Two-dimensional (2D) layered nanostructures have received increasing interest due to their unique nanoscale phenomena and their potential applications ranging from electronics and energy to catalysis.[1] Recent investigation has revealed that laterally confined layered nanocrystals (LCLN) have remarkably enhanced electrochemical properties compared to their bulk counterparts owing to nanoscale characteristics that include large surface areas, finite lateral sizes, and enhanced open-edge morphologies.[2] Among the variety of layered materials that have been described, tin sulfides are of particular interest because of their unique structural properties.[3] SnS$_2$ has a layered CdI$_2$-type structure, composed of tin atoms sandwiched between two layers of hexagonally disposed close-packed sulfur atoms. The 2D layered characteristics of this substance are revealed in alkali metal intercalation phenomena,[4] and by investigating anisotropy of properties such as electric and photoelectric conductivity.[5]

Owing to their large theoretical capacities for battery applications, bulk or micron sized tin-based materials have been extensively studied as possible alternatives for commercially available carbon electrodes.[6] However, the main drawback of this system has been stemming from the large volume changes and accompanying sharp decrease in capacity that occur during electrochemical cycles.[7] Aifantis et al. have reported that active sites with spherical and smaller volume fraction could improve electrochemical properties of anode materials from the viewpoint of fracture mechanics.[8] Other researchers also have reported that nanoscale tin sulfide-based materials would lead to an improvement in the cycling stability.[9,10] Though various morphologies of SnS$_2$ materials including fullerene-like nanoparticles,[11,12] nanoflakes,[12,13] and nanobelts[12,14] have been fabricated using variety of synthetic methods, thus far the preparation of high quality 2D layered SnS$_2$ nanoparticles has remained a significant challenge.

In this communication, we report the results of investigations that have led to the development of a facile synthesis of laterally confined (<150 nm) 2D layered SnS$_2$ nanoparticles. Owing to its unique morphology, consisting of a finite lateral sized and well-defined layered structure, this material has significantly enhanced host capabilities as an active Li ion battery electrode. Below, we discuss the morphological and electrochemical properties of this substance and their utilization as an electrode material.

Laterally confined 2D SnS$_2$ nanoparticles were synthesized by using thermal decomposition of the precursor, Sn(S$_2$CNEt$_2$)$_2$,[13] in an organic solvent at elevated temperature. Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) images clearly showed that the SnS$_2$ nanocrystals obtained by this procedure are 2D hexagonal nanoplates with a lateral size of ca. 150 nm and size distribution ($\sigma \approx 30\%$) (Fig. 1a and b). The X-ray diffraction pattern (XRD) supports the assignment of a 2T-type layered structure (JCPDS card #: 23-677) to the SnS$_2$ nanoplates (Fig. 1c). The thickness of SnS$_2$ nanoplates was estimated as ca. 15 nm according to the (001) peak by the Scherrer equation.

Tilting analysis of the TEM holder stage by 90° along the [001] direction shows a side view of the nanoplate and reveals a thickness of 16 ± 5 nm (Fig. 2a and b) which is complying with the estimated thickness by XRD peaks. The patterns from selected area electron diffraction (SAED) analyses confirm that the SnS$_2$ nanoparticles are single crystals having a 2D layered structure with hexagonal symmetry (Fig. 2a and b, inset). A more revealing feature of the crystallographic structures of the 2D SnS$_2$ nanoplates comes from a high resolution TEM (HRTEM) analysis (Fig. 2c and d). Specifically, the SnS$_2$ nanoplate lying flat on substrate with the zone axis of [001] has lattice fringes with interplanar distances of 3.2 and 1.8 Å. These distances are consistent with the respective (100) and (−1−10) planes of the hexagonal 2T-SnS$_2$ (Fig. 2c). The fast Fourier transformation (FFT) image of the SnS$_2$ nanoplates shows the characteristic spots for a hexagonal structure with the inner six spots and outer six spots indicating reflections of the [100] and [110] planes, respectively (Fig. 2c, inset). The side view has a
lattice fringe with an interplanar distance of 5.9 Å corresponding to (001) planes and shows the nanoplates are composed of ca. 30 layers (Fig. 2d). The FFT image (Fig. 2d, inset) also shows strong reflections associated with {001} planes. This demonstrates that the layers of SnS₂ are stacked along the [001] direction enforced by van der Waals interactions. Based on the analyses, the combined results from viewing different crystallographic orientations show that the SnS₂ nanoplates are single crystalline and have a 2D layered structure with hexagonal symmetry.

