Titanium Disulfide Coated Carbon Nanotube Hybrid Electrodes Enable High Energy Density Symmetric Pseudocapacitors

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While electrochemical supercapacitors often show high power density and long operation lifetimes, they are plagued by limited energy density. Pseudocapacitive materials, in contrast, operate by fast surface redox reactions and are shown to enhance energy storage of supercapacitors. Furthermore, several reported systems exhibit high capacitance but restricted electrochemical voltage windows, usually no more than 1 V in aqueous electrolytes. Here, it is demonstrated that vertically aligned carbon nanotubes (VACNTs) with uniformly coated, pseudocapacitive titanium disulfide (TiS$_2$) composite electrodes can extend the stable working range to over 3 V to achieve a high capacitance of 195 F g$^{-1}$ in an Li-rich electrolyte. A symmetric cell demonstrates an energy density of 60.9 Wh kg$^{-1}$—the highest among symmetric pseudocapacitors using metal oxides, conducting polymers, 2D transition metal carbides (MXene), and other transition metal dichalcogenides. Nanostructures prepared by an atomic layer deposition/sulfurization process facilitate ion transportation and surface reactions to result in a high power density of 1250 W kg$^{-1}$ with stable operation over 10 000 cycles. A flexible solid-state supercapacitor prepared by transferring the TiS$_2$–VACNT composite film onto Kapton tape is demonstrated to power a 2.2 V light emitting diode (LED) for 1 min.

Transition metal dichalcogenide (TMDC) materials, such as MoS$_2$, WS$_2$, and MoSe$_2$, have been widely studied in electrochemical applications as sensors,[1] catalysts,[2] and energy storage materials.[1,3] Among all TMDCs, TiS$_2$ is the lightest and cheapest[4] with the following potential benefits for lithium-based energy storage systems: (1) highest energy density storage capability among TMDCs,[4] (2) fast ion transportation rate,[5] (3) low volume expansion during reversible charge–discharge cycles,[6] and (4) no phase change during lithium ion intercalation.[4] However, TiS$_2$ suffers from mechanical degradation during ionization and deionization and has less desirable electrical conductivity.[7] Conformal coating of TiS$_2$ onto highly conductive 3D porous networks such as vertically aligned carbon nanotubes (VACNTs) improves electrical conductivity, increases surface areas, and helps the mechanical stability in electrochemical reactions.[8,9] Potential methods include chemical vapor deposition (CVD),[10] electro- and electroless plating,[11] and atomic layer deposition (ALD).[12] Both CVD- and plating-based processes encounter challenges in uniform coverage and crystallinity while the ALD deposition can achieve uniform and conformal coverage on porous, high-aspect-ratio structures such as VACNTs.[13] Not only does conventional ALD of TiS$_2$ use TiCl$_4$ and highly toxic H$_2$S as precursors, the subsequent production of sulfur contaminates ALD chambers.[12] In contrast, here we developed a two-step process that combines ALD of TiN with a following CVD...
sulfurization to fabricate TiS$_2$ composite-coated VACNT electrodes with desired nanostructures. Such ALD/sulfurization process could further be expanded to construct uniform coaxial coatings of chalcogenide (MoS$_2$, WS$_2$, etc.) onto high-aspect-ratio templates. Further characterizations demonstrate that the pseudocapacitive electrodes show a capacitance of 195 F g$^{-1}$ within a potential range of 3 V in a lithium-rich aqueous electrolyte, corresponding to an energy density of 60.9 Wh kg$^{-1}$ for a symmetric cell, which is exceptional among reported symmetric pseudocapacitors.

