The role of carbon nanotubes in enhanced charge storage performance of VSe$_2$: experimental and theoretical insight from DFT simulations†

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Herein, we report the hybrid structure of metallic VSe$_2$ and multi-walled carbon nanotube (MWCNT) based hybrid materials for high performance energy storage and high power operation applications. The dominance of capacitive energy storage performance behaviour of VSe$_2$/MWCNT hybrids is observed. A symmetric supercapacitor cell device fabricated using VSe$_2$/80 mg MWCNT delivered a high energy density of 46.66 W h kg$^{-1}$ and a maximum power density of 14.4 kW kg$^{-1}$ with a stable cyclic operation of 87% after 5000 cycles in an aqueous electrolyte. Using density functional theory calculations we have presented structural and electronic properties of the hybrid VSe$_2$/MWCNT structure. Enhanced states near the Fermi level and higher quantum capacitance for the hybrid structure contribute towards higher energy and power density for the nanotube/VSe$_2$.

1 Introduction

The growing demands for energy resources and the limitations of fossil fuels have stimulated intense research on alternative high-performance energy storage devices. Batteries and supercapacitors are the most favourable devices for these purposes. Batteries can store more energy than supercapacitors but the faradaic reaction to store energy in batteries hinders their use in high power operations. Unlike batteries, supercapacitors have higher power density which helps them to accumulate and provide more energy for a shorter period compared to batteries. Their high cycling life and reversibility also give them an edge over other energy storage devices. According to the energy storage mechanism, supercapacitors can be categorized into three types i.e. (1) electric double-layer capacitors (EDLCs), (2) pseudocapacitors and (3) battery like capacitors. In a conventional EDLC, charge storage occurs due to the formation of an electric double layer at the electrode–electrolyte interfaces. The occurrence of a faradaic electron transfer in the energy storage makes the device a battery-like supercapacitor. In the case of pseudocapacitors, rapid faradaic reactions occur at the surface or near-surface of the electrode and there is no solid-state diffusion like batteries. Transition metal dichalcogenides (TMDs) are rigorously expedited 2D materials for electrochemical energy storage applications. Properties like large surface area, polytypic structure (2H and 1T), easiness to functionalize, flexibility toward the controlled strain and variable oxidation state make them the most desirable candidates for both EDLC and pseudocapacitors based energy storage devices. Among TMDs, 1T-VSe$_2$ is one of the attractive electrode material having high electrical conductivity and surface area.

The basic structure of 1T-VSe$_2$ (ref. 17) is the octahedral vanadium atom coordination in a tetragonal symmetry with an offset arrangement of layers held together by weak van der Waal force. This layered structure, highly active edges and basal sites bestowed prepossessing energy storage properties to VSe$_2$. 1T structure of VSe$_2$ evinced metallic behaviour in nature. The unpaired d electron of vanadium is responsible for the high electronic conductivity. The van der Waal gaps in metallic TMDs can electrochemically intercalate cations with higher efficiency and plays important role in exhibiting superior charge storage properties. However, the high Gibbs’s free energy makes 1T-VSe$_2$ less stable. Interestingly, with the help of highly porous carbonaceous materials such as graphene and CNTs, it is possible to obtain high stability in long cycle operations along with enhanced electrochemical properties due to the active sites and enhanced electronic conductivity.

Behera and co-workers successfully synthesized VSe$_2$/RGO composites for supercapacitor applications with an energy density of 212 W h kg$^{-1}$ at a power density of 0.9 kW kg$^{-1}$. The multi-walled carbon nanotube (MWCNT) can improve the electrochemical activity of 1T-VSe$_2$ due to its large surface area.
high electronic conductivity, better chemical stability and excellent flexibility. Wu et al. fabricated VSe2/CNT based in-plane supercapacitor which although improves the stability of the material but there is no noticeable increase in capacitance. Coexistence of improved energy density, power density and cyclic stability of 1T-VSe2 based electrodes is very much required for the commercial viability.

