$Mo$_3$Se$_6$, and CoMoS [18–20], have been investigated as a promising class of electrode materials for promising energy storage and conversion devices because of their higher electrochemical activities and capacities than monometal sulfides/selenides, e.g., MoS$_2$, CoSe$_2$, NiSe$_2$, and FeSe$_2$ [21–27]. However, in the field of SIBs, there have been few reports on the application of bimetallic selenides because of the challenge in material synthesis. Up to date, some synthetic methods and applications of bimetallic selenides in SIBs have been carried out [28–30]. Among them, Co and Mo, as transition metal elements with abundant resources and high redox chemical valences [31–35], are promising components as anode materials. Additionally, carbon cloth with highly textured surface and good electrical conductivity is a good substrate for electrode materials, which can enable fast electron transport and produce large electrode–electrolyte contact areas [37, 38].

In this regard, we demonstrated 3D-networked CoMoSe$_4$ nanosheet arrays on network fibers of the carbon cloth (CoMoSe$_4$@C) by direct chemical conversion through the plasma-assisted selenization of CoMoO$_4$ nanosheet arrays prepared by the hydrothermal process on network fibers of the carbon cloth (CoMoO$_4$@C) as the anode in SIBs for the first time. Interestingly, with the assistance of plasma-assisted process on selenization process, the conversion of O atoms by Se can be achieved at a low temperature of 450 °C without any morphology change. The CoMoSe$_4$@C shows better sodium storage performance than that of the unselenized CoMoO$_4$@C. With synergetic effects from both transition metal species, a highly reversible capacity of 475 mA h g$^{-1}$ at 0.1 A g$^{-1}$ and a high capacity retention of over 80% even after 50 cycles at 0.5 A g$^{-1}$ were accomplished using the CoMoSe$_4$@C composite as the electrode in SIBs. Furthermore, this composite electrode can deliver excellent rate capabilities with the discharge capacities changing from 475 to 230 mA h g$^{-1}$ as current densities were stepwisely added ranging from 0.1 to 5 A g$^{-1}$, exhibiting a good sodium storage property. This work developed a new pathway of synthesizing bimetallic selenides, which may be adopted in other related materials for the sodium energy storage or other applications [39–43].

**Experimental Section**

**Synthesis of CoMoO$_4$ Nanosheet Arrays by the Hydrothermal Process**

Firstly, 0.4234 g Na$_2$MoO$_4$·2H$_2$O (purity ≥ 99%, Sigma-Aldrich), 0.5093 g Co(NO$_3$)$_2$·6H$_2$O (purity ≥ 98%, Alfa Aesar), 0.074 g NH$_4$F (purity ≥ 98%, Alfa Aesar), and 0.49 g CO(NH$_2$)$_2$ (purity ≥ 99.5%, Echo Chemical Co., Ltd.) were added to 35 mL of distilled (DI) water under constant intense stirring. Then, the mixture was transferred to the Teflon-lined stainless autoclave, containing a piece of carbon cloth (CC) (CeTech Co., Ltd., Taiwan), followed by heating at 180 °C for 12 h in an oven. After the hydrothermal growth, the as-synthesized sample was taken out and carefully cleaned, followed by the vacuum-drying at 60 °C for 12 h. Finally, the as-synthesized sample was annealed in pure argon at 300 °C for 2 h to obtain the CC coated with CoMoO$_4$ nanosheet arrays.

**Direct Conversion of CoMoSe$_4$ Nanosheet Arrays by Plasma-Assisted Selenization Process**

The plasma-assisted selenization system (Syskey Technology Ltd.) was used to selenize the as-produced CoMoO$_4$ nanosheet arrays. The selenium heater at the top of the machine is separated from the lower sample holder to independently control the temperature of the Se source and substrate, respectively. In the synthesis process, the selenium particles were firstly placed on the selenium (Se) heater and were heated to 300 °C to generate Se vapors. At the same time, the vaporized Se gas was carried out to the substrate by a vertical flow of a mixed carrier gas containing N$_2$/H$_2$ gas (N$_2$:H$_2$ = 40:80) at the steady flow rate to maintain the amount of Se in the vapor. Subsequently, the substrate previously placed on the sample holder was heated to the reaction temperature of 450 °C. Once the substrate temperature was stable, the plasma was initiated at 250 W to ionize Se vapors into Se radicals to promote the chemical reaction.

