

High Performance Pseudocapacitor Based on 2D Layered Metal Chalcogenide Nanocrystals

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Supporting Information

ABSTRACT: Single-layer and few-layer transition metal dichalcogenides have been extensively studied for their electronic properties, but their energy-storage potential has not been well explored. This paper describes the structural and electrochemical properties of few-layer TiS₂ nanocrystals. The two-dimensional morphology leads to very different behavior, compared to corresponding bulk materials. Only small structural changes occur during lithiation/delithiation and charge storage characteristics are consistent with intercalation pseudocapacitance, leading to materials that exhibit both high energy and power density.



KEYWORDS: TiS₂, chalcogenides, in-situ synchrotron diffraction, pseudocapacitors, intercalation kinetics, electrochemical energy storage

T he extraordinary properties of graphene have ignited renewed interest in other two-dimentional (2D) layered materials including transition metal oxides (TMOs) and transition metal dichalcogenides (TMDs).¹⁻³ The latter have received considerable interest in monolayer and few-layer forms as TMDs exhibit a wide range of interesting mechanical,^{4,5} catalytic,^{6,7} optical,^{8–10} and electronic properties.^{11,12} In particular, a great deal of activity has been directed toward electronic and optoelectronic devices because the TMD family of materials can possess metallic, semimetallic, semiconducting, and charge density wave behavior¹³ depending upon the chemistry and polytype of the compound.

The present paper reports on the energy storage properties of few-layer TiS_2 (2D-TiS₂). The energy storage properties of TMDs as bulk materials were well investigated during the 1970s. In fact, the first lithium-ion batteries brought to the pilot-plant stage used TiS₂ as the positive electrode.¹⁴ One reason for using TiS_2 as an energy storage electrode is that it is the lightest of all the layered dichalcogenides.^{15–17} The energy storage mechanism for TiS₂ is based on Li⁺ intercalation, which is controlled by both electron transfer and lithium ion diffusion into the host structure. A benefit of TiS2 is that it is a semimetal,¹⁸ so no conductive additive was needed in the electrode structure, permitting a higher energy density. Another advantage is that TiS₂ has the same crystallographic symmetry over the entire composition range of $\text{Li}_x \text{TiS}_2$ for $0 \le x \le 1$.¹⁹ The lack of a discontinuous phase change enables all the lithium to be removed reversibly without need for two-phase coexistence and the nucleation of new phases, a process that often leads to sluggish reaction kinetics.

Another type of energy storage mechanism that emerged during the 1970s was pseudocapacitance. In this case, reversible faradaic reactions lead to capacitor-like behavior.²⁰ These charge transfer reactions generally occur from ion adsorption or ion insertion at the surface or near-surface of the active material and lead to high levels of charge storage. The interest for such materials is the prospect of achieving high specific capacitance values (>1000 F g⁻¹) associated with fast redox reactions, while preserving the good power capability and cycle life of traditional electrochemical capacitors.²¹ Designing new pseudocapacitive materials is therefore a promising direction for energy storage research, as the prospect exists to achieve high energy density at discharge rates typical of capacitors (<1 min).

In the 1990s, Conway suggested that TiS_2 exhibited pseudocapacitive characteristics, but it was not clear whether the intercalation kinetics really differed significantly from bulk TiS_2 .^{20,22} One route to obtaining pseudocapacitive behavior is to decrease the particle size.²³ Thus, if TiS_2 materials can be scaled down to their most basic structural component of either a single layer or a few layers, it might be possible to circumvent the semi-infinite diffusion characteristics of the bulk material and achieve capacitive-controlled kinetics, leading to capacitor-like behavior. Nanostructuring TiS_2 has been shown previously to enhance electrode performance,¹⁶ but detailed work on the dimensionality has not been studied.

Investigations of energy storage in monolayer and few-layer TMDs are at their inception. $^{\rm 24}~\rm MoS_2$ has received the most

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Figure 1. (a) Schematic of anisotropic growth; (b) TEM images of TiS_2 nanocrystals with diameters Φ of 50 ± 8 , 100 ± 18 (with electron diffraction pattern), and 270 ± 55 nm (histogram in Supporting Information Figure S3); (c,d) side view of TiS_2 nanocrystals (50 nm).