The structure of the TiS$_2$-coated VACNT hybrid electrodes is illustrated in Figure 1a, in which a TiN layer is deposited by ALD and sulfurized to be TiS$_2$ composite via annealing in sulfur powder at relatively low temperature (300 °C), maintaining conformal coating on VACNTs during the entire process. Such electrodes show high electrochemical capacitance due to the intercalation of Li ions with TiS$_2$ composite. Furthermore, the electrode material successfully operates within a large potential window of 3 V in a lithium-rich “water-in-salt” electrolyte that has only been applied in battery.$^{[15,16]}$ As such, the energy density of the supercapacitor cell, proportional to the capacitance multiplied by voltage squared, outperforms most state-of-the-art symmetric pseudocapacitors using metal oxides, metal chalcogenides, and metal carbides$^{[17–24]}$ with comparable results to Li-ion batteries (Figure 1b). TiS$_2$–VACNT composites in ultrahigh-concentration LiTFSI electrolyte represents a specific energy 900 times that of bare VACNTs using a 0.5 m H$_2$SO$_4$ electrolyte. Furthermore, when compared to other electrodes of similar structures made of VACNT forests coated with pseudocapacitive materials, such as RuO$_x$,$^{[13]}$ TiN,$^{[14]}$ and MoS$_2$,$^{[18]}$ TiS$_2$–VACNTs show superior capacitance, energy density, and power density. Moreover, TiS$_2$ composite coated on carbon nanotube (CNT) inherits the low phase transformation rate in lithiation and delithiation cycles$^{[4]}$ while maintaining a low deformation ratio (<5%) and high capacitance retention (>95%) after 10 000 cycles of cyclic voltammetry testing (Figure 1c). The CNT forest network helps immobilize the TiS$_2$ coating layer to release the stress and deformation in the charging–discharging cycles to improve the mechanical stability of TiS$_2$ for high cycle operations.$^{[7]}$

The conductive, porous VACNT forest is grown on a silicon or stainless steel substrate$^{[8]}$ and the diameter of an as-grown CNT is 13 ± 5 nm (Figure S1, Supporting Information). Afterward, 500 cycles of ALD TiN are deposited for a uniform and conformal coating of TiN with a final TiN/CNT diameter of 130 ± 15 nm (Figure S2, Supporting Information). Deposition rate varies from 0.06 to 0.25 nm per cycle depending on temperature and cycle numbers; the average growth rate for 500 cycles is ≈0.11 and ≈0.12 nm per cycle for 800 cycles (Figure S2, Supporting Information).$^{[25,26]}$ Under sulfur vapor annealing at 300 °C for 30 min, the amorphous TiN layer is converted to polycrystalline TiS$_2$ composite (Figure 2a) and maintains conformal coating on CNTs (Figure 2b). High-resolution transmission electron microscopy (Figure 2c) reveals that the resulting

*Figure 1. TiS$_2$–VACNT hybrid fabrication process and advantage as pseudocapacitor electrodes. a) TiS$_2$–VACNT composite electrodes synthesized by a two-step process: TiN is coated onto VACNT by atomic layer deposition and converted to TiS$_2$ composite in a sulfur vapor environment. The high capacitance energy storage in Li$^+$ electrolyte is achieved by electron-double-layer and TiS$_2$ composite–Li intercalation. b) Ragone plot for state-of-the-art energy storage systems showing TiS$_2$–VACNT composite with the highest energy density among various families of noncarbon materials, including metal oxides, metal chalcogenides, and metal-carbide-based system.$^{[17–26]}$ c) Long-term cyclability of the TiS$_2$–VACNT composite electrode in the 21 m LiTFSI electrolyte.*
materials are hexagonal-shaped structures with characteristic polycrystalline diffraction rings, in-plane 0.3 nm lattice distance, and (001) zone axis of the CdI₂-type symmetry. X-ray diffraction (XRD) shows standard peaks of TiS₂ composite with the low angle at 16.6° due to the (001) stacking structures, and the (110) and (101) peaks by using a Co X-ray diffraction source (Figure 2d). XRD of cycled TiS₂ electrodes is also shown in Figure 2d for comparison. Split Ti 2p peaks indicate composite Ti⁴⁺ and Ti³⁺ (residual TiN) with different spin–orbit splitting showing different energy difference (Figure 2e). Figure 2f reveals S 2p₁/₂ and S 2p₃/₂ spin splitting with energy different of 1.39 eV. Sulfur peaks of S 2s at the binding energy of 228.8 eV and S 2p at the binding energy of 164.8 eV are observed after one and three times of repeated sulfur annealing while the relative distance and intensity of the peaks are almost the same (Figure S3, Supporting Information), implying that additional sulfurization does not contribute to further material conversions from TiN to TiS₂ composite.