**Characterization**

Morphologies of as-produced materials were characterized by scanning electron microscopy (SEM) (Hitachi UHR FE-SEM SU8010). Further observations of the difference in structures before and after the plasma-assisted selenization were examined using a high-resolution transmission electron microscope (HRTEM) (JEOL, JEM-F200 CFEGTEM, 200 kV). The elemental analyses were conducted by electron energy loss spectroscopy (EELS) via HRTEM (JEOL, JEM-F200). The formation of CoMoSe$_4$@C was examined by Raman spectroscopy (HORIBA, LabRAM, HR800) with the green laser (532 nm) excitation. The crystal structures of CoMoO$_4$ and CoMoSe$_4$ were then characterized by X-ray diffraction (XRD) (Ultima IV, Rigaku). The chemical bonding and the depth profile of materials were established by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI 1600) facility. Electrochemical testing of the prepared CoMoSe$_4$@C was carried out using a CR2032 coin cell, consisting of a CoMoSe$_4$@C electrode and a sodium metal cathode separated by glass fibers.
CoMoSe₄@C was directly used as an anode electrode, and its corresponding weight was calculated by subtracting the weight of the carbon cloth from the CoMoSe₄@C composite. The electrolyte is 1 M sodium trifluoromethanesulfonate (NaCF₃SO₃) dissolved in diethylene glycol dimethylether (DEGDME). To investigate the electrochemical performance of the assembled electrodes, cyclic voltammetry (CV) was performed in 0.5–3 V potential ranges at 0.1 mV s⁻¹ on a Bio-Logic VSP potentiostat, and the electrochemical impedance was conducted using electrochemical impedance spectroscopy (EIS) over the frequency ranges of 0.01 Hz–100 kHz. Charging/discharging measurements were conducted under 0.5–3 V on Land Battery Measurement System at room temperature.

Results and Discussion

The synthesis of 3D CoMoSe₄ nanosheet arrays converted directly from hydrothermally processed CoMoO₄ by the plasma-assisted selenization process is schematically shown in Scheme 1. Basically, as a proof of concept, CoMoO₄ nanosheets were grown on network fibers of a carbon cloth through hydrothermal process as displayed in Scheme 1a₁, followed by the plasma-assisted selenization process as displayed in Scheme 1a₂. CoMoO₄@C directly converted into CoMoSe₄ nanosheets. It can be demonstrated that the O atoms were nearly replaced by Se atoms after the plasma-assisted selenization process (Additional file 1: Figure S1). Detailed steps of CoMoSe₄ nanosheets converted directly by the plasma-assisted selenization process were mentioned in the experimental part.

Figure 1 a shows a SEM image of fibers taken from a carbon cloth where the inset shows a low-magnification SEM. After a hydrothermal process, CoMoO₄ nanosheet arrays with a well-established texture structure were successfully grown on the fibers of the carbon cloth denoted as CoMoO₄@C as shown in Fig. 1b. Figure 1 c shows a magnified SEM image taken from Fig. 1b where the nanosheet arrays with uniform in the diameter of approximately ~ 13 μm, consisting of high-density 3D nanosheets (Fig. 1d) with the networked morphology, can be clearly observed. After the plasma-assisted selenization under a power of 250 W at 450 °C for 1 h, nanosheet structures still remain as shown in Fig. 1e. However, there are slight changes in the morphology of the individual nanosheet, with which nanograins can be found on the surface instead of the smooth surface after the plasma-assisted selenization process as shown in Fig. 1f. The EDS elemental mapping images of Co, Mo, and Se on a randomly selected composite fiber as demonstrated in Fig. 1g soundly prove the successful production of CoMoSe₄ on the carbon cloth with the uniform distribution around the individual fiber. Without the plasma-assisted treatment, the CoMoO₄ cannot be completely converted into CoMoSe₄ under the identical condition (250 W and 450 °C) as shown in Additional file 1: Figure S2a. These characteristic resonance modes of CoMoO₄ still maintain after the selenization process without the plasma-assisted treatment (blue curve in Additional file 1: Figure S2a) while the black curve in Additional file 1: Figure S2a represents characteristic resonance modes of CoMoSe₄. Clearly, it can be expected that the Se radicals ionized from Se atoms...
by plasma-assisted treatment can speed up the chemical reaction between Co, Mo, and Se to form CoMoSe₄ at the lower selenization temperature.

