Solution Synthesis of VSe₂ Nanosheets and Their Alkali Metal Ion Storage Performance

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ABSTRACT: Vanadium diselenide (VSe₂) is a transition metal dichalcogenide with metallic conductivity, which makes it a potentially promising electrode material for electrochemical applications. However, the development of VSe₂ electrodes for such applications has been severely hampered by the difficulty of preparing nanosized products. In this work, a new facile solvothermal synthesis process is developed and optimized to synthesize ultrathin VSe₂ nanosheet assemblies. To obtain the ultrathin nanosheets, N-methyl pyrrolidone, which has similar surface energy to many transition metal dichalcogenides, was used as the solvent to limit the crystal growth along the *c*-axis direction. The resulted ultrathin VSe₂ nanosheets exhibit good performance toward the alkaline ions (Li⁺ and Na⁺) storage, which can be significantly enhanced by carbon coating. Specifically, the carbon-coated VSe₂ nanosheets can deliver high capacities of 768 mA h g⁻¹ (Li⁺ storage) and 571 mA h g⁻¹ (Na⁺ storage) along with outstanding stability.

KEYWORDS: VSe₂, solution synthesis, 2D materials, energy storage

The ever-increasing demand for electrical energy storage devices is providing great opportunities and challenges, especially for the rechargeable ion batteries. Alkali metal ions (e.g.

Li^+ and Na^+) are significant energy carriers with commercial potential[1, 2]. Over the past several decades, researchers have mainly focused on the development of electrode materials with efficient and reversible storage of alkali ions[3]. Among them, two dimensional (2D) materials have received considerable attentions and witnessed tremendous progress because of the unique physical and chemical properties, as well as the structural features[4-12].

Layered transition metal dichalcogenides (TMDs) with the general formula MX_2 ($\text{M} = \text{Mo}, \text{W}, \text{V}, \text{Nb}, \text{Ti}, \text{etc}$; $\text{X} = \text{S}, \text{Se}, \text{Te}, \text{etc}$) are a family of 2D materials, which possess similar layered structure to graphene with adjacent layers linked together by van der Waals interaction[13, 14]. However, most of recent efforts have been devoted to developing Mo- and W-based dichalcogenides, such as MoS_2 [15, 16], WS_2 [17, 18], MoSe_2 [19, 20], and WSe_2 [21], which are believed to have great impact on energy storage applications. While other TMDs like V- and Nb-based (both are group V transition metals) materials have rarely been explored[22]. In addition, it is worth noting that the synthetic Mo- and W-based dichalcogenides are originally in semiconducting 2H phases and need to be converted into metastable metallic 1T polymorph to further enhance their electrochemical performance[23, 24]. In contrast, the V- and Nb-based TMDs exhibit intrinsic metallic conductivity[22], therefore are expected to show even better electrochemical performance[23, 25, 26].

VSe_2 , as a layered metallic TMD, has a very similar sandwich structure (see crystal structure in **Figure 1A**) as that of MoS_2 . The strong electron coupling interaction between V^{4+} - V^{4+} pairs in VSe_2 induces the metallic properties[22, 27, 28]. Further, it has been demonstrated that VSe_2 exhibits good electrocatalytic activity[29] and versatile electronic properties[27], which suggest that VSe_2 may also have great potential in energy storage applications. As early as in 1978, Whittingham has reported the electrochemical characteristics of VSe_2 in lithium cells[30].

Recently, VSe₂ has attracted renewed attention for electrochemical applications such as electrocatalysis and supercapacitors and so forth[29, 31-35]. However, the further exploration of the electrochemical properties of VSe₂ has been seriously limited by the difficulty in preparing VSe₂ nanostructures, especially thin nanosheets. This, to a large extent, is because that the V⁴⁺ is less stable and tends to be reduced or oxidized into more stable V³⁺ or V⁵⁺ species. In general, vapor phase methods such as chemical vapor deposition (CVD) might be applied to the synthesis of VSe₂ with high crystalline quality[36] as they have shown efficacy in synthesizing other TMDs such as MoS₂[7, 37, 38] and WS₂[38], but they often require high reaction temperature (normally around 600-900 °C depending on the precursors), thus are more energy costly. In contrast, low temperature solution synthesis provides an economic approach that is more suitable for large-scale renewable energy applications. Unfortunately, there are only a few reports on the solution synthesis of VSe₂[28] and the resulting products are normally disordered bulk structures.