Figure 2. (a) Illustration of the crystal structure of TiS_2 . (b) In situ variation of the *a*-axis and *c*-axis lattice parameter of lithium titanium sulfides as a function of the potential during the first intercalation for B-TiS₂ (open circles) and 2D-TiS₂ (solid squares).

attention, as methods exist to prepare these materials by CVD or exfoliation.^{25–29} Other TMDs³⁰ reported recently include $WS_{2\nu}^{31} TaS_{2\nu}^{32} ZrS_{2\nu}^{33}$ and $VS_{2\cdot}^{34,35}$ A popular means of investigating these TMDs has been to prepare hybrid materials, in which the TMD is mixed with graphene or reduced graphene oxide to improve electron transfer properties. For the most part, these studies are directed at investigating TMDs as negative electrodes for Li-ion batteries. Only a limited number of studies have considered the supercapacitor properties of few-layer TMDs.^{24,34} While device performance was well-characterized, there was little information regarding the influence of the 2D morphology on charge storage kinetics or capacity.

In the work presented here, we characterize the structural and electrochemical properties of few-layer $2D-TiS_2$ nanocrystals ($2D-TiS_2$) and determine how their kinetics and charge storage mechanism compare to micron-sized TiS_2 particles ("Bulk", B-TiS_2). The 2D morphology dominates the charge storage properties as it leads to a highly reversible, high rate, capacitive mechanism that is very different from that of bulk TiS_2 . The use of in situ synchrotron XRD enables us to connect

the novel electrochemical behavior in 2D-TiS₂ to the structural changes occurring during electrochemical lithiation.

2D-TiS₂ nanocrystals were synthesized through a hot injection route which has been reported previously.³⁶ A benefit of this approach is that it can be used to control the size of TiS_2 nanocrystals. Details of the preparation of TiS₂ are described in Supporting Information. Briefly, 2D-TiS₂ is prepared by injection of CS₂ in a solution of TiCl₄ and oleylamine at 300 °C under N₂ flow for 15 min of reaction time. TEM analysis reveals that 2D-TiS₂ nanocrystal size can be adjusted by modifying the reaction conditions, producing TiS₂ nanocrystals with average diameters Φ of approximately 50, 100, and 270 nm and thicknesses of 2-3, 4-5, and 7-10 layers, respectively (Figure 1, Supporting Information Figure S10). The 2D-TiS₂ nanocrystals are composed of (001) layers with an interplanar spacing of ~5.7 Å (Figure 1). Each layer of TiS_2 is comprised of S-Ti-S triatomic layers corresponding to the 1T phase of TiS₂ (Figure 2). The hexagonal TiS_2 phase is observed for both small 2D-TiS₂ nanocrystals as well as the corresponding bulk material (Supporting Information Figure S4). In agreement with TEM analysis, X-ray diffraction also indicates preferred crystal growth in the (hk0) directions, as observed from the fact that the (110) diffraction peak shows both significantly greater intensity and narrower width than the (101) or (001) diffraction peaks. The electron diffraction patterns (Supporting Information Figure S4), also confirm these results. Crystallite sizes are related to the integral breadth β through the Scherrer equation ($\tau = (\kappa \lambda / \beta \cos \theta)$). Here τ is the Scherrer size, which is related to the actual crystallite size in a given direction by a shape parameter that is usually of order unity. These τ values are listed in Supporting Information Table S1. The ratio τ_{110}/τ_{101} indicate that the crystallites become thinner when their size decreases. Since the XRD size values (τ_{110}) are smaller than the size of the nanocrystals (ϕ_{TEM}), this implies that the 2D-TiS₂ nanocrystals are either polycrystalline or contain defects that limit the periodic domain size.