Furthermore, TEM results also demonstrate the nanosheet morphology in the as-prepared CoMoO₄ as shown in Fig. 2a, which is consistent with SEM images. In addition, a polycrystalline feature can be found in a CoMoO₄ nanosheet where small single crystals can be well recognized by high-resolution TEM image as shown in Fig. 1b, c. As displayed in Fig. 1c, spaced lattice fringes in the distance of around 0.157 nm and 0.335 nm can be measured, which can be indexed to the crystal planes of (024) and (002), confirming the phase of CoMoO₄. To further confirm the phase difference between CoMoO₄ and CoMoSe₄, Raman results were measured as shown in Additional file 1: Figure S2b. Before the plasma-assisted selenization process, the characteristic resonance modes at 330, 817, and 930 cm⁻¹ are measured to well confirm the formation of the CoMoO₄ phase (black curve in Additional file 1: Figure S2b) [44, 45]. However, significant changes in the corresponding resonance modes can be found in the Raman spectra.
before and after the plasma-assisted selenization process on the CoMoO 4@C, with which the resonance mode at 168 cm\(^{-1}\) originated from CoSe\(_2\) [46], and typical MoSe\(_2\) features with \(E^{1/2}_L\) and \(A_{1g}\) modes located at 233 and 280 cm\(^{-1}\) verified the production of CoMoSe\(_4\) (red curve in Additional file 1: Figure S2b) [47]. The CoMoO\(_4\) and CoMoSe\(_4\) phases can be also evidenced by XRD spectra as shown in Additional file 1: Figure S3 where monoclinic CoMoO\(_4\) (JCPDS No. 21-0868), orthorhombic CoSe\(_2\) (JCPDS No. 53-0449), and hexagonal MoSe\(_2\) nanocrystals (JCPDS No. 29-0914) were confirmed, respectively. Additionally, the uniform distribution of Co, Mo, and O elements throughout the nanosheet can be confirmed by EDS elemental mapping images as shown in Fig. 2d indicating the homogeneous synthesis of the CoMoO\(_4\) after the hydrothermal process. The as-selenized CoMoSe\(_4@C\) preserved the nanosheet structure, presenting the polycrystallinity as shown in Fig. 2e, f and characterized by Raman and XRD measurements (Additional file 1: Figures S2b and S3). The high-resolution TEM image as shown in Fig. 2g exhibits well-recognized lattice fringes separated by ~ 0.27 and ~ 0.65 nm, corresponding to (110) and (002) crystal planes of CoSe\(_2\) and MoSe\(_2\), respectively, confirming the successfully plasma-assisted selenization process to form the CoMoSe\(_4\). Similarly, the homogeneous transformation can be claimed with the uniform distribution of Co, Mo, and Se elements within the CoMoSe\(_4\) nanosheets as shown in Fig. 2h.

In order to investigate the chemical composition of the selenized CoMoSe\(_4\), XPS measurements were carried out in the CoMoSe\(_4@C\) composite, with which only Co, Mo, Se, C, and O elements can be identified within the instrumental limit as shown in Fig. 3a. Further narrow-scan spectra of Co 2p, Mo 3d, and Se 3d orbitals in both raw data and fitted curves were laid out in Fig. 3b–d. The 2p orbital-related peak of Co element splits into well-defined 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks at 778.37 and 793.92 eV (Fig. 3b), suggesting that Co exists in the form of Co\(^{2+}\), and their satellite peaks marked as “Sat.” appeared at 780.37 and 783.52 eV, respectively [48, 49]. Two peaks at 232.25 and 229.53 eV (Fig. 3c) correspond to Mo 3d\(_{3/2}\) and Mo 3d\(_{5/2}\), indicating that Mo is in its Mo (IV) state [50, 51]. Additionally, peaks located at 54.59 and 55.46 eV in both raw data and fitted curves can be well-resolved corresponding to the Se 3d\(_{5/2}\) and Se 3d\(_{3/2}\) energies as shown in Fig. 3d [36, 52, 53]. Clearly, the peak observed at 59.64 eV is associated with SeO\(_x\), which was formed by the surface oxidation of CoMoSe\(_4@C\) during sample handling [54]. The compositional analysis results show that the atomic ratio of Co:Mo:Se is about 1:0.88:3.84, indicating the stoichiometric of CoMoSe\(_4\).