Here, we propose a one-step hydrothermal technique to synthesize VSe2/MWNTs hybrid electrodes with enhanced ionic conductivity, long cycle life and very high energy and power density. We have provided a comprehensive understanding of the energy storage mechanism involved in VSe2/MWNTs with different concentration of CNTs suitable for commercial application. Theoretical simulations have been carried out to support experimental findings from electronic properties, bonding mechanism and quantum capacitance of the hybrid structure as well as diffusion and charge transfer performance of the electrolyte ions.

2 Experimental section

2.1 Synthesis of VSe2/MWCNT composites

High purity MWCNTs (<5% impurities, 1–10 μm length and 3–15 number of walls) was purchased from PlasmaChem GmbH, Berlin. The nanotubes were functionalized using an acidic solution of H2SO4 and HNO3 mixed together in a 3:1 ratio. The VSe2/MWCNT hybrids are synthesised by following the one-step hydrothermal method. 1 mM of ammonium metavanadate (NH4VO3), 2 mM of selenium dioxide (SeO2), 5 ml formic acid and different concentrations of functionalized multi-walled carbon nanotube (MWCNT) were added into 35 ml distilled water and stirred until a uniform solution was obtained. The above solution then transferred into a Teflon lined autoclave and heated up to 200 °C for 24 h. After the autoclave reaches room temperature, the precipitate is washed in distilled water and ethanol, followed by drying in ambient conditions. Pristine VSe2 also synthesised in the same method without the addition of nanotubes.

2.2 Material characterization

The morphological and structural characterisations of VSe2/MWCNT composites were carried out using Field Emission Scanning Electron Microscope (FESEM, JEOL JSM-7100F, JEOL Ltd., Singapore, with maximum operating accelerating voltage as 30 kV), Transmission Electron Microscope (TEM, TALOS F200s G2 with 200 kV, FEI, CMOS Camera 4k x 4k) and X-ray Diffraction (XRD) (Rigaku Ultima IV X-ray diffractometer having Ni-filter for Cu Kα radiation (wavelength, λ = 0.1541 nm)). FESEM has also been used to colour map the elements present in the material. The surface area measurements were done by BET surface area analyzer (Belsorp max, Japan).

2.3 Electrochemical measurements

The electrochemical measurements were studied using Wuhan Corrtest electrochemical workstation version 5.3 using a Swagelok cell in two electrode configuration with 0.5 M K2SO4 as an aqueous electrolyte. Electrochemical impedance spectroscopy (EIS) for the symmetric device was performed within the frequency range between 0.05 Hz and 100 kHz with operating ac field amplitude of 5 mV.

2.4 Computational details

We have used plane wave based Density Functional Theory (DFT) code VASP with PAW-GGA as exchange–correlation functional for the simulations. The cutoff energy is considered as 500 eV and the Brillouin zone is integrated employing a Monkhorst–Pack mesh of 7 x 7 x 1 k-points for (001) plane of VSe2 and hybrid VSe2/CNT (carbon nanotube). To describe the weak van der Waals forces between VSe2 and CNT, we have considered Grimme DFT-D2 dispersion scheme.

3 Results and discussions

3.1 Morphological and structural characterization of VSe2/MWCNT hybrid sheets

The morphology of VSe2/MWCNT and pristine VSe2 were studied through field emission scanning electron microscopy (FESEM) which is shown in Fig. 1a–d. FESEM images revealed that the pristine VSe2 forms as hexagonal nanosheets. In VSe2/MWCNT composite, VSe2 exhibits a similar hexagonal structure formation with 0.5 M K2SO4 as an electrolyte. The SPR peak at 262 nm observed in pristine VSe2 is not observed in VSe2/MWCNT nanocomposite.

The HRTEM analysis showcases the concatenated structure of VSe2 and MWCNT. To describe the weak van der Waals forces between VSe2 and CNT, we have considered Grimme DFT-D2 dispersion scheme.