In Figure 3a, cyclic voltammetry (CV) results show that TiS₂ composite–VACNT in 21 m (mol kg⁻¹) LiTFSI electrolyte exhibits over ≈100 times the specific capacitance (per projected surface area) of as-grown VACNT electrode in 0.5 M H₂SO₄ electrolyte. Two key mechanisms are believed to assist this significant increase: (1) intercalation of Li–S into and out of the TiS₂ composite and (2) the increase of working voltage window from 1 to 3 V. It is found that the specific capacitance increases ≈4 times from the VACNT–H₂SO₄ system to the VACNT–LiTFSI system and 26.8 times from the VACNT–LiTFSI system to the TiS₂ composite–VACNT–LiTFSI system; the total increase is more than 100 times higher capacitance. Furthermore, the length of VACNT is found to slightly affect the performance of the TiS₂ composite–VACNT electrode systems (Figure S3b; Figure S4, Supporting Information). The system made of 4 µm thick VACNT grown on stainless steel has about 15% higher specific capacitance (195 F g⁻¹) as compared with that of the system made of 40 µm thick VACNT grown on silicon (168 F g⁻¹), as shown in Figure S4 (Supporting Information). Systems made of shorter VACNT electrodes could benefit from increased sulfur diffusion in the annealing process for the conversion of TiS₂ composite and smoother ion diffusion during the charge–discharge process. In the fitted capacity versus reverse of the square root of scan rate in Figure 3c, the larger constant of ½ than the interception constant indicates a near 2:1 ratio of diffusive to capacitive behavior in the cyclic voltammetry curve, consistent with the nature of Li⁺–Ti–S intercalation. It is also noted that even with over 60% diffusive capacitance, there is no obvious lithiation peak, which we could attribute to the limited, nanoscale TiS₂ depth and high surface area of VACNT forest that lead to more surface reactions at relatively high scan rates as compared to battery discharge rate. Similarly, if the 10 m LiCl electrolyte is used as the electrolyte (Figure S5, Supporting Information),
no lithiation peaks are observed at 10 mV s$^{-1}$ with only a small peak at 2 mV s$^{-1}$. Due to such observations, as well as two other facts including no plateaus shown in the chronopotentiometry charge–discharge tests (Figure 3d) and stable operation in symmetric two-electrode cells, we consider our composite electrodes as pseudocapacitive instead of battery like.

It is estimated that the density of the TiS$_2$–VACNT composite electrodes is 0.9 g cm$^{-3}$ (Supporting Information) and the volumetric specific capacitance up to $\approx$216 F cm$^{-3}$ (Figure S4, Supporting Information), such that chronopotentiometry current density of 1 mA cm$^{-2}$ is equivalent to 1.11 A g$^{-1}$ (Figure S6a, Supporting Information). A low Coulombic efficiency has been observed in the test, which can be caused by two possible reasons. One is the slow chemical kinetics of Li$^{+}$ intercalations in chalcogenide materials. The other is the self-discharging of the device caused by the leakages through Ohmic resistance and side reactions, which exist in all electrochemical energy storage devices. Nevertheless, the specific capacitance of electrodes tested between $-1$ to $-0.8$ V results in similar values and kinetics under different voltage scanning rates. Although the high capacitance is demonstrated with the 3 V working window (Figure S6b,c, Supporting Information), high voltage operations could induce aging for electrodes and electrolyte such that a slightly smaller working window such as 2.7 V is recommended for longer lifetime. When a 1.5 mA cm$^{-2}$ current density source is used, it takes about 15 s to charge–discharge the system to 3 V (Figure 3d). It is found that the TiS$_2$–VACNT composite network helps to mechanically stabilize the system during the cycling tests: >95% of original capacitance is maintained after 10 000 operation cycles (Figure 1c). Results show that the capacitance increases slightly during the initial cycles and drops in the last few thousands of cycles. We think that the slight increase of the capacitance in the initial cycling process is caused by two possible mechanisms: (1) the ion insertion and dissociation processes improve the conductivity and (2) the surface wettability improves. On the other hand, the reason for performance decay is likely the decreased lithiation depth. From the X-ray photoelectron spectroscopy (XPS) and XRD results, we see ions in LiTFSI gradually diffuse or intercalate into the lattice after cycling. Even though there is no solid electrolyte interface formed, the deformed surface layer could possibly block the further ion transportation.

