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

We hereby submit our manuscript “Titanium Disulfide Coated Carbon Nanotube Hybrid Electrodes Enable High Energy Density Symmetric Pseudocapacitors” to Advanced Materials for your consideration. The merits of this work are addressed as below:

This work provides potential solution for the dilemma of high capacitance and high operating window of pseudo-capacitors, by employing nanocrystalline TiS2 composite coated vertical aligned carbon nanotube (VACNT) electrodes with ultra-high concentration Li-ion electrolyte. The operating voltage is popped to 3V which can compete with organic electrolyte, while merit of high capacitance in aqueous electrolyte is maintained. TiS2-VACNT hybrid provides most high energy density (60.9 Wh/kg) among pseudocapacitance materials, which is inspiring for the design of energy storage systems. The process to fabricate such electrodes by the atomic layer deposition (ALD)/sulfurization process is inspiring for transition material chalcogenide synthesis and deposition onto versatile substrate, which could further broaden their application in a wide range of set up. The interesting performance of TiS2 composite-Li interaction could also provide input for Li battery design and development. Thus, we believe this work could attract interest of broad range of researchers in energy storage materials, nanotechnology, electrochemistry and ALD synthesis, many of whom are readers of Advanced Materials.

Finally, the contents in this manuscript are original, have not been previously published, and are not under consideration by any other journals. All authors approved the manuscript and its submission to this journal.

Thank you for considering our manuscript for review. We appreciate your time and look forward to your favorable response.

Sincerely

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

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Keywords: Transition metal dichalcogenide (TMDC), Titanium sulfide, Atomic layer deposition (ALD), Vertically aligned carbon nanotubes (VACNT), High energy density storage.

Abstract: While electrochemical supercapacitors often show high power density and long operation lifetimes, they are plagued by limited energy density. Pseudo-capacitive materials, in contrast, operate by fast surface redox reactions and have been shown to enhance energy storage of supercapacitors. Furthermore, several reported systems exhibit high capacitance
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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 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 electro-less 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\textsuperscript{[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\textsuperscript{[12]. In contrast, here we developed a two-step process that combines ALD of TiN\textsuperscript{[14]} 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 co-axial coatings of chalcogenide (MoS$_2$, WS$_2$, and etc) onto high aspect ratio templates. Further characterizations demonstrate that the pseudocapacitive electrodes show a capacitance of 195 F/g within a potential range of 3 V in a lithium-rich aqueous electrolyte, corresponding to an energy density of 60.9 Wh/kg 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 which has only been applied in battery\textsuperscript{[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\textsuperscript{[17-24]} with comparable results to Li-ion batteries (Figure 1b). TiS$_2$-VACNT composites in ultra-high-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$_x$\textsuperscript{[13]}, TiN \textsuperscript{[14]}, and MoS$_2$\textsuperscript{[18]}, TiS$_2$-VACNTs show superior capacitance, energy density, and power density. Moreover, TiS$_2$ composite coated on CNT inherits the low phase transformation rate in lithiation and de-lithiation cycles \textsuperscript{[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\textsuperscript{[7]}.

The conductive, porous VACNT forest is grown on a silicon or stainless steel substrate \textsuperscript{[8]} and the diameter of an as-grown CNT is 13±5 nm (Figure S1). Afterwards, 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). Deposition rate varies from 0.06 nm/cycle to 0.25 nm/cycles depending on temperature and cycle numbers; the average growth rate for 500 cycles is ~0.11 nm/cycle and ~0.12 nm/cycle for 800 cycles (Figure S2) \textsuperscript{[25, 26]}. Under sulfur vapor annealing at 300 °C for 30 minutes, 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 (HRTEM) (Figure 2c) reveals that the resulting materials are hexagonal-shaped structures with characteristic polycrystalline diffraction rings, in-plane 0.3 nm lattice distance, and (001) zone axis of the CdI$_2$ type symmetry. X-ray Diffraction (XRD) shows standard peaks of TiS$_2$ 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 TiS$_2$ electrodes is also shown in Figure 2d for comparison. Split Ti$_{2p}$ peaks indicate composite Ti$^{4+}$ and Ti$^{3+}$ (residual TiN) with different spin-orbital splitting showing different energy difference.
Figure 2e. Figure 2f reveals $S_{2p}^{1/2}$ and $S_{2p}^{3/2}$ 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 1 and 3 times of repeated sulfur annealing while the relative distance and intensity of the peaks are almost the same (Figure S3), implying that additional sulfurization does not contribute to further material conversions from TiN to TiS$_2$ composite.