The sodium storage performance of the CoMoSe\(_4@C\) anode was evaluated using coin-type half cells with the unselenized CoMoO\(_4@C\) electrode for the comparison. As can be seen in the cyclic voltammogram (CV) curves of the CoMoSe\(_4@C\) electrode as shown in Fig. 4a, two peaks at ~ 1.14 and 1.05 V during the first cathodic sweep can be resolved corresponding to the insertion process by Na\(^+\) ion while the two oxidation peaks at around 1.79 V and 1.86 V are related to the extraction process of the Na\(^+\) ion. Starting from the second cycles, the CV curves in this composite as the anode material exhibit overlaps with the subsequent cycle, indicating the good electrode stability. The corresponding galvanostatic charge/discharge curves as displayed in Fig. 4b are consistent with the CV results and demonstrate the stable Na\(^+\) insertion/extraction behaviors within the first five cycles except for some irreversible reactions. It should be mentioned that the fiber structure of the carbon cloth almost contributed nothing in the capacity evidenced by the cycling measurements as shown in Additional file 1: Figure S4. For the comparison, CV and charge/discharge curves of the CoMoO\(_4@C\) electrode at the same measured conditions are displayed in Additional file 1: Figure S5. Note that the poor electrochemical activity in the CoMoO\(_4@C\) composite as the anode for SIBs can be confirmed. Undoubtedly, the plasma-assisted selenization of CoMoO\(_4@C\) is quite constructive to produce more suitable electrode materials for sodium storage.

Additional file 1: Figure S6 shows the raw experimental and fitted Nyquist plots for CoMoSe\(_4@C\) and CoMoO\(_4@C\) as well as the corresponding equivalent circuit (inset of Additional file 1: Figure S6). Clearly, the fitting results confirm that the charge transfer resistance (Rct) of CoMoSe\(_4@C\) and CoMoO\(_4@C\) is 19 and 157 \(\Omega\), respectively. EIS results reveal the electrochemical mechanisms of improved sodium storage capability in the CoMoSe\(_4@C\) composite electrode, in which the better electrical conductivity can be characterized in the plasma-assisted selenized composite to facilitate the faster Na\(^+\) insertion/extraction even at high current densities than those in the CoMoO\(_4@C\) composite. Moreover, the superior rate performance in the CoMoSe\(_4@C\) electrode was accomplished comparing with the CoMoO\(_4@C\) as demonstrated in Fig. 4c with the current densities stepwisely increasing from 0.1 to 5 A g\(^{-1}\). Specifically, a high reversible capacity of 475 mA h g\(^{-1}\) at 0.1 A g\(^{-1}\) was shown by the CoMoSe\(_4@C\) electrode with the contrast to only 198 mA h g\(^{-1}\) in the CoMoO\(_4@C\) anode. As current densities are stepwisely increased from 0.1 to 0.2, 0.5, 1, 2, and 5 A g\(^{-1}\), reversible capacities in the CoMoSe\(_4@C\) electrode dropped from 475 to 458, 371, 320, 277, and 230 mA h g\(^{-1}\), indicating the good rate capability. As a comparison, the discharge capacities in the CoMoO\(_4@C\) anode experienced a reduction from 198 to 140, 93, 65, 45, and 26 mA h g\(^{-1}\), respectively. Furthermore, the similar phenomena...
Fig. 3  

(a) The wide-scan XPS spectrum and narrow-scan spectra of (b) Co2p, (c) Mo3d, and (d) Se3d in the composite of CoMoSe4@C.

Fig. 4  

(a) CV curves of CoMoSe4@C at 0.1 mV s \(^{-1}\) under 0.5–3 V versus Na/Na\(^+\). (b) Discharge/charge curves of the CoMoSe4@C electrode within the first five cycles at 0.1 A g \(^{-1}\). (c) Capabilities of the CoMoSe4@C and CoMoO4@C electrodes at different charging rates under 0.5 to 3 V with its corresponding Coulombic efficiency. (d) Cycling performances of the CoMoSe4@C and CoMoO4@C electrodes for 50 cycles at 0.5 A g \(^{-1}\).
can be found in the cycling testing results of the CoMoSe4@C and CoMoO4@C electrodes as presented in Fig. 4d. The CoMoSe4@C exhibited a better cycling stability with a high capacity of 301 mAh g−1 at 0.5 A g−1 maintained even after 50 cycles compared to 46 mA h g−1 in the CoMoO4@C electrode. Compared with the anode materials previously reported (Table 1), CoMoSe4@C composite electrode exhibits considerable reversible capacity and rate performance, thus CoMoSe4@C composite can be used as a potential electrode material for SIBs.