The broadening of EIS for the symmetric device was performed within the frequency range between 0.05 Hz and 100 kHz with operating ac field amplitude of 5 mV.

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The XRD patterns of VSe2 and VSe2/MWCNT composites are shown in Fig. S3. All the peaks of VSe2 and VSe2/MWCNT composites are facsimiled with the JCPDS card number 89-1641. The XRD patterns of VSe2 and VSe2/MWCNT revealed the formation of the metallic VSe2, but in the case of hybrids with a high concentration of nanotubes, low content of vanadium oxide coexists. During the synthesis process, the functional groups attached to the CNT surface facilitate the grafting of this low content of vanadium oxide layer on it. The widening of (002) plane in VSe2/100 mg MWCNT may be due to the increased strain in VSe2 sheets. The interconnection of VSe2
sheets by MWCNT causes a strain which leads to lattice distortion and peak broadening.35 The growth and slight shift of (002) peak and diminution of highly intense (011) peak can be explained by the possible increase of interlayer spacing between the VSe2 layers.25,36 In the case of the hybrids VSe2/50 mg MWCNT and VSe2/80 mg MWCNT, prominent peaks of MWCNT are not observed due to formation of high crystalline metallic VSe2 and its dominance over CNTs. In the case of the VSe2/100 mg MWCNT, a less intensified broad (002) peak of MWCNT is observed around 26°. The specific surface area of metallic VSe2 and VSe2/80 mg MWCNT was calculated using Brunauer–Emmett–Teller (BET) analysis. The 1T-VSe2 shows a specific surface area of 3.5478 m2 g−1 and the VSe2/80 mg MWCNT composite exhibits an enhanced specific surface area of 93.047 m2 g−1 (Fig. S4 of ESI†).

The charge storage mechanism in a supercapacitor electrode involves three major contributors: (1) the formation of an electric double layer in the electrode–electrolyte interface of the cell, (2) pseudocapacitive process arising from a non-faradaic surface redox reaction or diffusion free intercalation of ions into layers of the electrode material and (3) faradaic reaction arising from the intercalation mechanism. The first two mechanisms convoluted to the capacitive type storage and the third mechanism contributes to diffusive type charge storage. The faradaic and non-faradaic components are given in eqn (1) and (2) respectively.37

\[
\text{(VSe2)\text{surface} + K^+ + e^- \rightleftharpoons (VSe_2^- - K^+)\text{surface}} \quad (2)
\]

The charge storage contributions from both faradaic and capacitive components can be calculated from the CV curves by using the Power’s law (eqn (3)).38

\[
i = a v^b
\]

According to the Power’s law, \(i\) (A) is the current at a particular voltage, \(v\) (V s−1) is the scan rate and \(a\) and \(b\) are the two adjustable parameters.38 The \(b\) parameter can be obtained from the slope after plotting \(\log i\) against \(\log v\) at a particular potential (\(V\)). Generally, if the \(b\) value is equal to 1 then it shows a diffusion free capacitive behaviour.39 If the \(b\) value is equal to 1/2 impute an ideal diffusion dependant faradaic contribution which satisfies Cortell’s equation \(i = a v^{1/2}\). Therefore, current value \(i\) (A) at a fixed potential \(V\) from CV can be written as the sum of surface redox reactions and diffusion dependent faradaic reactions (eqn (4a) and (4b))

\[
i(V) = a_1 v + a_2 v^{1/2}
\]

(4a)

\[
i(V) = a_1 v^{1/2} + a_2
\]

(4b)

The values of \(a_1\) and \(a_2\) can be determined from the slope and intercept of the \(i(V)/v^{1/2}\) vs. \(v^{1/2}\) plot at specific potential values.40