In Figure 3a, cyclic voltammetry (CV) results show that TiS$_2$ composite-VACNT in 21 m (mol/kg) LiTFSI electrolyte exhibits over ~100 times the specific capacitance (per projected surface area) of as-grown VACNT electrode in 0.5 M H$_2$SO$_4$ electrolyte. Two key mechanisms are believed to assist this significant increase: (1) intercalation of Li-S into and out of the TiS$_2$ composite and (2) the increase of working voltage window from 1 V to 3 V. It is found that the specific capacitance increases ~4 times from the VACNT-H$_2$SO$_4$ system to the VACNT-LiTFSI system, and 26.8 times from the VACNT-LiTFSI system to the TiS$_2$ 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 TiS$_2$ composite-VACNT electrode systems (Figure 3b and Figure S4). The system made of 4 µm-thick VACNT grown on stainless steel has about 15% higher specific capacitance (195 F/g) as compared with that of the system made of 40 µm-thick VACNT grown on silicon (168 F/g), as shown in Figure S4. Systems made of shorter VACNT electrodes could benefit from increased sulfur diffusion in the annealing process for the conversion of TiS$_2$ composite and smoother ion diffusion during the charge/discharge process. In the fitted capacity vs reverse of the square root of scan rate in Figure 3c, the larger constant of $v^{1/2}$ 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 TiS$_2$ 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), no lithiation peaks are observed at 10 mV/s with only a small peak at 2 mV/s. 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 ~216 F/cm$^3$ (Figure S4), such that chronopotentiometry current density of 1 mA/cm$^2$ is equivalent to 1.11 A/g (Figure S6a). 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 -1V~0.8V results in similar values and kinetics under different voltage scanning rates. Although the high capacitance is demonstrated with the 3V working window (Figure S6b,c), high voltage operations could induce aging for electrodes and electrolyte such that a slightly smaller working window such as 2.7V is recommended for longer lifetime. When a 1.5 mA/cm$^2$ current density source is used, it takes about 15 seconds 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 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).
The TiS₂ shows limited lattice expansion after cycling (Figure 2d). The (001) peak is
broadened and shifted, while the (110) and (101) peaks shifted from 30.4° to 29.4° and
33.1° to 31.9°, respectively, indicating lattice deformation of 3.1% and 4.5%,
respectively. Meanwhile XPS spectrum of cycled TiS₂ 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). 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).

Effects of different electrolytes, 0.5M H₂SO₄, 1 m LiTFSI in NMP(N-Methyl-2-
pyrrolidone), 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 DI water
(Table 1 and Figure S10) due to the lower ionic activity in organic solvent [27]. 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 in Figure S11). As a result, the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) depopulate to broaden the stable operation voltage window [16]. Specifically, high concentrations of LiTFSI extend the electrochemical window from 1.9 V (1 m) to 3 V (21 m), and high concentrations of LiCl extend the window from 1.4 V (1 m) to 2.35 V (20 m). Furthermore, the large TFSI anion forms higher Helmholtz layer potentials to increase the threshold of oxygen evolution swing to 1.7 V (Cl⁻ solution occurs at 1.05 V). On the other hand, electrolytes based on H₂SO₄ and NaCl (H⁺ or Na⁺ ions) do not exhibit intercalation with TiS₂ composite. In fact, H⁺ increases the probability of hydrogen evolution by lowering overpotential in the hydrogen evolution reaction (HER), decreasing the electrochemical voltage window. Furthermore, high LiTFSI concentration increases the conductivity of ions and lowers electrolytic impedance [28] (Figure 3f). These characteristics in high-concentration LiTFSI solution work to improve both energy density and power density of Li-ion-based storage systems.