Herein we report the synthesis of the ultrathin (~10 nm) VSe₂ nanosheet assemblies (NSA) by a facile one-pot solvothermal method for the first time, where N-methyl pyrrolidone (NMP) was used to stabilize the VSe₂ and the nanosheet morphology. The effect of synthetic parameters on the morphology and nanostructure of VSe₂ NSA were investigated in detail. The VSe₂ NSA were then evaluated as lithium and sodium ion battery electrodes and showed good performance, which can be further enhanced by *in-situ* carbon coating. The VSe₂ NSA/C can deliver high specific capacities of 768 mA h g⁻¹ and 571 mA h g⁻¹, respectively, at 100 mA g⁻¹, along with outstanding rate performance and stability.

Hierarchical VSe₂ NSA were synthesized by reacting vanadyl acetylacetonate (VO(acac)₂) and SeO₂ with formic acid (HCOOH) in NMP (see details in Experimental section). The NMP was used as solvent because its surface energy is close to that of TMDs. It can adsorb on the surface of the VSe₂ (and other TMDs as well) and retard the growth along the *c*-axis, thus favor the formation of ultrathin 2D nanostructures. In fact, NMP is commonly used as solvent for the liquid-exfoliation of TMDs[39, 40]. During the reaction, HCOOH reacts with SeO₂ firstly and produces highly active H₂Se gas, which then reacts with vanadium precursor to form the VSe₂. It should be noted that the excess H₂Se gas is very easy to be oxidized into Se on the surface of VSe₂ upon air exposure. Therefore, the post-annealing treatment is critically important for obtaining phase pure VSe₂, but it also improves VSe₂ crystallinity. The structures of the obtained VSe₂ NSA and VSe₂ NSA/C were then examined by X-ray diffraction (XRD). As shown in **Figure 1B**, well-defined diffraction peaks are obtained for both samples and can be assigned to hexagonal VSe₂ (JCPDS no. 89-1641) without any impurity. Even though no diffraction peaks are observed for carbon in the VSe₂ NSA/C sample, which may be due to the trace amount of carbon[41], Raman analysis does confirm the existence of carbon, indicating successful carbon coating. The Raman spectra of VSe₂ NSA and VSe₂ NSA/C are almost identical except for the broad peaks at ~ 1350 and 1580 cm⁻¹ (inset of Figure 1C), which can be assigned to the D and G bands of the amorphous carbon.[42, 43] The characteristic Raman peaks at 280.8 and 406.8 cm⁻¹ are similar to those observed in VS₂[40, 44] and are likely due to the E_{2g} and A_{1g} vibration modes of VSe₂[40], respectively, as schematically illustrated in **Figure S1**. In addition, the high-resolution X-ray photoelectron spectroscopy (XPS) spectra (Figure 1D-E) of V 2p and Se 3d confirm the presence of V⁴⁺ and Se²⁻ in the as-obtained products[31, 32]. The binding energies of V and Se shift by ~0.1 eV after carbon coating, which suggests the electronic structure of VSe₂ has been modified by carbon coating. These results

indicate that we have successfully synthesized pure VSe₂ and carbon-coated VSe₂ composites. The electronic conductivity of pure VSe₂ was determined to be 525 S cm⁻¹ (**Figure S2**) at room temperature, further confirming its relatively high conductivity.

The morphological features of products were then examined by scanning electron microscopy (SEM). As shown in **Figure 2A and Figure S3**, the VSe₂ NSA present a highly open hierarchical structure. A close observation reveals that these VSe₂ NSA are composed of many ultrathin nanosheets (**Figure 2B and C**). Such a 3D assembly can minimize the agglomeration and restacking of the nanosheets, providing a fast and efficient access to the inner of the electrode material and leading to fast electron transfer. The nanosheet subunits were almost transparent under the SEM electron beam (**Figure 2C**, dashed box), indicative of its ultrathin nature. The thickness of individual sheets in the NSA was measured by SEM and Atomic force microscopy (AFM) analysis. As shown in **Figure S4**, the thickness of individual nanosheets is found to be around 10 nm by both methods. Further confirmation of the individual sheet thickness was obtained by transmission electron microscope (TEM), as shown in **Figure 2E**. In addition, the TEM image (**Figure 2D**) further indicates that the ultrathin nature of the nanosheet by the light contrast. The lattice fringes of 0.605 nm measured from the high resolution TEM (HRTEM) image can be ascribed to (001) plane of VSe₂ (**Figure 2E**). Furthermore, the scanning TEM-energy dispersive spectroscopy (STEM-EDS) elemental mapping reveals the uniform distribution of V and Se in a nanosheet (**Figure 2F-G**). These results suggest phase-pure VSe₂ was successfully synthesized by our facile solvothermal method.