![Fig. 1](image-url)
Fig. 2c shows the voltage–current profile of VSe$_2$/80 mg MWCNT composite at a scan rate of 20 mV s$^{-1}$ and the shaded region accounts for the capacitive controlled region. The dominance of capacitive contribution for the charge storage in VSe$_2$/80 mg MWCNT electrodes is evident from Fig. 2c. In VSe$_2$/80 mg MWCNT, the capacitive contribution is found to be around 82.89%. A gradual increase in capacitive contribution for VSe$_2$/80 mg MWCNT is found with increasing scan rate, at a higher scan rate of 100 mV s$^{-1}$, segregation of capacitive contribution over diffusion is around 92.75% (Fig. S8a of ESI†). We can take an assumption that the majority of the charge storage phenomena in VSe$_2$/80 mg MWCNT electrode is due to the capacitive contribution, whereas fast intercalation of K$^+$ ions contributes towards the diffusion process.

With the help of Trasatti method, the charge storage mechanism inside and outside of the VSe$_2$/80 mg MWCNT electrode can be further explained (Fig. S8b and c of ESI†). From the y-intercept of $1/q$ vs. $v^{1/2}$ (where $v = 0$), the total charge stored ($Q_{\text{total}}$) can be calculated and charge stored on the outer surface of the electrode ($Q_{\text{outer}}$) can be obtained from the y-intercept of $q$ vs. $v^{-1/2}$ (where $v = \infty$). The total charge stored in the electrode and on the surface of the electrode is calculated to be 217.86 C g$^{-1}$ and 54.23 C g$^{-1}$ respectively and the charge stored inside the electrode is 163.63 C g$^{-1}$. This upholds the faradaic component in the charge storage operation along with the dominance of capacitive contribution. The sharp increase in the intensity of (002) peak and diminution of highly intense (011) peak observed in the XRD spectrum of VSe$_2$/80 mg MWCNT after 5000 cycles, explain a possible intercalation effect of the cation in the gap between the VSe$_2$ layers. This observation further provides the insights to the observed enhanced pseudocapacitive energy storage performance arising from the intercalation of cations (Fig. S8d ESI†).

Fig. 2b, S6b and f illustrate the GCD curves of VSe$_2$ and VSe$_2$/MWCNT hybrids at varying current densities. The energy storage performance of VSe$_2$/MWCNT is found to be very much superior compared to the pristine VSe$_2$ sheets. VSe$_2$/80 mg MWCNT shows superior supercapacitor performance than that of all other electrodes with a specific capacitance of 233.33 F g$^{-1}$ at a current density of 2 A g$^{-1}$ Fig. 2f. The dominance of MWCNT content and its aggregation in the VSe$_2$/100 mg MWCNT composite can be accounted for the truncated electrochemical performance compared to VSe$_2$/80 mg MWCNT. The coulombic efficiency of VSe$_2$/80 mg MWCNT increases with increase in current density (Fig. S9 of ESI†). At
lower current density the electrode might undergo some parasitic reactions, which may be originated from the diffusion and responsible for the low coulombic efficiency of VSe$_2$/80 mg MWCNT at lower current density.$^{45}$–$^{47}$ The VSe$_2$/80 mg MWCNT possesses high cyclic stability with 87% of capacitive retention after 5000 GCD cycles and a 95% of coulombic efficiency which provides high reversibility and higher power operation (Fig. 2f).$^{48}$ The interconnection of 2D VSe$_2$ sheets and 1D MWCNT not only enhances the aspect ratio of the stored ions but gives a shorter ion transport pathways to the inner side of the material. Besides, VSe$_2$/80 mg MWCNT exhibits a much small $iR_{\text{drop}}$ compared to the pristine VSe$_2$ and this leads to the reduction of equivalent series resistance (ESR) from 20.96 $\Omega$ cm$^2$ to 12.67 $\Omega$ cm$^2$. The reduction observed in ESR is probably due to the enhancement in ionic conductivity of VSe$_2$/80 mg MWCNT.$^{49}$