The electrochemical voltage window is further determined by the coated active material (VACNT works as an inert electrode). Experimentally, stable ranges of -1.3 V to 1.7 V vs Ag/AgCl (1.9 V to 4.9 V vs Li/Li⁺) for the TiS₂-VACNT composite electrodes under the 21 m LiTFSI electrolyte are observed (Figure 4a), higher than the other three tested pseudocapacitive materials, RuOₓ, MoS₂, and TiN. Both RuOₓ-VACNT and MoS₂-VACNT electrode systems act as HER/OER catalysts and decrease the stable operation voltage window [29, 30]. 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 [31]. 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 TiS$_2$-VACNT composite system can result in the
largest enclosed area in the CV tests than those of tested RuO$_x$-, MoS$_2$-, and TiN-
VACNT systems with a scanning rate of 100 mV/s (Figure 4b), and has the highest
capacitance density under various scan rates (Figure 4c). In Figure 4c, specific
capacitance at 10 mV/s maintains 120F/g which corresponds to charging 12 C/g within
5 min. Such high charging rate is difficult to achieve in a battery system. Although
RuO$_x$ is considered one of the highest capacitance materials [32], it is incapable of
effective Li$^+$ intercalation in Li-rich electrolytes. MoS$_2$ has a higher density (5.06
g/cm$^3$) than that of TiS$_2$ composite (supplementary materials) which leads to
unfavorable gravimetric capacitance and energy density. In this work, MoS$_2$-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). TiN shows good electrical conductivity but its electrochemical
performance is not comparable with TiS$_2$ 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 TiS$_2$-VACNT hybrid
systems to the large working voltage window and intercalation-induced capacitance.
Although some oxide materials (such as RuO$_x$ and MnO$_x$) also provide high
capacitance, smaller operation voltage windows in conventional acidic and basic electrolytes limit their energy density (Table S2). Using conventional organic solvent may promotes cell voltage by eliminating hydrolysis but low ionic conductivity and diffusion coefficient degrade the performance\cite{33}. Since the aqueous electrolyte can be easily made in ambient conditions to eliminate possible safety issues, the TiS$_2$-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 rates from 2 to 100 mV/s (Figure 5a). The Nyquist plot shows the internal resistance to be about 1000 Ω, consistent with single cell impedance testing result of 400 Ω (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 semi-solid 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. This device is able to power a 2.2 V LED for 1 min (Figure 5c). In the future, larger 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\cite{34,35}.

Three factors allow for exceptionally high energy density (reaching a maximum of 60.9 Wh/kg 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 ultra-high concentration, 21 m LiTFSI electrolyte; (b) effective intercalation of Li$^+$ into TiS$_2$-VACNT composite for high gravimetric capacitance of 195 F/g; and (c) nano-crystallinity of TiS$_2$ composite and ultra-high surface area of VACNT framework.
promotes surface reactions instead of bulk behavior for a maximum power density of 1250 W/kg (~1.13mW/cm³) and cycleability of more than 10,000 charge/discharge cycles with >95% capacitance retention. TiS₂-VACNT composite electrodes are compared with prepared RuOₓ-, MoS₂-, 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 [8]. Alternatively, the VACNT electrodes are synthesized on a stainless-steel substrate with a passivation layer of atomic layer deposited (ALD) Al₂O₃ (Cambridge
Fiji F200 Plasma ALD). The same ALD tool is used to coat TiN onto the VACNT framework, with TDMAT (0.05 s) and N₂ plasma (5 s, 300W) as precursors and 5 s argon purge at 300°C. The TiN-VACNT forest is annealed in sulfur vapor at 150 °C, 250 °C, 300 °C, or 350 °C in a furnace (Lindbergh Thermal) for 30 minutes.

**Synthesis of RuOₓ-VACNT electrodes**

RuOₓ 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 1s and 10s, respectively, with 5s argon gas purge. During the ALD process, substrates were heated to temperatures ranging from 270 °C 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 °C, 650 °C 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 (XRD, 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-, RuOₓ 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.
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Reference


Titanium Disulfide (TiS$_2$) is coated coaxially onto Vertical Aligned Carbon nanotube forests via an ALD-sulfurization process. TiS$_2$-VACNTs provide exceptional high specific capacitance of ~195 F/g and working voltage window up to 3V in a Li$^+$ ion rich (21m) electrolyte. Energy density of supercapacitor based on TiS$_2$-VACNT electrodes is promoted to 60.9 Wh/kg, which outperforms most of the pseudocapacitance materials.

**Keyword:** Transition metal dichalcogenide (TMDC), Titanium sulfide, Atomic layer deposition (ALD), Vertically aligned carbon nanotubes (VACNT), High energy density storage.