The growth mechanism for 2D-TiS₂ nanocrystals was also investigated. One of the reasons for the anisotropic growth is the large difference in surface energies between the various facets of 1T structure; the (100) and (010) surfaces exhibit higher surface energy than the (001) surfaces³⁶ (Figure 1a). One reason for the stability of the (001) surface is that the bonding between layers is relatively weak and is controlled by van der Waals forces, not covalent bonding. The difference in surface energy for the various crystalline planes is further increased by the preference for the oleylamine ligand to stabilize the (001) facet of TiS_2 , which is rich in sulfur.^{37,38} As the reaction time increases, agglomeration and coalescence of TiS₂ sheets occurs and results in both larger and thicker hexagonal 2D-nanocrystal (Supporting Information Figure S2). We expect epitaxial attachment to have a significant influence on the growth of 2D-TiS₂ polycrystalline nanocrystals.³⁹ The presence of oleylamine further controls the two-dimensional nature of the epitaxial growth.

The structural changes occurring during Li⁺ intercalation within B-TiS₂ and 2D-TiS₂ materials were followed by in situ synchrotron XRD (Figure 2). Li-ions are preferentially inserted and stored in the (001) plane; therefore, following changes in the c-axis lattice parameter during electrochemical lithiation provides important insight into the nature of charge storage processes in 2D-TiS₂.^{16,40} In a previous XRD investigation, Whittingham showed that micrometer-sized TiS₂ particles maintain the same crystallographic symmetry during Li⁺ insertion with *n*-butyl lithium, although Li⁺ insertion is associated with a ~ 0.5 Å change in the *c*-axis lattice parameter from 5.7 to 6.2 Å.¹⁹ Figure 2a shows the crystal structure of TiS₂ while Figure 2b compares the lattice parameters at different voltages for B-TiS₂ with those from 2D-TiS₂ nanocrystals. The diffraction patterns (Supporting Information Figures S5 and S6) show the (110) and (101) reflections that were used to calculate the *a*-axis and *c*-axis lattice parameters for B-TiS₂ and 2D-TiS₂ shown in Figure 2b. In situ synchrotron XRD during electrochemical insertion of Li-ions into B-TiS₂ produced results that are consistent with other reported in situ studies on bulk materials, providing confidence in our methods. Before Li-ion insertion, the *c*-axis lattice parameter for B-TiS₂ is calculated to be 5.66(6) Å and the *a*-axis lattice parameter is calculated to be 3.41(5) Å. These measured lattice parameters are consistent with previously reported experimental values for the c-axis (5.69 Å) and the a-axis (3.41 Å) of TiS_2 .^{16,40,41} During lithiation of both B-TiS₂ and 2D-TiS₂, the (110) and (101) peaks shift toward lower values of Q (where $Q = 2\pi/d$), indicating an increase in the interplanar distance, d (Supporting Information Figures S5 and S6). This observed increase in the a-lattice parameter is consistent with the presence of larger Ti³⁺

cations (ionic radius, 0.810 Å) in Li_xTiS₂ as compared to the smaller Ti⁴⁺ cations (ionic radius, 0.745 Å) in TiS₂. Furthermore, Li⁺ intercalation in the van der Waals planes of the TiS₂ structure forces the layers to expand to accommodate the guest ion in the host material, resulting in an increase in the c-lattice parameter. Lithium intercalation into B-TiS₂ leads to a *c*-axis lattice expansion to 6.17 Å and an *a*-axis lattice expansion to 3.43 Å, which are consistent with previous in situ X-ray diffraction⁴² and in situ neutron studies⁴³ on bulk TiS₂.

Markedly different structural characteristics emerge for 2D-TiS₂ compared to B-TiS₂ during Li-ion charge storage. The unit cell volume of 2D-TiS₂ is larger than B-TiS₂ in the pristine state. The *c*-axis lattice parameter is calculated to be 5.80(5) Å while the *a*-axis lattice parameter is calculated to be 3.43(1) Å. The larger lattice parameter in the as-synthesized state could be due to a combination of excess Ti cations in the van der Waals gaps¹⁶ and/or disorder induced increases in the lattice constant. This nanosize effect was shown for LiCoO₂ nanoparticles⁴⁴ as well as for mesoporous thin films after heat treatment.⁴⁵ Upon lithiation, 2D-TiS₂ undergoes a much smaller c-axis lattice expansion (to just 5.93 Å) as compared to B-TiS₂. The lattice volume change is only 2% upon lithiation in 2D-TiS₂ compared to a 10% lattice volume expansion in B-TiS₂. This is direct structural evidence that the large volume change that occurs in B-TiS₂ is reduced in this nanoscale material during lithiation. Moreover, these measurements show that reversible Li⁺ intercalation/extraction after the first cycle occurs without significant crystallographic change in 2D-TiS₂ (Supporting Information Figure S7).