To further enhance the electrochemical performance, we synthesized the carbon-coated VSe₂ NSA by simply adding 0.1 M glucose into the reaction solution that was used for the preparation of VSe₂, followed by a post-annealing process (see Experimental section for details). After carbon

coating, the overall nanosheet morphology is retained though the surface becomes rougher (**Figure 2H-I and Figure S5**). The energy dispersive X-ray spectroscopy (EDS, **Figure S6A**) analysis suggests that the ratio of V and Se is 1:2.08, which is close to stoichiometric ratio of VSe_2 . Furthermore, after carbon coating, it is obviously that the intensity of carbon is much stronger than that of the bare VSe_2 (possibly ~~comes~~ coming from contamination), suggesting the successful introduction of carbon. It should be noted that the oxygen signal originates from the surface oxidation because of the exposure to ~~the~~ air. The HRTEM image reveals that the thickness of the carbon coating layer is ~ 5 nm (**Figure 2J**). Such thin layer could help alleviate the volumetric change of VSe_2 upon cycling but without affecting the ion transport. The measured inter-planar spacing of 0.169 nm from **Figure 2J** corresponds to the (110) plane of VSe_2 . The elemental mapping further confirms the uniform distribution of V, Se and the outer carbon layer (**Figure 2K-M, Figure S7 and S8**) in the NSA.

To gain insights into the structural and phase evolution of VSe_2 NSA during the reaction, intermediate products obtained with different reaction times were collected and analyzed via XRD, which suggests that the pure VSe_2 can be only obtained for reaction time more than 24 h (**Figure S7**). SEM observation (**Figure S9B-I**) reveals the formation of large smooth branches at the initial stage (e.g. 4 h). As reaction time increases, many thin nanosheets grow on the surface of these branches (8 h) and eventually form the hierarchical VSe_2 NSA structure. There is no significant difference in the phase and morphology of the products obtained at 24 and 30 h, suggesting the reaction is almost completed at around 24 h. It is worth mentioning that that NMP plays a crucial role in the formation of the ultrathin nanosheets. This is confirmed by the control experiment that used water instead of NMP as solvent, while keeping other conditions unchanged, which leads to the formation of thick nanoplates of around 200-300 nm (**Figure S10**). In an effort to further reduce

the thickness and improve the dispersibility, we evaluated several surfactants including Pluronic P123 (P123), polyvinyl pyrrolidone (PVP), and cetyltrimethyl ammonium bromide (CTAB) under hydrothermal conditions with water as solvent. The thickness of the nanosheets indeed reduces; unexpectedly, we did not get the pure VSe₂ phase (**Figure S11**). This result further supports the extremely important role of NMP, which not only produces thin nanosheets, but also stabilizes the V⁴⁺ (which is easily transformed to the more stable V³⁺ and V⁵⁺ ions) during the solvothermal reaction. To further demonstrate the critical role of NMP, we conducted a control experiment in DMF (Dimethylformamide), another commonly used solvent for synthesis and exfoliation of 2D materials. The result shows that pure VSe₂ can be also obtained, but the product consists of both microrods and microflowers (**Figure S12**), unlike the uniform flower-like assembly that we obtained in NMP. This difference is mainly attributed to the different ion diffusion rates in solvents. NMP has a higher viscosity (1.65 cp at 25 °C) than that of DMF (0.80 cp at 25 °C), which results in slow diffusion of ions and the crystal products therefore tend to form structures with low surface energy (e.g. spheres or spherical aggregates such as the flower-like nanosheet assembly in our work). Whereas in DMF, the diffusion limitation of the precursors is mitigated and often lead to anisotropic structures. Besides the solvent, different vanadium and selenium precursors were used to prepare the VSe₂ in NMP as well. The product synthesized using NH₄VO₃ or V₂O₅ consists of thin nanosheets but less aggregated (**Figure S13**), possibly due to the higher solubility of these precursors in NMP that results in a relatively fast ion diffusion rate. Similar phenomenon was also found in the literature[40]. However, when selenourea was used instead of SeO₂, no VSe₂ phase is obtained. This is likely because of the difficulty in releasing Se²⁻ as the hydrolysis of selenourea is suppressed in NMP. Indeed, selenourea is more often used in hydrothermal reactions using

weakly alkaline aqueous solution (with abundant OH^- to promote its hydrolysis) to produce metal selenides.[45, 46]