A comparative Ragone plot of VSe$_2$ and VSe$_2$/MWCNT hybrids is shown in Fig. 2g. VSe$_2$/80 mg MWCNT exhibits an energy density of 46.66 W h kg$^{-1}$ at a high power density of 4.8 kW kg$^{-1}$ and retains 13.6 W h kg$^{-1}$ of its energy density at a power density of 14.4 kW kg$^{-1}$ which further underlines the high power operation of VSe$_2$/80 mg MWCNT. All the VSe$_2$ based hybrid materials we discussed above possess an excellent power capability. From the Ragone plot, it is evident that the high power density in the composites came from the metallic nature of VSe$_2$ and the addition of nanotubes enhances the energy density of the composites. The VSe$_2$/80 mg MWCNT hybrid possesses high cyclic stability with 87% of capacitive retention after 5000 GCD cycles (Fig. 2h).$^{48}$ A comparison of delivering a high energy density at a higher power density in TMD based devices along with the present work is given in Table 1; which further underlines the superior performance of VSe$_2$/80 mg MWCNT.

With the help of electrochemical impedance spectroscopy (EIS) measurement, the charge transfer property and resistivity of these materials have been explored. The Nyquist plots for the pristine VSe$_2$ and VSe$_2$/MWCNT composites with their Randles equivalent circuit (inset) are shown in Fig. 2i and $S7c$ EIS spectrum of MWCNT has also been shown. All the composites show far better charge transfer as compared to the pristine VSe$_2$. However, VSe$_2$/80 mg MWCNT exhibits higher charge transfer than any other composites which further proves its excellent capacitance.$^{45}$ The synergistic mechanism between VSe$_2$ sheets and multi-walled carbon nanotube in VSe$_2$/80 mg MWCNT improves the electronic conductivity and diminishes resistivity which further sheds light on the enhanced power operation of this electrode material.$^{34,47,48}$ The charge storage mechanism and reduced redox kinetics of VSe$_2$/80 mg MWCNT can be further understood by its fast charge transfer kinetics.

### 3.2 Theoretical study of VSe$_2$/MWCNT hybrids using Density Functional Theory (DFT)

We have provided theoretical support using Density Functional Theory (DFT) simulations. Computational details are given in Section 2.4.

First, we have generated (001) surface of VSe$_2$ and performed geometry optimization. The relaxed structure of the (001) plane of VSe$_2$ is displayed in Fig. 3a. Then we have put single walled carbon nanotube (SWCNT) with chirality of (8,0) and allow the hybrid structure to relax. The hybrid VSe$_2$–SWCNT is depicted in Fig. 3b. The separation between VSe$_2$ and SWCNT is around 3 Å. Here we mention that for theoretical simulations we have considered only single walled carbon nanotube (SWCNT) as taking more layers connected by weak van der Waals interactions is computationally expensive and does not provide much additional information. To get the electronic properties of the hybrid structure, we have computed the density of states (DOS). The DOS for pristine VSe$_2$, VSe$_2$/20 wt% of SWCNT (~VSe$_2$/50 mg MWCNT) and VSe$_2$/33 wt% SWCNT (~VSe$_2$/80 mg MWCNT) are shown in Fig. 4a. We can notice the enhancement of states near Fermi level in the hybrid structure compared to pristine materials.

#### Table 1 Comparative table on the energy storage performance of existing literature on TMDs based supercapacitor devices and the present work