Electrochemical kinetics of Li^+ insertion into TiS_2 materials was investigated using a 3-electrode flooded cell with lithium foils as both the reference and counter electrodes, and 1 M LiClO_4 in EC/DMC as the electrolyte (see electrochemical characterization in the Supporting Information for more details). The electrochemical lithium insertion process is described by the following equation:

$$\operatorname{TiS}_{2} + x\operatorname{Li}^{+} + xe^{-} \leftrightarrow \operatorname{Li}_{x}\operatorname{TiS}_{2} \tag{1}$$

The maximum theoretical storage in TiS₂ is obtained at x = 1 (226 mAh g⁻¹), obtained using, x = QM/mF. In this equation, Q is the stored charge, M the molecular weight, m the mass, and F is Faraday constant. The cyclic voltammograms (CVs) at 1 mV s⁻¹ for different size 2D-TiS₂ nanocrystals are compared to B-TiS₂ particles in Figure 3. First, we observe that 2D-TiS₂ nanocrystals exhibit much higher levels of charge storage compared to the B-TiS₂ material. The CVs show prominent redox peaks around 2.3 V (vs Li/Li+) for both the 50 and 100 nm samples.

To provide more insight about the charge storage mechanism in these 2D-TiS₂ nanocrystals, we investigated the kinetics of the TiS₂ materials (Figure 4) using analytical approaches that provide quantitative information about differences between diffusion controlled and capacitive charge storage processes. In Figure 4a, the capacity of the TiS₂ materials is plotted versus the square root of the inverse sweep rate (i.e., $\nu^{-1/2}$) from 1 to 100 mV s⁻¹. In this plot, the linear regions are those that are limited by semi-infinite diffusion, as described in eq 2

$$Q_{\rm tot} = Q_{\infty} + \alpha(\nu^{-1/2}) \tag{2}$$

where Q_{tot} is the total amount of charge storage, Q_{∞} refers to charge stored on accessible surfaces (i.e., capacitive controlled



Figure 3. CVs (10 cycles) at 1 mV s⁻¹ in a Li⁺ electrolyte for 2D-TiS₂ nanocrystals, comparing 50 nm (red) and 100 nm (green) diameters to B-TiS₂ particles (black).

processes) and $\alpha(\nu^{-1/2})$ describes the less accessible sites (diffusion limited), where α is a constant and ν is the sweep rate. The extrapolated infinite sweep-rate capacitances are estimated from the *y*-intercept (when $\nu^{-1/2} \rightarrow 0$) and the results are given in Supporting Information Table S2. For the B-TiS₂ materials, the kinetics are characterized by diffusioncontrolled behavior as shown by the linear dependence of capacity on $\nu^{-1/2}$. For 2D-TiS₂, two regions are evident. At sweep rates below 20 mV s⁻¹, charge storage is relatively independent of $\nu^{-1/2}$ indicating that the kinetics are not controlled by semi-infinite diffusion. At sweep rates greater than 20 mV \cdot s⁻¹, the capacity changes in a linear manner corresponding to diffusion-controlled behavior. From this analysis, we are able to determine the relative amount of charge storage that occurs from capacitive processes (both double layer and pseudocapacitance) and those involving the slower diffusion-controlled kinetics. At 10 mV s^{-1} , the capacitive contribution is estimated to be $\sim 6\%$ for the bulk material, 91% for 100 nm, and 84% for the 50 nm diameter material. The capacity of 167 mA h g^{-1} observed at 1 mV s^{-1} for 2D-TiS₂ 50 nm nanocrystals corresponds to storage of 0.74 Li^+/TiS_2 . Moreover, the data at 10 mV s⁻¹ indicates that over 50% of the theoretical capacity (226 mA h g^{-1}) is stored within 150 s. To the best of our knowledge, the kinetic response for 2D-TiS₂ is the fastest charging rate reported for a transition metal chalcogenide. Finally, it should be noted that when the

surface area of the material is estimated using the nanosheet size, the capacitance is much higher than 100 μ F cm⁻² (see in Supporting Information Table S4), which is an indication that nearly all the capacitance arises from pseudocapacitive processes and not from the electrical double layer.^{20,46}