Inspired by the high performance that metallic 2D compounds have achieved in electrochemical energy storage applications[47-49], we then evaluated the alkali metal ion storage in VSe_2 . Two-electrode coin cell with lithium metal as the counter electrode was used to evaluate the lithium storage performance of pristine VSe_2 NSA and VSe_2 NSA/C hybrid. **Figure 3A** presents the cyclic voltammetry (CV) profiles of VSe_2 NSA/C for the first 3 cycles at a scan rate of 0.1 mV s^{-1} . For the VSe_2 NSA/C composite, the stabilized curves exhibit two reversible cathodic peaks at ~ 2.0 and $\sim 1.43 \text{ V}$, with two anodic peaks at ~ 1.83 and $\sim 2.23 \text{ V}$. The broad peak at 0.41 V in the first cycle corresponds to the formation of irreversible solid electrolyte interface (SEI). Similar to VS_2 , the lithiation of VSe_2 is supposed to proceed with the Li^+ intercalation into the VSe_2 layers, followed by conversion reaction. Thus, we concluded that the $2.0/2.23 \text{ V}$ redox pair can be attributed to the intercalation reaction, while the $1.43/1.83 \text{ V}$ redox pair can be assigned to the conversion reaction to metallic V and Li_2Se and its counter reaction to VSe_2 and Li . The CV curves for the pristine VSe_2 NSA (**Figure S14**) shows similar features.

Consistent result was obtained from the galvanostatic charge/discharge (CD) plots of VSe_2 NSA/C at the current density of 100 mA g^{-1} . As shown in **Figure 3B**, the first discharge curve exhibits three plateaus at ~ 2.0 , ~ 1.41 and $\sim 0.5 \text{ V}$, while the first charge curve shows two distinct plateaus at ~ 1.82 and 2.2 V , in good agreement with the CV profile for VSe_2 NSA/C and previous reports[50]. Meanwhile, the overlapped charge/discharge curves after 5 cycles reveal that the high reversibility and stability of the electrodes. The VSe_2 NSA/C electrodes achieve a high initial discharge capacity of 981 mA h g^{-1} and charge capacity of 745 mA h g^{-1} , corresponding to a coulombic efficiency of 76% in the first cycle. The capacity loss can be ascribed to the formation

of SEI film. In addition to the large initial capacity, VSe₂ NSA/C also demonstrate good cycling performance, as depicted in **Figure 3C**. After the first cycle, the discharge capacity drops to 772 mA h g⁻¹ in the second cycle and then stabilized. The coulombic efficiency jumps to over 98 % in the second cycle and reaches nearly 100% in the subsequent cycles. After 50 CD cycles, a reversible capacity as high as 766 mA h g⁻¹ is maintained. By contrast, the pure VSe₂ NSA displays a high initial discharge capacity of ~1000 mA h g⁻¹, however, an inferior cycling performance. After 50 cycles, only 555 mA h g⁻¹ discharge capacity can be remained. The poor cycling performance and capacity loss mainly result from the big volumetric expansion during the lithium insertion. As expected, the VSe₂ NSA/C electrode also exhibits excellent rate capability at high current densities. **Figure 3D** depicts the rate performance of VSe₂ NSA/C and bare VSe₂ NSA at different current densities range from 100 to 2000 mA g⁻¹. The VSe₂ NSA/C electrode shows good capacity retention, varying from 768 to 725, 705, 656, 629, 571 mA h g⁻¹ at the current densities from 100 to 300, 500, 800, 1000, 2000 mA g⁻¹, respectively. When the rate is changed back to 100 mA g⁻¹, a reversible capacity of 755 mA h g⁻¹ with 98% capacity retention is obtained. In comparison, the VSe₂ NSA electrode only retains specific capacities of 457 and 370 mA h g⁻¹ at 1000 and 2000 mA g⁻¹, respectively. In addition to that, when the current density reduces to 100 mA g⁻¹, the reversible capacity is only 486 mA h g⁻¹, and drops quickly upon cycling. Furthermore, we note that the high rate did not compromise the cycling performance of VSe₂ NSA/C. A specific capacity of ~614 mA h g⁻¹ is retained after 300 cycles at a high current of 800 mA g⁻¹ (**Figure S15**), while only 315 mA h g⁻¹ can be maintained for bare VSe₂. These results suggest the Li⁺ storage performance of VSe₂ NSA can be significantly enhanced by carbon coating.