Conclusions
A facile approach to prepare a binary transition metallic selenide to serve as the anode material in SIBs was demonstrated via the plasma-assisted selenization process of a binary transition metallic oxide. In this work, three-dimensional (3D) CoMoSe4 nanosheets on network fibers of a carbon cloth denoted as CoMoSe4@C directly converted from CoMoO4 nanosheets prepared by hydrothermal process on network fibers of a carbon cloth through the plasma-assisted selenization as the anode for SIBs were demonstrated for the first time. A large sodium-ion storge of 475 mA h g−1 at 0.1 A g−1 can be generated from the plasma-assisted selenized composite electrode with the capacity retention of over 80% maintained even after 50 cycles, while the discharge capacity of 230 mA h g−1 still can be obtained even at 5 A g−1. Excellent Na-ion storage capabilities benefit from its well-developed nanostructure and good electrical conductivity. The work highlights the promising application of binary transition metallic selenides as electrode materials in SIBs and the simple synthesis method which might be employed in the production of other bimetallic selenides for a variety of applications, such as powering sustainable vehicles and portable energy storage devices.

### Table 1: Electrochemical properties of various anode materials applied as sodium-ion batteries reported in the previous literature

| Materials description | Voltage range (V vs Na+/Na) | Specific capacity (mAh g−1)/current density | Cycling data (mAh g−1)/cycles/current density | Reference |
|-----------------------|-----------------------------|--------------------------------------------|---------------------------------------------|-----------|
| MoSe2/CNT            | 0.001–2.5 V                 | 382/2.0 A g−1                              | 296/250th/1 A g−1                           | [31]      |
| CoSe2@N-PGC/CNTs     | 0.001–3 V                   | 482/2.0 A g−1                              | 424/100th/0.2 A g−1                         | [32]      |
| FeSe2                | 0.5–2.9 V                   | 447/1.0 A g−1                              | 372/200th/1 A g−1                           | [24]      |
| MoO2@MoSe2           | 0.01–3 V                    | 1136/0.1 A g−1                             | 520/4/400th/2 A g−1                         | [36]      |
| CoSe2                | 0.001–3 V                   | 521/0.1 A g−1                              | 467/40th/0.5 A g−1                          | [25]      |
| CoSe2/(NiCo)Se2      | 0.001–3 V                   | 554/0.2 A g−1                              | 497/80th/0.2 A g−1                          | [29]      |
| Ni3S2Se/C            | 0.01–3 V                    | 397/0.2 A g−1                              | 390/100th/0.2 A g−1                         | [26]      |
| WSe2/C               | 0.01–3 V                    | 294/0.1 A g−1                              | 270/50th/0.2 A g−1                          | [12]      |
| MoSe2/Gr             | 0.01–3 V                    | 432/0.1 A g−1                              | 380/50th/0.4 A g−1                          | [27]      |
| SnSe/RGO             | 0.01–2 V                    | 500/0.1 A g−1                              | 385/50th/0.5 A g−1                          | [13]      |
| Sb2Se3@N-Gr          | 0.01–3 V                    | 705/0.1 A g−1                              | 548/6/50th/0.2 A g−1                        | [14]      |
| VSe2/Gr              | 0.01–3 V                    | 559/0.2 A g−1                              | 632/60th/0.1 A g−1                          | [15]      |
| CoMoSe4@C            | 0.5–3 V                     | 475/0.1 A g−1                              | 301/50th/0.5 A g−1                          | This work |

Acknowledgements
Not applicable.

**Authors’ Contributions**
SZ and YFA initiated the idea and designed the experiments. SZ performed the experiments and drafted the manuscript. SCW, HJK, TYS, JHC, CHW, LL, YZC, BBX, SYT, DCW, and SSL take part in the experiments and discussed the results. YLC, JL, JYK, and JY guided the idea and the simulations and checked the figures. All authors read and approved the final manuscript.

**Funding**
This work is financially supported by the National Basic Research Program of China (Grant No.2015CB932301 and 2017YFB0040101), National Natural Science Foundation of China (Grant No. 61675173, 61505172 and 11405253), Natural Science Foundation of Fujian Province of China (Grant No.2017H6022 and 2018 J01102), and National Natural Science Foundation of Guangdong Province (Grant No.2015A030311002). In addition, this research is also supported by the Ministry of Science and Technology through Grant nos. 2017YFA0700102, 2017YFA0700202, 2017YFA0700302, and 2017YFA0700402. Y.L. Chueh greatly appreciates the use of the facilities at CNMM.