A related analysis can be performed regarding the behavior of the peak current by assuming the current, i, obeys a power-law relationship with the sweep rate

$$i = a\nu^b \tag{3}$$

Here a is a constant and ν is the sweep rate. The b-value can change from 0.5 (semi-infinite diffusion) to 1 (capacitive processes). The slope of log(i) versus $log(\nu)$ gives the *b*-value, as shown for 100 nm 2D-TiS₂ in Supporting Information Figure S11. In that figure, the redox peaks shift with increasing sweep rate because of the diffusion-controlled nature of the redox processes as discussed above. The b-value analysis was performed using the CV data between 1.8 and 2.5 V (vs Li/Li +). In Figure 4b, the *b*-values for the 50 and 100 nm $2D-TiS_2$ nanocrystals are compared with bulk TiS₂. As expected, the *b*value for the bulk is close to 0.5 for all potentials. The 2D nanocrystals are characterized by two different regions. At 2.3 V (vs Li/Li+) the value extends toward b = 0.5, while at lower potentials, the values are much closer to b = 1.0 (b = 0.95 for 100 nm and $b \sim 0.83$ for 50 nm). The charge storage behavior for 2D-TiS₂ nanocrystals is vastly different from that of B-TiS₂. The latter exhibits a diffusion-controlled mechanism (b = 0.5) while the TiS₂ nanocrystals exhibit capacitive-controlled behavior, except in the potential range where redox processes are apparent. The smaller b-values for 50 nm 2D-TiS₂ nanocrystals in comparison to 100 nm may be associated with a more disordered structure (Supporting Information Figure S4) and also the presence of excess sulfur.

Using another analysis, it is possible to determine the potential regions where the capacitive contributions occur in the CV plots (Figure 5). In this method, the current at a particular voltage is considered to contain contributions from capacitive (k_1) and diffusion (k_2) controlled processes

$$i = k_1 \nu + k_2 \nu^{1/2} \tag{4}$$

For 2D-100 nm sample, the amount of charge stored due to both diffusion and surface limited processes at 1 mV s^{-1} is presented in Figure 5. In this analysis, it is generally most insightful to determine the different contributions at 1 mV s^{-1} ,



Figure 4. Kinetic analysis of 2D-TiS₂ and B-TiS₂ cycled in a Li⁺ electrolyte at various sweep rates from 1–100 mV·s⁻¹. (a) Capacity versu $\nu^{-1/2}$, (b) determination of the anodic *b*-values as indicated in eq 4. A complete example of the analysis is shown in Supporting Information Figure S11 for the 100 nm 2D-TiS₂. The capacitive fraction for many samples and sweep rates is give in Supporting Information Table S2.



Figure 5. Capacitive and diffusion-controlled contributions to charge storage in 100 nm 2D-TiS₂ cycled in a Li⁺ electrolyte at 1 mV s⁻¹. Capacitive contributions are in black.

as this enables one to maximize the diffusive contribution to charge storage. The best capacitive materials have minimal diffusion contributions, even at slow sweep rates⁴⁷ and that is what we observe here. Around 85% of the total current (and therefore, the capacity) is capacitive at 1 mV s⁻¹. The diffusion-controlled currents are located predominantly in the peak regions of the CV, as redox peaks are expected to be diffusion limited. The remaining regions are almost entirely capacitive.