It is worth noting that the reversible capacity of 768 mA h g⁻¹ for VSe₂ NSA/C, or 710 mA h g⁻¹ for bare VSe₂ NSA at a current density of 100 mA g⁻¹ exceeds the theoretical capacity of 513

mA h g⁻¹ (assuming an uptake of 4 mol Li into 1 mol VSe₂). This phenomenon has also been observed in many other layered TMDs[50-53]. This might be due to the reversible interfacial Li storage, which is proposed by Maier[54]. Specifically, the Li will be stored through the following steps: in the initial stage, Li ions are homogeneously inserted into the metallic VSe₂ and the discharge curve is slightly sloped, with additional possible anomalies due to structural transitions. After reaching the solubility limit, new phases (V, Li₂Se) and interfaces are formed. Although these phases no longer dissolve Li, further storage is possible *via* interfacial charging until the chemical potential of Li is equal to that of metallic Li. It should be noted that all cases of interfacial storage resemble the characteristic of a capacitor (a typical CV curve can be seen in our case, **Figure 3A**, at the potential below 1.0 V). Such an interfacial charging has been proposed to be very reversible[55]. To further understand the charge storage kinetic in the host materials, we quantitatively distinguished the capacitive and diffusion-controlled contributions from the measured current using sweep voltammetry (see Experimental section for details). As shown in **Figure 3E**, 60% of the current can be ascribed to capacitive response at a scan rate of 0.3 mV s⁻¹, suggesting that the solid-solution reactions are mainly limited by the reaction rate itself rather than the ion diffusion rate[56]. What's more, the *b*-values (**Figure 3F** and **Figure S16**) of different redox peaks are determined to be 0.97, 0.65, 0.8, 0.96, 0.85 and 0.91, respectively, clearly indicating the capacitive-like kinetics. All these results explain the high reversible capacity and the good rate performance of the VSe₂ NSA/C.

We also assessed the sodium storage performance for as-obtained VSe₂ NSA/C and bare VSe₂ NSA. CV curves for bare VSe₂ NSA are depicted in **Figure S17**. Two sharp peaks at 1.65 and 1.74 V disappear in the subsequent cycles, which could be assigned to the irreversible intercalation of Na⁺ into the VSe₂ layers. However, in the CV profile of VSe₂ NSA/C electrode (**Figure 4A**), it

shows a broad peak at around 1.7 V instead of the sharp peaks. One possible reason is that the carbon coating, to a certain degree, prohibits the Na^+ intercalation. **Figure 4B** shows the typical galvanostatic CD plots at a rate of 100 mA g^{-1} for VSe_2 NSA/C, which is in good agreement with the CV result. The specific charge and discharge capacities of 530 and 650 mA h g^{-1} can be achieved for VSe_2 NSA/C electrode at first cycle, corresponding to a coulombic efficiency of 81.5%. **The VSe_2 NSA/C electrode also exhibits much superior stability performance than bare VSe_2 NSA (Figure 4C and Figure S18).** Moreover, the rate performance of VSe_2 NSA/C is much better than that of bare VSe_2 NSA. As shown in **Figure 4D**, for VSe_2 NSA/C, when the current ramps stepwise, the measured capacity reduces from 576 to 571, 564, 510 and 450 mA h g^{-1} at 50, 100, 200, 300 and 500 mA g^{-1} , respectively. However, for bare VSe_2 NSA, the capacities are only 525, 459, 421, 402 and 350 mA h g^{-1} , respectively. Also, the capacitive contribution is determined to be 65% at a scan rate of 0.3 mV s^{-1} (**Figure 4E**), which confirms the Na ion storage in VSe_2 NSA/C is the surface-mediated capacitive mechanism instead of the diffusion-limited Faradaic mechanism[56, 57]. The b -values (**Figure 4F and Figure S19**) of different peaks were 0.85, 0.98, 0.94 and 0.92, respectively, which further demonstrates the capacitive-like kinetics.