Compared to bulk materials with large (>µm) 2D planar structures, highly crystalline, laterally confined 2D SnS₂ nanoplates possess superior physicochemical properties which arise from the greater accessibility of Li ions and the enlarged surface area. These properties make diffusion of Li ions and electron transfer within the host matrix more facile (Fig. 3a).[14]

A nanomaterial-based working electrode was fabricated by mixing SnS₂ nanoplates with Super P carbon black and polyvinylidene fluoride binder. Cycling tests were carried out on the resulting electrode by using coin-type half cells (2016 type) with a Li counter electrode. First cycle-life performance of SnS₂ electrode showed that a large irreversible discharge capacity (1311 mAhg⁻¹) (Fig. 3b) existed, which is highly likely a result of the formation of metallic Sn and subsequent generation of Li-Sn alloy (Eqs. 1 and 2).[14]

SnS₂ + 4Li → Sn + 2Li₂S (1)
Sn + 4.4Li+ ↔ Li₄.₄Sn (2)

The discharge capacity of the first cycle was found to be close to the sum of theoretical irreversible capacity (587 mAhg⁻¹) and maximum theoretical reversible capacity (645 mAhg⁻¹).[10] Analysis of the voltage profile of the SnS₂ electrode shows that a plateau and shoulder exist at ca. 1.21 V and at ca. 0.35 V, respectively, that are likely responsible for the irreversible and reversible processes (Fig. 3c). The decomposition of SnS₂ into metallic Sn and Li₂S, and the subsequent Li-Sn alloy proceeded at this voltage region. The discharge capacity of the second cycle was measured to 645 mAhg⁻¹, which is close to the maximum theoretical capacity. After the second cycle, the cycle-life performance was observed to be fairly stable and reversible up to 30th cycles. The average discharge capacity was determined to be 583 mAhg⁻¹, which is 90% of the maximum theoretical reversible value, and 1.6 times higher

Figure 1. a) TEM image and b) FESEM image of SnS₂ nanoplates. c) XRD patterns. These patterns are matched with the reference (vertical line, JCPDS card #: 23–677).
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than that of a commercialized carbon electrode (372 mAh g\(^{-1}\)).\(^{[15]}\)

The observed cycle-life performance demonstrates that the discharge capacity of SnS\(_2\) nanocrystals is maintained up to 85% of the first reversible capacity after 30 cycles, representative of an excellent retention property. The enhanced electrochemical properties associated with SnS\(_2\) nanoplates can be attributed to their 2D layered characteristics, including finite lateral size and enhanced open-edges, which can facilitate Li ion diffusion through the active materials and decrease the overvoltage for associated with the Li-Sn alloying reaction, thus driving a faster electrode reaction and providing a higher charge/discharge capacity and excellent cycling stability.\(^{[14]}\)

In summary, we have presented a facile synthesis of 2D layered SnS\(_2\) nanoplates which have nanoscale lateral size of 150 nm. Their unique nanoscale characteristics, including finite lateral 2D morphology, make electrodes fabricated from SnS\(_2\) nanoplates have remarkably high discharge capacities that are close to the theoretically limiting values. The laterally confined 2D nanoplates constructed in this effort can be feasible alternative electrode materials for the next generation lithium ion batteries.