Finally, composite electrodes comprised of 2D-TiS₂ nanocrystals were fabricated with the objective of determining how these materials perform in a rechargeable Li-ion device. TiS₂/ electrolyte/lithium Swagelok-type cells were fabricated and characterized (see Supporting Information for details). Here the cathode is a free-standing 2D-TiS₂ membrane obtained by filtration of a 2D-TiS₂ solution. One centimeter diameter (1.6 mg) samples were formed as shown in Supporting Information Figure S12. Galvanostatic cycling was used to study the amount of lithium inserted during repetitive charge-discharge cycles at specific currents between 0.5 and 10 A g^{-1} (Figure 6). The charge-discharge curves do not exhibit any plateaus, which are generally associated with discontinuous or first order phase transitions of the host material upon Li⁺ insertion. The effect of discharge and charge rates on capacity is shown in Figure 6b. The TiS₂ exhibited excellent stability for the 10 cycles at each of the different rates, although there is a significant decrease in capacity at the higher rates. At a rate of 2.2C (0.5 A/g), 0.66 mol of lithium is reversibly inserted and deinserted. Increasing the current density to 44C (10 A/g) decreases the capacity to 70 mAh/g, corresponding to 0.31 mol of lithium insertion.

The results obtained in Swagelok cells for the 2D-TiS₂ materials are promising for pseudocapacitor-based energy storage devices. Indeed, this work shows that the high-rate pseudocapacitive properties demonstrated with 2D nanocrystal-line TiS₂ can be extended to practical TiS₂ membrane electrodes. The 2D-TiS₂ membranes exhibit reasonably high specific capacitance levels of 320 F g⁻¹ with a 30 s charge–discharge time.

A key feature in our studies on 2D-TiS₂ is that only small structural changes occur during cycling. The lattice volume in 2-D TiS₂ undergoes only a 2% change, while B-TiS₂ shows a 10% change, as calculated from in situ XRD. This indicates the presence of facile ion migration pathways in 2D-TiS₂ that can promote rapid charge storage with little need for slow atom rearrangements. The small 2% lattice expansion in 2D-TiS₂ also enables the material to function well as a binder-less membrane electrode because volume changes do not disrupt the integrity of the porous electrode geometry. Indeed, after the first deinsertion, the c-axis parameter decreases by $\sim 1\%$ from the starting value and shows little change upon Li⁺ insertion, and for the second cycle there is an additional small contraction. Small dimensional changes are consistent with the capacitive storage mechanism occurring in 2D-TiS₂. The kinetic analysis (Figure 5) shows that a large fraction of the stored charge comes from a capacitive process. This behavior is likely the result of the 2D morphology in that the electrolyte can readily access the entire surface. Thus, it is not surprising that the rate controlling step (Figure 4) is surface limited and not solid-state diffusion. Another important consideration in our study is that charge storage associated with Li⁺ insertion does not induce a phase change. We believe that by designing materials that undergo very small changes during lithiation/delithiation, there is an opportunity to realize electrode materials that exhibit both high energy and power density.

The results presented here illustrate that a 2D morphology leads to electrochemical and structural properties that are not exhibited by the corresponding bulk material. TiS₂ displays



Figure 6. (a) Charge-discharge curves for a membrane made from 50 nm 2D-TiS₂ (1.6 mg/cm²) cycled in a Swagelok cell. Cells were cycled at $0.5-10 \text{ A} \cdot \text{g}^{-1}$ between 1.5 and 3 V. (b) Rate capability at various charge and discharge rates for 2D-TiS₂ and B-TiS₂ film.

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highly reversible and high-rate charge storage characteristics that are consistent with intercalation pseudocapacitance:²¹ currents that are linearly dependent on sweep rate, redox peaks whose potentials do not shift significantly with sweep rate, and a structure that does not experience a phase transition upon intercalation. Because of the specific 2D nanocrystal morphology, the rate limiting step for lithium ion storage is a quasi-2D process, similar to that of 2D surface adsorption reactions.²⁰ Experiments with composite materials show that thicker samples maintain their high power density. To date, the electrochemical properties of only a small number of few-layer dichalcogenide nanocrystals have been reported. However, as our 2D-TiS₂ results show, the opportunity for advances in energy storage using these types of materials represents an exciting direction for the future.

ASSOCIATED CONTENT

S Supporting Information

Details of the synthesis, characterization, and electrochemical measurements for TiS_2 . This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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