There is also no obvious change in the morphology of the electrodes (Figure S7, Supporting Information). The TiS$_2$ shows limited lattice expansion after cycling (Figure 2d). The (001) peak is broadened and shifted from 30.4$^\circ$ to 29.4$^\circ$ and 33.1$^\circ$ to 31.9$^\circ$, indicating lattice deformation of 3.1% and 4.5%, respectively. Meanwhile XPS spectrum of cycled TiS$_2$ implies residual Li$^{+}$ in the lattice indicated by the slight Ti 2p shift and electrolyte absorption with S 2p side peak presented (Figure S8 and Table S1, Supporting Information). Furthermore, the system made of an 800-cycle ALD TiN does not show obvious improvement of specific capacitance as compared with the system made of 500-cycle ALD TiN; longer sulfurization annealing does not significantly improve performance (Figure S9, Supporting Information).

Figure 3. Electrochemical testing results of TiS$_2$–VACNT composite electrodes in the 21 m LiTFSI electrolyte. a) CV results from three systems: as-grown VACNT electrodes in 0.5 m H$_2$SO$_4$ electrolyte, in 21 m LiTFSI electrolyte, and TiS$_2$–VACNT composite electrodes in 21 m LiTFSI electrolyte. b) CV results of TiS$_2$–VACNT composite electrode in 21 m LiTFSI electrolyte under different scanning rates from 1 to 50 mV s$^{-1}$. c) Analysis of the energy storage capacity versus $v^{1/2}$, d) Repeating chronopotentiometry charge–discharge tests of TiS$_2$ composite/CNT in 21 m LiTFSI with a discharging current density of 300 µA cm$^{-2}$. e,f) CV and Nyquist plots of TiS$_2$–VACNT composite electrodes in multiple electrolytes.
Effects of different electrolytes. 0.5 m H₂SO₄, 1 m LiTFSI in N-methyl-2-pyrrolidone (NMP), and 1 m LiTFSI (Figure 3e) were observed under different operation voltage windows and organic NMP-based electrolyte presented slightly higher working windows. However, the TiS₂–VACNT composite electrode system in 1 m LiTFSI electrolyte dissolved in NMP can produce only about one-third of specific capacitance than that of the same electrode system in 1 m LiTFSI electrolyte dissolved in distilled (DI) water (Table 1; Figure S10, Supporting Information) due to the lower ion activity in organic solvent. Other key results from the Li⁺-rich electrolytes are summarized in Table 1. Working voltage window was found to scale with Li⁺ concentration as the activity of water molecule is suppressed by the high concentration of cathodic Li⁺ and anodic TFSI⁻ or Cl⁻ (additional results are provided in Figure S11 in the Supporting Information). As a result, the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) depopulate to broaden the stable operation voltage window. Specifically, high concentrations of LiTFSI extend the reaction (OER) depopulate to broaden the stable operation voltage window. However, the TiS₂–VACNT composite electrode system in 1 m LiTFSI electrolyte dissolved in NMP can produce only about one-third of specific capacitance than that of the same electrode system in 1 m LiTFSI electrolyte dissolved in distilled (DI) water. The TiN–VACNT electrode system shows an undesirable broad electrochemical peak near −0.4 V which could be attributed to either hydrolysis or TiN–TiO₂ impurity transition reactions due to the instability of TiN in acidic media. As such, the TiS₂–VACNT composite electrode system provides unique characteristics in the 21 m LiTFSI: (1) a large stable electrochemical operation voltage window, (2) high specific capacitance, (3) high power density, and (4) high energy density as compared with the other electrode systems. Specifically, experimental results show that the TiS₂–VACNT composite system can result in the largest enclosed area in the CV tests than those of tested RuO₂⁺, MoS₂⁻, and TiN–VACNT systems with a scanning rate of 100 mV s⁻¹ (Figure 4b), and has the highest capacitance density under various scan rates (Figure 4c). In Figure 4c, specific capacitance at 10 mV s⁻¹ maintains 120 F g⁻¹ which corresponds to charging 12 C g⁻¹ within 5 min. Such high charging rate is difficult to achieve in a battery system. Although RuO₂ is considered one of the highest capacitance materials, it is incapable of effective Li⁺ intercalation in Li-rich electrolytes. MoS₂ has a higher density (5.06 g cm⁻³) than that of TiS₂ composite (supplementary materials) which leads to unfavorable gravimetric capacitance and energy density. In this work, MoS₂–VACNT electrodes are also shown to suffer from poor coverage onto the individual CNT electrodes as most of the deposition forms a layer on the top of the VACNT structure (Figure S12, Supporting Information). TiN shows good electrical conductivity but its electrochemical performance is not comparable with TiS₂ composite in Li⁺ or non-Li⁺ electrolytes. Figure 4d summarizes the nominal energy density and working potential window for the tested electrodes presented in this paper. Figure 4e shows the measured energy density and power density of all tested electrodes under different scan rates to show high energy density and high power density of the different electrodes. Figure 4f records the relationships between capacitance density, energy density, and power density for all tested electrodes.