Experimental

Materials and Instruments: All chemicals were purchased from Aldrich and all were used as received. TEM and high resolution TEM (HRTEM) analyses were performed by using a JEM 2100 at 200 kV or a JEOL-ARM1300S at 1250 kV. XRD studies were conducted by using a Rigaku DMAX-RB equipped with a graphite-monochromatized Cu-K radiation source (40 kV, 120 mA).

Synthesis of SnS\(_2\) Nanoplates: 2D SnS\(_2\) nanoplates were synthesized through thermal decomposition of a molecular precursor, Sn(S\(_2\)CNEt\(_2\))\(_4\) \(^{[13]}\), in an organic solvent at elevated temperature. In a typical preparation, 60 mg of Sn(S\(_2\)CNEt\(_2\))\(_4\) was added to a 50 mL three neck round bottom flask containing 5 mL of distilled and dried oleyamine under an Ar atmosphere. The reaction mixture was heated to 280 °C at a rate of 10 °C min\(^{-1}\) and maintained for 10 min at 280 °C. During the process, the initial orange-colored solution gradually became yellow and the reaction was quenched by the addition of cold toluene (6 mL). The resulting solution was treated with 20 mL of...
acetone to precipitate yellow nanoparticles (15 mg), which were separated by centrifugation.

Electrochemical Properties of SnS$_2$ Nanoplates as Electrodes in Lithium-ion Batteries: The working electrode was fabricated by mixing SnS$_2$ nanoparticles, which were annealed at 500 °C for 1 h, and Super P carbon black and polyvinylidene fluoride binder in a respective weight ratio of 8:1:1. Cycling tests were carried out by using coin-type half cells (2016 type) with a Li counter electrode and a 1 M solution of LiPF$_6$ in ethylene carbonate (EC)/diethylene carbonate (DEC) (1:1 vol %) as the organic electrolyte. The cells were discharged from an initial open-circuit voltage to 1 mV, and cycled between 1 mV and 1.1 V under constant current of 323 mAg$^{-1}$ for up to 30 cycles.

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Figure 3. Electrochemical properties of SnS$_2$ nanoplates for Li ion batteries. a) A schematic of lithiation processes for bulk versus nanoplates. Facile Li-Sn alloying processes are observed for laterally confined nanoplates b) cycle-life performance, and c) voltage profile of the SnS$_2$ electrode.


Aqueous suspension droplets of monodisperse latex or latex and gold nanoparticles mixtures assume a spherical shape on superhydrophobic substrates. The drying sessile droplets serve as macroscopic templates for assembling microspheres into closed-packed structures. Upon illumination, the supraparticles display discrete colored rings because of the periodic arrangement of latex particles in the surface layer. The physical origin of the colored patterns is explained in detail.

Quantitative energy transfer from CdSe nanocrystals to a single, conjugated organic dye is observed in the system shown. The energy transfer can be modulated by altering the surface chemistry of the CdSe nanocrystal. The ability of one dye molecule to capture the exciton energy from a semiconductor nanocrystal effectively enhances the absorption cross section of the dye.

Rigid particles as well as soft capsules can be ingested by cells and stored in acidic compartments around the nucleus. TEM and fluorescence images show that the rigid particles retain their original spherical shape whereas the hollow and thus more flexible capsules are deformed and squeezed upon the incorporation process. Though soft capsules are deformed upon uptake, the cargo loaded into the capsules is not released into the cytosol.

Photonic Crystals
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Synthesis of Light-Diffracting Assemblies from Microspheres and Nanoparticles in Droplets on a Superhydrophobic Surface

Batteries
Two-Dimensional SnS₂ Nanoplates with Extraordinary High Discharge Capacity for Lithium Ion Batteries

Energy Transfer
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Complete Quenching of CdSe Nanocrystal Photoluminescence by Single Dye Molecules

Polymeric Materials
Uptake of Colloidal Polyelectrolyte-Coated Particles and Polyelectrolyte Multilayer Capsules by Living Cells