**Availability of Data and Materials**
All data generated or analyzed during this study are included in this published article and its supplementary information files.
Competing Interests
The authors declare that they have no competing interests.

Author details
1 Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Pen-Tung Sah Institute of Micro-Nano Science and Technology/Department of Physics, Xiamen University, Xiamen 361005, Fujian, China. 2 Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan, Republic of China. 3 Frontier Research Center on Fundamental and Applied Sciences of Matters, National Tsing Hua University, Hsinchu 30013, Taiwan, Republic of China. 4 College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China. 5 Department of Physics, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, Republic of China.

Received: 17 April 2019 Accepted: 30 May 2019
Published online: 25 June 2019

References
1. Kundu D, Talai E, Duffort V, Nazar LF (2015) The emerging chemistry of sodium ion batteries for electrochemical energy storage. Angewandte Chemie 54:3431–3448
2. Xiang Z, Zhang K, Chen J (2015) Recent advances and prospects of cathode materials for sodium-ion batteries. Adv Mater 27:3543–3564
3. Kim H, Kim H, Ding Z, Lee MH, Lim K, Yoon G, Kang K (2016) Recent progress in electrode materials for sodium-ion batteries. Adv Energy Mater 6:1600943
4. Slater MD, Kim D, Lee E, Johnson CS (2013) Sodium-ion batteries. Adv Funct Mater 23:947–958
5. Cao Y, Xiao L, Sushko ML, Wang W, Schwenzer B, Xiao J, Nie Z, Saraf LV, Cao Y, Zhang Z, Li Z, Yin L (2018) Hollow prism NiCo2S4 linked with MoSe2 nanosheets as anode material for sodium-ion batteries. Adv Funct Mater 29:1700606
6. Luo W, Shen F, Bommier C, Zhu H, Ji X, Hu L (2016) Na-ion battery anodes: materials and electrochemistry. Acc Chem Res 49:231–240
7. Er D, Li J, Naguib M, Gogotsi Y, Shenoy VB (2014) TiC2 MXene as a high capacity electrode material for metal (Li, Na, K) ion batteries. ACS Appl Mater Interfaces 6:11173–11179
8. Hu Z, Liu Q, Chou SL, Dou S-X (2017) Advances and challenges in metal sulfides/selenides for next-generation rechargeable sodium-ion batteries. Adv Energy Mater 29:1601188
9. Chao D et al (2016) Pseudocapacitive Na-ion storage boosts high rate and areal capacity of soft-branched 2d layered metal chalcogenide nanoarrays. ACS nano 10:102121–10219
10. Pan Y, Cheng X, Gong L, Shi L, Deng Y, Zhang H (2018) Highly reversible Na ion storage in N-doped polyhedral carbon-coated transition-metal chalcogenides by optimizing the nanostructure and surface engineering. J Mater Chem A 6:18823–18832
11. Zhang F, Xia C, Zhu J, Ahmed B, Liang H, Velusamy DB, Schwingenschlögl U, Alshareef HNE (2016) SnSe2 2D anodes for advanced sodium ion batteries. Adv Energy Mater 6:1601188
12. Zhang Z, Yang X, Fu Y (2016) Nanostructured WS2/C composites as anode materials for sodium-ion batteries. RSC Advances 6:12726–12729
13. Yang X, Zhang R, Chen N, Meng X, Yang P, Wang C, Zhang Y, Wei Y, Chen G, Du F (2016) Assembly of SnSe2 nanoparticles confined in graphene for enhanced sodium-ion storage performance. Chemistry 22:1445–1451
14. Zhao W, Li CM (2017) Mesh-structured N-doped graphene@MoS2 hybrids as an anode for large capacity sodium-ion batteries. J Colloid Interface Sci 488:356–364
15. Wang Y, Qian B, Li H, Liu L, Chen L, Jiang H (2015) VSe2/graphene nanocomposites as anode materials for lithium-ion batteries. Mater Lett 141:35–38
16. Zhang Y, Liu Z, Zhao H, Du Y (2016) MoSe2 nanosheets grown on carbon cloth with superior electrochemical performance as flexible electrode for sodium ion batteries. RSC Advances 6:1440–1444