In this paper, we attribute the exceptional energy density of TiS₂–VACNT hybrid systems to the large working voltage window and intercalation-induced capacitance. Although some oxide materials (such as RuO₂ and MnO₃) also provide high capacitance, smaller operation voltage windows in conventional acidic and basic electrolytes limit their energy density (Table S2, Supporting Information). Using conventional organic solvent may promote cell voltage by eliminating hydrolysis but low ionic conductivity and diffusion coefficient degrade the performance. Since the aqueous electrolyte can easily be made in ambient conditions to eliminate possible safety issues, the TiS₂–VACNT composite electrode system with 21 m LiTFSI electrode is preferable to conventional Li⁺-rich solutions for various systems.

As a practical demonstration, a full symmetric cell device is constructed using a two-electrode design on filter paper (Fisher Scientific, P5 grade) and tested under a broad range of scan windows.

<table>
<thead>
<tr>
<th>V vs Ag/AgCl</th>
<th>Min. potential [V]</th>
<th>Max. potential [V]</th>
<th>Potential window [V]</th>
<th>Capacitance F g⁻¹ [10 mV s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 m H₂SO₄</td>
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<td>1.0</td>
<td>1.2</td>
<td>10.4</td>
</tr>
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<td>0.1</td>
<td>0.5</td>
<td>0.2</td>
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<tr>
<td>1 m LiCl</td>
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<td>1.0</td>
<td>1.4</td>
<td>18.75</td>
</tr>
<tr>
<td>10 m LiCl</td>
<td>−0.5</td>
<td>1</td>
<td>1.5</td>
<td>30</td>
</tr>
<tr>
<td>20 m LiCl</td>
<td>−1.3</td>
<td>1.05</td>
<td>2.35</td>
<td>80</td>
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<tr>
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<td>1.1</td>
<td>1.9</td>
<td>86</td>
</tr>
<tr>
<td>10 m LiTFSI</td>
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<td>1.2</td>
<td>2.3</td>
<td>102</td>
</tr>
<tr>
<td>21 m LiTFSI</td>
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<td>1.7</td>
<td>3</td>
<td>120</td>
</tr>
<tr>
<td>1 m LiTFSI in NMP</td>
<td>−1.5</td>
<td>0.9</td>
<td>2.4</td>
<td>31.25</td>
</tr>
</tbody>
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Table 1. TiS₂ composite–VACNT electrodes in different electrolytes (NMP: N-methyl-2-pyrrolidone).
rates from 2 to 100 mV s\(^{-1}\) (Figure 5a). The Nyquist plot shows the internal resistance to be about 1000 \(\Omega\), consistent with single cell impedance testing result of 400 \(\Omega\) (Figure 5b). By transferring two TiS\(_2\)–VACNT composite film structures onto Kapton tape with filter paper as the separator, a flexible, fully operational cell is built. The semisolid 21 m LiTFSI/5% PVA electrolyte is applied to measure a capacitance of 60 mF cm\(^{-2}\) at a scan rate of 15 mV s\(^{-1}\). This device is able to power a 2.2 V LED for 1 min (Figure 5c). In the future, large-scale TiS\(_2\)–VACNT can be transferred and patterned onto versatile substrates with better elastic properties and structural designs in order to make flexible and stretchable energy storage devices with high energy densities.\[^{34,35}\]