Indeed, the VSe_2 NSA/C electrode shows superior performance than bare VSe_2 NSA owing to the carbon coating. **It is noted that VSe_2 can be easily oxidized upon heating or even stirring and ultrasonication, which was confirmed by our experiments as well as literature[33]. The oxides layer can possibly be formed on the surface during the electrode fabrication process and thus lowers the conductivity though VSe_2 itself is a metal. The introduction of carbon coating layer can not only prevent the VSe_2 from being oxidized, but also help to alleviate the structural expansion upon cycling as we discussed earlier, as well as to further improve the conductivity. Indeed, the Nyquist plots of pristine electrodes (Figure S20) confirm that the VSe_2 NSA/C has a much lower**

electrochemical resistance than that of bare VSe_2 . We further investigated the electrochemical behavior by monitoring the electrochemical impedance of the electrodes for lithium- and sodium-ion batteries after different cycles (1st, 5th, 20th, 50th, and after cycling). The result shows that the diameter of the semicircle (represents for the charge-transfer resistance) of VSe_2 NSA/C electrodes becomes smaller from 1st cycle to ~50th cycle (**Figure S20B and D**), indicating the decrease in charge-transfer resistance in the first 50 cycles, which is possibly due to the activation process and enhanced reversibility of the electrodes. Subsequently, the charge-transfer resistance increases after cycling for 300 or 200 cycles, likely due to the dissolution of vanadium and/or the accumulative deposition of insulating Li_2Se (or Na_2Se) on the surface of lithium (sodium) metal during the extended cycles. However, the initial electrochemical impedance of VSe_2 NSA electrodes is much larger than that of VSe_2 NSA/C (**Figure S20A and C**), and the semicircle immediately increases after only ~5 cycles and finally becomes much larger than the initial state. The result shown here further confirms that the thin carbon coating plays an important role for the long-term stability of the electrodes. In addition, we also investigated the morphological and elemental changes of different electrodes after cycling. For both electrodes, the V:Se ratio is similar and close to 1:2 (**Figure S21**). However, SEM images reveal that the bare VSe_2 NSA electrodes suffer from the big volumetric expansion and thus the structural collapse (**Figure S22 A and B**). In contrast, the nanosheet structures of VSe_2 NSA/C samples were well preserved thanks to the surface carbon coating layer (**Figure S22C and D**). From these results, it is safe to conclude that the outmost carbon coating serves as a conducting buffer layer that not only helps electronic transport and prevents VSe_2 NSA from being oxidized, but more importantly, also alleviates the internal strain during the lithium/sodium uptake and thus guarantee a high reversible capacity and superior stability.

In summary, we have developed a new chemical synthesis process to prepare hierarchical two-dimensional VSe₂ nanosheets. Different reaction parameters were investigated in detail to obtain the optimized process. When assessed as electrode materials for lithium/sodium ion batteries, the in-situ carbon-coated VSe₂ showed excellent performance including a high specific capacity of 768 mA h g⁻¹ and 571 mA h g⁻¹, for lithium and sodium ion batteries, respectively (at 100 mA g⁻¹), as well as the good rate performance and stability. Our study shows that VSe₂, which has been difficult to prepare, can be synthesized using proper solvents without any surfactants. In addition, our study demonstrates a great potential for VSe₂ in electrochemical applications, especially energy storage applications.

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Figures

Figure 1. Structural characterization of VSe₂ NSA and VSe₂ NSA/C. (A) Crystal structure of VSe₂. (B) XRD patterns, (C) Raman spectra, and (D, E) XPS spectra of VSe₂ NSA and VSe₂ NSA/C.

Figure 2. Microscopic characterizations of VSe₂ NSA and VSe₂ NSA/C. (A-C) SEM images of VSe₂ NSA; (D) TEM and (E) HRTEM images of VSe₂ NSA; (F-G) STEM-EDS elemental mappings for V and Se of VSe₂ NSA, respectively; (H-I) SEM images of VSe₂ NSA/C; (J) HRTEM image of VSe₂ NSA/C; (K-M) STEM-EDS element mappings for V, Se and C of VSe₂ NSA/C.