| Active material          | Type of supercapacitor | Energy density          | Cyclic stability%/cycles | Ref.   |
|-------------------------|------------------------|-------------------------|--------------------------|--------|
| Flower-like MoS$_2$/GNS | Asymmetric             | 78.9 W h kg$^{-1}$ at 284.1 W kg$^{-1}$ | 90/5000                  | 49     |
| MoS$_2$                 | Symmetric              | 34.0 W h kg$^{-1}$ at 333.3 W kg$^{-1}$ | 81.6/3000                | 50     |
| NiSe$_2$/MoSe$_2$       | Asymmetric             | 32.6 W h kg$^{-1}$ at 415 W kg$^{-1}$ | 91.4/5000                | 51     |
| MoSe$_2$/graphene       | Asymmetric             | 26.6 W h kg$^{-1}$ at 0.8 kW kg$^{-1}$ | 88/3000                  | 52     |
| WS$_2$                  | Symmetric              | 31.9 W h kg$^{-1}$ at 333.3 W kg$^{-1}$ | 77.4/3000                | 50     |
| WS$_2$/rGO              | Symmetric              | 49 W h kg$^{-1}$        | 53                       |        |
| WS$_2$/rGO              | Symmetric              | 34.5 W h kg$^{-1}$ with 400 W kg$^{-1}$ | 98.7/3000                | 54     |
| SnS$_2$/GCA             | Asymmetric (sodium hybrid capacitor) | 108.3 W h kg$^{-1}$ at 130 W kg$^{-1}$ | 68.4% after 1500 cycles at 1 A g$^{-1}$ | 55     |
| NiSe$_2$ spheres        | Asymmetric             | 35.2 W h kg$^{-1}$ at 749.3 W kg$^{-1}$ | 97.3/10 000              | 56     |
| CoSe$_2$                | Asymmetric             | 32.2 W h kg$^{-1}$ at 1914.7 W kg$^{-1}$ | 94.5/5000                | 57     |
| Co$_2$                  | Symmetric              | 11.8 W h kg$^{-1}$ at 0.3 kW kg$^{-1}$ | 58                       |        |
| 1T-MoTe$_2$             | Asymmetric             | 56.4 W h kg$^{-1}$ at 800 W kg$^{-1}$ | 59                       |        |
| TiS$_2$/VACNT           | Symmetric              | 60.9 W h kg$^{-1}$      | >95/100 000              | 60     |
| VS$_2$                  | Symmetric              | 25.9 W h kg$^{-1}$ at 1.5 kW kg$^{-1}$ | 89/6000                  | 61     |
| VS$_2$/MWCNTs           | Symmetric              | 42 W h kg$^{-1}$ at 2.8 kW kg$^{-1}$ | 93.2/5000                | 37     |
| VSe$_2$/rGO             | Symmetric              | 212 W h kg$^{-1}$ at 0.9 kW kg$^{-1}$ | 81/10 000                | 25     |
| VSe$_2$/MWCNTs          | Symmetric              | 46.66 W h kg$^{-1}$ at 4.8 kW kg$^{-1}$ | 87/5000                  | This work |
pristine VSe$_2$. The enhancement is stronger with the increase in SWCNT content. Electronic structures with more states near Fermi level may point towards an increase in conductivity of VSe$_2$ when it is hybridized with SWCNT which supports our experimental observations. Fig. 4c depicts the partial density of states of C 2p orbital and V 3d orbital for pristine SWCNT, pristine VSe$_2$ and for the hybrid structure. We can observe that the states of V 3d near Fermi level gets reduced in the hybrid structure compared to pristine VSe$_2$. Also, the states of C 2p orbital near Fermi level gets enhanced for the hybrid structure compared to pristine SWCNT. The reduction of states of V 3d orbitals and increase in states for C 2p orbitals near Fermi level for the hybrid structure indicates a possible charge transfer between V 3d orbital and C 2p orbitals. To visualize the charge transfer qualitatively, in Fig. 3c, we have plotted the charge density distribution for charge density difference between VSe$_2$/SWCNT and VSe$_2$ for isovalue of 0.05e. Charge gain region is shown by blue color and charge loss region by red color. We can see more blue color iso-surface in SWCNT indicating the charge gain by C 2p orbital from V 3d orbital. This is consistent with the charge transfer as seen from the analysis of the partial density of states presented in Fig. 4c.

From the density of states, we have computed the quantum capacitance using the relation

$$C_Q = \frac{e^2}{8\pi^2} \int_{-\infty}^{\infty} D(E) F_T(E - \varphi_d) dE$$  \hspace{1cm} (5)

where the parameters are $D(E)$ = density of states, $\varphi_d$ = electrode potential, $F_T(E)$ = thermal broadening function.