Three factors allow for exceptionally high energy density (reaching a maximum of 60.9 Wh kg\(^{-1}\) and 54.8 mWh cm\(^{-3}\)) for TiS\(_2\)–VACNT composite electrodes: (1) large electrochemical voltage window of 3 V due to the chemical stability of TiS\(_2\) composite in ultrahigh concentration, 21 m LiTFSI electrolyte;
(2) effective intercalation of Li⁺ into TiS₂–VACNT composite for high gravimetric capacitance of 195 F g⁻¹; and (3) nanocrystallinity of TiS₂ composite and ultrahigh surface area of VACNT framework promote surface reactions instead of bulk behavior for a maximum power density of 1250 W kg⁻¹ (≈1.13 W cm⁻³) and cyclability of more than 10 000 charge–discharge cycles with >95% capacitance retention. TiS₂–VACNT composite electrodes are compared with prepared RuO₂−x, MoS₂−x, TiN–VACNT and bare VACNT electrode systems and compared with other published works of various high-performance oxide, chalcogenide, and MXene energy storage systems. The TiS₂–VACNT composite electrode system in 21 m LiTFSI electrolyte achieves the highest maximum energy density among these supercapacitors. Furthermore, by decreasing the thickness of TiS₂ composite while increasing surface area of the highly porous VACNT network, we are able to achieve high power density. As a result, the large volumetric deformation during the charge–discharge operations is prevented to preserve the long-term stability of TiS₂ composite. So far, only a few graphene/activated graphene with extremely high surface areas report slightly higher energy densities in organic electrolyte or ionic liquid.[36,37] With further efforts to modify the composition of TiS₂ composite and decrease the impurities/defects, the performance of hybrid TiS₂ composite–VACNT LiTFSI systems could be further enhanced. Other aspects of such supercapacitors materials will be studied, including volumetric and areal capacitance[38] for potential applications with specific requirement.

**Experimental Section**

**Synthesis of TiS₂–VACNT Composite Electrodes:** A thermally grown silica layer on silicon serves as the basis of the VACNT substrate. A 50/10/5 nm Mo/Al/Fe thin film is evaporated as the catalyst layer and VACNTs are grown by CVD in a carbon-rich environment. The height (thickness) of the VACNT forest is controlled by processing time.[10] Alternatively, the VACNT electrodes are synthesized on a stainless-steel substrate with a passivation layer of atomic layer deposited Al₂O₃ (Cambridge FIII F200 Plasma ALD). The same ALD tool is used to coat TiO onto the VACNT framework, with TDMAT (0.05 s) and N₂ plasma (5 s, 300 W) as precursors and 5 s argon purge at 300 °C. The TiN–VACNT forest is annealed in sulfur vapor at 150, 250, 300, or 350 °C in a furnace (Lindbergh Thermal) for 30 min.

**Synthesis of RuO₂–VACNT Electrodes:** RuO₂ is deposited onto the VACNT electrodes using ALD with bis(ethylcyclopentadienyl) ruthenium(II) (Ru(ETCp)₂) and oxygen (O₂) as precursors. Pulse times for Ru(ETCp)₂ and O₂ are 1 s and 10 s, respectively, with 5 s argon gas purge. During the ALD process, substrates were heated to temperatures ranging from 270 to 400 °C.[13]

**Synthesis of MoS₂–VACNT Electrodes:** MoS₂ is grown by a second CVD process, using stoichiometric sulfur and MoO₃ as precursors and 300 sccm of Ar as the carrier gas. The holders for sulfur, MoO₃, and CNT are separated in different locations and heated to 400, 650, and 650 °C, respectively.

**Materials Characterization:** Scanning electron microscopy (SEM, FEI Quanta 3D), transmission electron microscopy (TEM, FEI Tecnai) are employed to study the morphology and structure of as-grown VACNT, TiN–VACNT, and TiS₂ composite–VACNT. X-ray diffraction (Bruker, D8) is performed to study the crystallinity and X-ray photoelectron spectroscopy (CHI) is used to study the surface element components of samples. Cycled TiS₂–VACNT samples are washed by DI water and vacuum dried before XRD and XPS tests.

**Electrochemical Testing:** Ag/AgCl is used as the reference electrode to study VACNT, TiN–, TiS₂ composite–, RuO₂, and MoS₂–VACNT electrode systems for comparisons in different electrolytes. Linear sweep voltammetry, cyclic voltammetry, chronopotentiometry, and EIS impedance tests are performed by an electrochemistry workstation (Gamry Ref 600) with different modules.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

atomic layer deposition (ALD), high energy density storage, titanium sulfides, transition metal dichalcogenides (TMDC), vertically aligned carbon nanotubes (VACNTs)

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