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

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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 non-carbon materials, including metal oxides, metal chalcogenides, and metal carbide-based system [17-24]. (c) Long term cyclability of the TiS$_2$-VACNT composite electrode in the 21 m LiTFSI electrolyte.
Figure 2. Material characterization of the TiS$_2$-VACNT composite electrodes. (a) SEM image after a 500-cycle ALD TiN deposition process followed up with a sulfurization step; (Inset) magnified SEM image showing individual electrodes with diameter of 210±13nm. (b) TEM image of CNT coated with sulfurized TiS$_2$ composite particles. (c) Zoomed in TEM image of hexagonal TiS$_2$ composite nanoparticles in (b). (d) XRD showing the (001) peak at 16.6°, (110) at 30.4°, and (101) at 33.1°. The (001) peak is broadened while the other two peaks shift to slightly smaller angles after intercalation in LiTFSI. (e) X-ray photoelectron spectroscopy (XPS) spectrum for TiS$_2$ composite-VACNT, in which split Ti$_2$p$^{1/2}$ and Ti$_2$p$^{3/2}$ peaks indicate different composition of TiS$_2$ and TiN. (f) XPS spectrum of sulfur peak of TiS$_2$ composite, with S$_2$p$^{1/2}$ and S$_2$p$^{3/2}$ split peaks.
Figure 3. Electrochemical testing results of TiS$_2$-VACNT composite electrodes in the 21 m LiTFSI electrolyte. (a) cyclic voltammetry (CV) results from three systems: as-grown VACNT electrodes in 0.5 M $\text{H}_2\text{SO}_4$ 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. (c) Analysis on the energy storage capacity vs $V^{1/2}$. (d) Repeating chronopotentiometry charge-discharge tests of TiS$_2$ composite/CNT in 21 m LiTFSI with discharging current density of 300μA/cm$^2$. (e) and (f) CV and Nyquist plots of TiS$_2$-VACNT composite electrodes in multiple electrolytes.

Table 1 TiS$_2$ composite-VACNT electrodes in different electrolytes. (NMP: N-Methyl-2-pyrrolidone)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Min potential (V)</th>
<th>Max potential (V)</th>
<th>Potential window (V)</th>
<th>Capacitance F/g (10mV/s)</th>
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<tr>
<td>0.5 M $\text{H}_2\text{SO}_4$</td>
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<td>1.2</td>
<td>10.4</td>
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<tr>
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<tr>
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<td>1</td>
<td>1.5</td>
<td>30</td>
</tr>
<tr>
<td>20m LiCl</td>
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<td>1.05</td>
<td>2.35</td>
<td>80</td>
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<tr>
<td>1 m LiTFSI</td>
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<td>1.9</td>
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<tr>
<td>10m LiTFSI</td>
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<td>1.2</td>
<td>2.3</td>
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<tr>
<td>1 m LiTFSI in NMP</td>
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<td>0.9</td>
<td>2.4</td>
<td>31.25</td>
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</table>
Figure 4. TiS$_2$-VACNT composite electrodes outperform other VACNT-based electrodes coated with high-energy pseudocapacitive materials such as RuO$_x$, TiN, and MoS$_2$. (a) Linear sweep voltammetry (LSV) results of as-grown VACNT, TiS$_2$ composite-, RuO$_x$-, TiN-, and MoS$_2$-VACNT electrodes in 21 m LiTFSI electrolyte under a scan rate of 5 mV/s. Both TiS$_2$ composite-VACNT and pristine VACNT electrodes exhibit a 3V stable operation window, while other electrodes have either broad redox peaks or hydrolysis reactions at a low voltage to reduce the electrochemical operation window. (b) CV results of four different electrodes in 21 m LiTFSI electrolyte under a scan rate of 100 mV/s. (c) Capacitance density vs. scan rate of the four electrode systems. (d) Operation voltage window vs. energy density for the four electrode systems. (e) Measured energy density vs. power energy density of the four electrode systems. (f) Measurement results and comparison of the energy density, power density, and capacitance of the four VACNT electrodes coated with different materials.
Figure 5. Demonstration for potential practical applications. (a) CV of a symmetric full cell made of a two-electrode design with a filter paper as the separator in between with the 21m LiTFST electrolyte. (b) Impedance measurement results. (c) A flexible fully cell energy storage system is built by transferring two TiS$_2$-VACNT film structures onto a Kapton tap with a filter paper in between as the separator with the LiTFSI/PVA/H$_2$O electrolyte to power up a 2.2V LED for 60 seconds.
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