The thermal broadening function is given by

$$F_T(E) = \frac{4K_B T}{C_0} \text{sech} \left( \frac{E}{2K_B T} \right)$$  \hspace{1cm} (6)
Fig. 4d shows the variation of quantum capacitance with the electrode potential for pristine VSe$_2$ surface and the hybrid VSe$_2$/SWCNT surface. We can notice that the quantum capacitance is higher for the hybrid VSe$_2$/SWCNT compared to pristine VSe$_2$ surface. Higher quantum capacitance for the hybrid structure qualitatively justifies the better supercapacitor performance of the hybrid structure. Here we clarify that quantum capacitance is significant for low dimensional system and in the experiment we measure the total capacitance which includes both quantum capacitance and electrical double layer capacitance.

K$_2$SO$_4$ aqueous electrolyte is used for the electrochemical energy storage of the present system. We have computed the average voltage of the system for different concentrations of K$^+$ ions using the eqn (7) (ref. 63)

$$V = \left(\frac{E_{K,1VSe_2} - \left(E_{K,2VSe_2} + (x_1 - x_2)E_K\right)}{(x_1 - x_2)e}\right)$$

(7)

Here $E_K$ and $E_{K,VSe_2}$ represent the energy of K$^+$ per ion and total energy of K$_x$VSe$_2$ per unit formula, respectively. We have chosen three different concentrations for K$^+$ ions with $x_1$, $x_2$, $x_3$ are 0.03333, 0.13333 and 0.26666 respectively. The computed average voltage for different concentration of K$^+$ ions is listed in Table S1 of ESI.† The voltage range is consistent with the theoretical predictions for a similar system in the literature.33 In Fig. S10 of ESI,† we have plotted the energy of the system for different concentration of K$^+$ ions.

As the mobility of the electrolyte ions increases, the system exhibits better super capacitance performance. The mobility of the ion is inversely proportional to the barrier potential offered by the system. We have computed the diffusion barrier of K$^+$ and Na$^+$ ions for the diffusion across the monolayer of VSe$_2$. The computed diffusion barrier of K$^+$ and Na$^+$ ions are 0.1023 eV and 0.1306 eV respectively. We can see that the diffusion barrier for K$^+$ ion is less compared to Na$^+$ ions attributing higher mobility and better charge transfer.

4 Conclusions

In summary, hybrid structures of metallic VSe$_2$ and MWCNT were synthesised by a one-step hydrothermal method. Enhanced electrochemical energy storage performance was observed in all the composites compared to pristine VSe$_2$. The VSe$_2$/80 mg MWCNT hybrid electrode shows high cyclic stability, good energy density and an attractive power density in comparison with other hybrids. A predominant capacitive contribution over diffusion-controlled contribution in the energy storage mechanism was observed in all the hybrid electrodes of VSe$_2$ and MWCNT. Synergistic effect of VSe$_2$ and MWCNT elucidates the enhancement of electrochemical properties of VSe$_2$/80 mg MWCNT and reduces the resistivity of the material. Besides the increase in interplanar spacing in VSe$_2$ with the incorporation of MWCNT provides a favourable condition for the intercalation of K$^+$ ions and improves the cyclic stability of the VSe$_2$/80 mg MWCNT electrode in high power operation. We have presented the electronic properties and quantum capacitance of the hybrid structure VSe$_2$/SWCNT to get theoretical insight for the enhanced charge storage performance of the hybrid structure. Enhanced states near Fermi level, charge transfer from V 3d orbital to C 2p orbitals and enhanced quantum capacitance of the hybrid structure provide theoretical justification for superior super capacitance performance of VSe$_2$/SWCNT as observed in experiments. The low diffusion barrier of K$^+$ ions (of K$_2$SO$_4$ electrolytes) compared to Na$^+$ ions predicts higher mobility and better charge storage characteristics.

Conflicts of interest

There are no conflicts to declare.

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