17. Yang X, Zhang Z, Fu Y, Li Q (2015) Porous hollow carbon spheres decorated with molybdenum diselenide nanosheets as anodes for highly reversible lithium and sodium storage. Nanoscale 7:10198–10203
18. Zhang Z, Li Z, Yin L (2018) Hollow prism NiCo2S4 linked with interconnected reduced graphene oxide as a high performance anode material for sodium and lithium ion batteries. New J Chem 42: 1467–1476
19. Guo Y, Yao Z, Shang C, Wang E (2017) P doped Co9S8Se nanosheets grown on carbon fiber cloth as an efficient hybrid catalyst for hydrogen evolution. J Mater Chem A 5:12043–12047
20. Dominguez N, Torres B, Barrera LA, Rincon JE, Lin Y, Chianelli RR, Ahsan MA, Novery CN (2018) Bimetallic CoMoS composite anchored to biocarbon fibers as a high-capacity anode for Li-ion batteries. ACS Omega 3:10243–10249
21. Xie X, Makaytan Y, Zhao M, Van Aken KL, Gogotyi Y, Wang G (2016) MoS2 nanosheets vertically aligned on carbon paper: a freestanding electrode for highly reversible sodium-ion batteries. Adv Energy Mater 6:1502161
22. Zhang K, Park M, Zhou L, Lee G-H, Li W, Kang Y-M, Chen J (2016) Uchirn-like CoSe2 as a high-performance anode material for sodium-ion batteries. Adv Functional Mater 26:6728–6735
23. Zhu S, Li Q, Wei Q, Sun R, Liu X, An Q, Mai L (2017) NiSe2 nanocathodes as an anode material for high-rate and long-life sodium-ion battery. ACS Appl Mater Interfaces 9:311–316
24. Zhang K, Hu Z, Liu X, Tao Z, Chen J (2015) Fe3Se4 microspheres as a high-performance anode material for Na-ion batteries. Adv Mater 27:3365–3369
25. Xia Y, Cai W, Wang Y, Song X, Neale Z, Wang H-E, Sui J, Cao G (2018) MoSe2 Nanosheets perpendicularly grown on graphene with Mo–C bonding for sodium-ion capacitors. Nano Energy 47:224–234
26. Kim JK, Kim JH, Kang YC (2018) Electrochemical properties of multicomponent oxide and selenide microspheres containing Co and Mo components with several tens of vacant nanorooms synthesized by spray pyrolysis. Chem Eng J 333:655–677
27. Park S-K, Kim JK, Chan Kang Y (2017) Metal–organic framework-derived CoSe2/NC–CoSe2 box-in-box hollow nanocubes with enhanced electrochemical properties for sodium-ion storage and hydrogen evolution. J Mater Chem A 5:18823–18830
28. Ali Z, Asif M, Huang X, Tang T, Hou Y (2018) Hierarchically porous Fe2CoSe4 binary-metal selenide for extraordinary rate performance and durable anode of sodium-ion batteries. Adv Mater Interfaces 5:2002745
29. Choi SH, Kang YC (2016) Fullerene-like MoSe2 nanoparticles-embedded Cnt balls with excellent structural stability for highly reversible sodium-ion storage. Nanoas 84:209–4216
30. Park S-K, Kim JK, Chan Kang Y (2017) Excellent sodium-ion storage performances of CoSe2 nanoparticles embedded within N-doped porous graphitic carbon nanocube/carbon nanotube composite. Chem Eng J 328:543–555
31. Chang U, Lee JT, Yun JM, Lee B, Lee SW, Oh H, Eom K, Fuller TT (2019) In situ self-formed nanoheterostructure of MoSe2/reduced graphene oxide material showing superior performance as a lithium-ion battery cathode. ACS Nano 13:1490–1498
32. Alarawi A, Ramalingam V, Fu HC, Varadhan P, Yang R, He JH (2019) Enhanced photoelectrochemical hydrogen production efficiency of MoS2–Si heterojunction. Opt Express 27:A352–A363
33. Wei R, Fang M, Dong G, Lan C, Shu L, Zhang H, Bu X, Ho JC (2018) High-index faceted porous Co3O4 nanosheets with oxygen vacancies for highly efficient water oxidation. ACS Appl Mater Interfaces 10:7079–7086
34. Zhao X, Sui J, Li F, Fang H, Wang H, Li J, Cai W, Cao G (2016) Lamellar MoSe2 nanosheets embedded with MoO3 nanoparticles: novel hybrid nanostructures promoted excellent performances for lithium ion batteries. Nanoas 8:17902–17910
35. Ai Y, Lou Z, Li L, Chen S, Park HS, Wang ZM, Shen G (2016) Metro-long flexible CoNiO2 nanowires@carbon fibers based wire-supercapacitors for wearable electronics. Adv Mater Technol 1:1600142