Figure 3. Electrochemical performance of the VSe₂ NSA and VSe₂ NSA/C electrodes for Li-ion storage. (A) CV plots for VSe₂ NSA/C. (B) Galvanostatic charge-discharge profiles for VSe₂ NSA/C electrode at 100 mA g⁻¹. (C) Cycle performance (discharge capacities) at 100 mA g⁻¹ for VSe₂ NSA/C and bare VSe₂ NSA. (D) Rate performances of VSe₂ NSA/C and bare VSe₂ NSA cathodes. (E) Capacitive contribution to the charge storage at 0.3 mV s⁻¹. (F) The *b*-values of different redox peaks, determined from the log(*i*) versus log(*v*) plots.

Figure 4. Electrochemical performance of the VSe₂ NSA and VSe₂ NSA/C electrodes for Na ion storage. (A) CV plots for VSe₂ NSA/C. (B) Galvanostatic CD profiles for VSe₂ NSA/C electrode at 100 mA g⁻¹. (C) Cycling performance at 100 mA g⁻¹ for VSe₂ NSA/C and bare VSe₂ NSA. (D) Rate performance of VSe₂ NSA/C and bare VSe₂ NSA cathodes. (E) Capacitive contribution to the charge storage at 0.3 mV s⁻¹. (F) The *b*-values of different redox peaks, determined from the log(*i*) versus log(*v*) plots.

Graphic abstract: Solution synthesis of ultrathin VSe₂ using NMP as the solvent. The simultaneously carbon-coated product exhibits excellent performance for both Li⁺ and Na⁺ storage.

Supporting Information

Solution Synthesis of VSe₂ Nanosheets and Their Alkali Metal Ion Storage Performance

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1. Experimental Section

Preparation of VSe₂ NSA and VSe₂ NSA/C: Typically, 2 mmol VO(acac)₂ and 4 mmol SeO₂ were added to 30 ml NMP, after stirring for 30 minutes, a brownish grey solution was obtained. 6 ml of formic acid (HCOOH) was added dropwise into the above solution, which was then stirred for another 15 minutes. Finally, the mixture was transferred to a 50 mL Teflon-lined stainless-steel autoclave and heated in an electric oven at 200 °C for 24 h. After naturally cooling to the room temperature, the black powder was collected by centrifugation, washed with DI water and ethanol several times and dried at 50 °C overnight. The VSe₂ NSA was obtained by annealing the above powder at 500 °C for 3 h under Ar atmosphere. It should be noted that post-annealing process is necessary to remove the surface selenium and to improve the crystallinity. For the preparation of VSe₂ NSA/C sample, the process is similar to the pure VSe₂ NSA except that, 0.1 M glucose was added into the reaction solution before the mixture was transferred into the autoclave.

Characterization: The phase and structure of the samples were identified using XRD (Bruker diffractometer, D8 Advance) with Cu K α radiation. The composition and surface oxidation state were probed by X-ray photoelectron spectroscopy using an AMICUS ESCA 3400 XPS with Al K α radiation. Raman spectra were collected on a Hariba Aramis spectrometer using He-Ne laser at 633 nm. Electronic conductivity was characterized by the MET-007 four-probe. The morphology of the product was characterized using a ZEISS Merlin scanning electron microscope (SEM) and a FEI Titan transmission electron microscopy (TEM).

Electrochemical Measurements: To prepare the working electrodes, the active materials were mixed with Super P carbon black and carboxymethyl cellulose binder in a weight ratio of 7:1.5:1.5, and uniformly dispersed in water. The slurry was then blade-coated onto a copper foil, followed by vacuum drying at 80 °C for 12 h. For electrochemical measurements, CR2032-type coin half cells were assembled in an Ar-filled glove box (both H₂O and O₂ concentrations less than 0.5 ppm) by using the working electrode and a piece of Li or Na foil. The separator was Celgard 3501 microporous membrane and the electrolyte was 1 M LiPF₆ in a 1:1 (v/v) ethylene carbonate/dimethyl carbonate (EC/DMC) for Li ion batteries or 1.0 M NaClO₄ in 1:1 (v/v) EC/DMC for Na ion batteries. Cyclic voltammetry was recorded on a Biologic VMP3 potentiostat in the voltage range of 0.01-3 V for Li ion batteries and 0.01-2.5 V for Na ion batteries. The galvanostatic charge/discharge experiments at different current densities were carried out using an Arbin BT-2043 battery testing system. Electrochemical impedance spectroscopy (EIS) tests were conducted using Biologic VMP3 in the frequency range from 1000 kHz to 0.01 Hz at open circuit voltage.