36. Liu B, Zhang J, Wang X, Chen G, Chen D, Zhou C, Shen G (2012) Hierarchical three-dimensional ZnCo2O4 nanowire arrays/carbon cloth anodes for a novel class of high-performance flexible lithium-ion batteries. Nano Letters 12:3005–3011
37. Gao W, Gou W, Zhou X, Ho JC, Ma Y, Qu Y (2018) Amine-modulated/engineered interfaces of NiMo electrocatalysts for improved hydrogen evolution reaction in alkaline solutions. ACS Appl Mater Interfaces 10:1728–1733
38. Lan C, Zhou Z, Wei R, Ho JC (2019) Two-dimensional perovskite materials: from synthesis to energy-related applications. Mater Today Energy 11:61–82
41. Le V-Q, Do T-H, Retamal JR'D, Shao P-W, Lai Y-H, Wu W-W, He J-H, Chueh Y-L, Chu Y-H (2019) Van Der Waals Heteroepitaxial AZO/NiO/AZO/muscovite (ana/muscovite) transparent flexible memristor. Nano Energy 56:322–329
42. Ouyang W, Teng F, He J-H, Fang X (2019) Enhancing the photoelectric performance of photodetectors based on metal oxide semiconductors by charge-carrier engineering. Adv Funct Mater 29:1807672
43. Zhou Z, Lan C, Wei R, Ho JC (2019) Transparent metal-oxide nanowires and their applications in harsh electronics. J Mater Chem C 7:202–217
44. Mai LQ, Yang F, Zhao YL, Xu X, Xu L, Luo YZ (2011) Hierarchical MnMoO4/CoMoO4 heterostructured nanowires with enhanced supercapacitor performance. Nat Commun 2:381
45. Li M, Wang Y, Yang H, Chu PK (2017) Hierarchical CoMoO4@Co3O4 nanocomposites on an ordered macro-porous electrode plate as a multi-dimensional electrode in high-performance supercapacitors. J Mater Chem A 5:17312–17324
46. Ali A, Oh W-C (2017) Ultrasonic synthesis of CoSe2-graphene-TiO2 ternary composites for high photocatalytic degradation performance. J Korean Ceram Soc 54:205–210
47. Wu C-T, Hu S-Y, Tiong K-K, Lee Y-C (2017) Anisotropic effects in the Raman scattering of Re-doped 2H-MoSe2 layered semiconductors. Results Physics 7: 4096–4100
48. Sun C, Dong Q, Yang J, Dai Z, Lin J, Chen P, Huang W, Dong X (2016) Metal-organic framework derived CoSe2 nanoparticles anchored on carbon fibers as bifunctional electrocatalysts for efficient overall water splitting. Nano Res 9:2234–2243
49. Kim JK, Park GD, Kim JH, Park SK, Kang YC (2017) Rational design and synthesis of extremely efficient macroporous CoSe2-Cnt composite microspheres for hydrogen evolution reaction. Small 13
50. Tang H, Dou K, Kaun C-C, Kuang Q, Yang S (2014) MoSe2 nanosheets and their graphene hybrids: synthesis, characterization and hydrogen evolution reaction studies. J Mater Chem A 2:360–364
51. Qu B, Yu X, Chen Y, Zhu C, Li C, Yin Z, Zhang X (2015) Ultrathin MoSe2 nanosheets decorated on carbon fiber cloth as binder-free and high-performance electrocatalyst for hydrogen evolution. ACS Appl Mater Interfaces 7:14170–14175
52. Wang H, Kong D, Johannes P, Cha JJ, Zheng G, Yan K, Liu N, Cui Y (2013) MoSe2 and WSe2 nanofilms with vertically aligned molecular layers on curved and rough surfaces. Nano Letters 13:3426–3433
53. Park GD, Kang YC (2016) One-pot synthesis of CoSe2-RGO composite powders by spray pyrolysis and their application as anode material for sodium-ion batteries. Chemistry 22:4140–4146
54. Park GD, Kim JH, Kang YC (2016) Large-scale production of spherical FeSe2-amorphous carbon composite powders as anode materials for sodium-ion batteries. Mater Charact 120:349–356

Publisher’s Note
Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Submit your manuscript to a SpringerOpen journal and benefit from:
► Convenient online submission
► Rigorous peer review
► Open access: articles freely available online
► High visibility within the field
► Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com