Estimation of the capacitive contribution and diffusion-limited contribution:

To quantitatively distinguish the capacitive and diffusion-controlled contributions to current, cyclic voltammetry curves at various sweep rates were recorded. Generally, the relationship between the measured peak current (i) and sweep rate (v) in a CV scan follows the power law:

$$i = av^b$$

$$\text{thus, } \log(i) = \log(a) + b \cdot \log(v)$$

Therefore, the b value can be acquired by fitting slope of the $\log(i)$ versus $\log(v)$ profile. A b value of 0.5 indicates a diffusion-controlled behavior while the b value of 1.0 corresponds to a capacitive behavior. The capacitive contribution and diffusion-controlled contribution can be further quantitatively distinguished assuming the current (i) is a combination of the capacitor-like and diffusion-controlled processes according to:

$$i = k_1v + k_2v^{1/2}$$

we can estimate the capacitive and diffusion limited contributions by determining k_1 .

2. Supporting Figures:

Figure S1. Illustration of the Raman vibration modes of E_{2g} and A_{1g} in VSe_2 .

Figure S2. Temperature-dependent electronic conductivity measured using the four-probe method.

Figure S3. SEM images of VSe₂ NSA at low magnifications.

Figure S4. (A) SEM and (B) AFM images for determining the thickness of the VSe₂ nanosheets.

Figure S5. SEM (left) and TEM (right) images of VSe₂ NSA/C.

Figure S6. EDS spectra of (A) VSe₂ NSA and (B) VSe₂ NSA/C.

Figure S7. STEM-EDS element mappings of VSe₂ NSA/C (V, Se, and C overlay).

Figure S8. SEM-EDS element mappings for V, Se and C of VSe₂ NSA/C.

Figure S9. (A) XRD patterns of the products obtained at various reaction periods. (B-I) SEM images of the products obtained after reaction for (B, C) 4, (D, E) 8, (F, G) 24 and (H, I) 30 h.

Figure S10. (A) XRD pattern and (B, C) SEM images of the product obtained using water as the solvent.

Figure S11. SEM images and XRD patterns for the products synthesized using different surfactants. (A, B) P123, (C, D) PVP and (E, F) CTAB.

Figure 12. XRD pattern and SEM images of VSe₂ obtained by using DMF as the solvent.

Figure S13. SEM images and XRD patterns for the products synthesized using different precursors. (A-C) NH₄VO₃ and SeO₂, (D-F) V₂O₅ and SeO₂, and (G-I) VO(acac)₂ and selenourea.

Figure S14. CV plots of VSe₂ NSA for Li ion storage.

Figure S15. Cycle performance at 800 mA g⁻¹ of VSe₂ NSA and VSe₂ NSA/C for Li ion storage.

Figure S16. Cyclic voltammetry curves of VSe₂ NSA/C at different scan rates for Li ion storage.

Figure S17. CV plots of VSe₂ NSA for Na ion storage.

Figure S18. Cycle performance at 500 mA g⁻¹ of VSe₂ NSA and VSe₂ NSA/C for Na ion storage.

Figure S19. Cyclic voltammetry curves of VSe₂ NSA/C at different scan rates for Na ion storage.

Figure S20. Nyquist plots of VSe₂ NSA and VSe₂ NSA/C after different cycles. VSe₂ NSA for (A) lithium ion battery and (C) sodium ion battery; VSe₂ NSA/C for (B) lithium ion battery and (D) sodium ion battery.

Figure S21. EDS mapping and corresponding percentage of VSe₂ NSA/C electrodes after 50 cycles for lithium (top panel) and sodium (bottom panel) storage, respectively.

Figure S22. SEM images of VSe₂ NSA and VSe₂ NSA/C after 50 cycles. VSe₂ NSA for (A) lithium ion battery and (B) sodium ion battery; VSe₂ NSA/C for (C) lithium ion battery and (D) sodium ion battery.