Two-Dimensional Tin Selenide Nanostructures for Flexible All-Solid-State Supercapacitors

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ABSTRACT Due to their unique electronic and optoelectronic properties, tin selenide nanostructures show great promise for applications in energy storage and photovoltaic devices. Despite the great progress that has been achieved, the phase-controlled synthesis of two-dimensional (2D) tin selenide nanostructures remains a challenge, and their use in supercapacitors has not been explored. In this paper, 2D tin selenide nanostructures, including pure SnSe2 nanodisks (NDs), mixed-phase SnSe–SnS2 NDs, and pure SnSe nanosheets (NSs), have been synthesized by reacting SnCl2 and trioctylphosphine (TOP)-Se with borane-tetraethylammonium complex (BTBC) and 1,3-dimethyl-4,5,6-tetrahydro-2(1H)-pyrimidinone. Utilizing the interplay of TOP and BTBC and changing only the amount of BTBC, the phase-controlled synthesis of 2D SnSe2 nanostructures is realized for the first time. Phase-dependent pseudocapacitive behavior is observed for the resulting 2D nanostructures. The specific capacitances of pure SnSe2 NDs (168 F g⁻¹) and SnSe NSs (228 F g⁻¹) are much higher than those of other reported materials (e.g., graphene-Mn₃O₄ nanorods and TiN mesoporous spheres); thus, these tin selenide materials were used to fabricate flexible, all-solid-state supercapacitors. Devices fabricated with these two tin selenide materials exhibited high areal capacitances, good cycling stabilities, excellent flexibilities, and desirable mechanical stabilities, which were comparable to or better than those reported recently for other solid-state devices based on graphene and 3D GeSe₂ nanostructures. Additionally, the rate capability of the SnSe₂ NDs device was much better than that of the SnSe NS device, indicating that SnSe₂ NDs are promising active materials for use in high-performance, flexible, all-solid-state supercapacitors.

KEYWORDS: tin selenide · 2D nanostructures · phase control · electrochemistry · supercapacitors · flexibility

The fabrication of high-efficiency energy storage devices has attracted widespread attention due to ever-increasing demands for renewable energy.¹ Supercapacitors (SCs), also known as electrochemical capacitors, are promising energy storage devices because they offer higher power densities, longer operating lifespans, and better safety tolerances than batteries.²⁻⁷ Recently, substantial efforts have focused on flexible and thin SCs to meet growing requirements for lightweight portable electronic devices, including devices capable of being rolled up.⁸⁻¹⁴ For these applications, it is necessary to find appropriate electroactive materials and integrate them into specific device configurations. Active materials with hierarchical pores, and tubular or layered structures, can promote charge transport and ion diffusion, enhancing power density and cycling stability of SCs.¹⁵ Additionally, the composition and phase of certain pseudocapacitive materials affect energy storage in devices fabricated from these materials.¹⁶ Certain nanostructured materials, such as carbon nanotubes,¹⁷ graphene and its composites,¹⁸⁻²⁴ layered hydroxides and oxides,²⁵⁻²⁹ and metal/oxide hybrids,³⁰ have been developed for use in SCs with desirable properties. The members of one class of important functional nanomaterials, two-dimensional (2D) layered metal chalcogenides (LMCs), exhibit unique electronic structures and physical properties due to their special geometric structures with weak
interlayer Van der Waals coupling, variable composition, and rich phase structure\textsuperscript{31–35} and thus provide a large library of materials for potential applications in flexible energy storage devices. However, only V$_2$ nanosheets (NSs) have been used as active materials in high-performance flexible SCs with in-plane configuration.\textsuperscript{36}

Tin selenides, which belong to one class of typical LMCs and are narrow band gap semiconductors, are promising candidates for use in infrared optoelectronic devices,\textsuperscript{37} solar cells,\textsuperscript{38,39} memory switching devices,\textsuperscript{40} and anodes for lithium-ion batteries.\textsuperscript{41} However, problems with the composition or phase of these materials are encountered frequently during their synthesis.\textsuperscript{41,42} The two main phases of tin selenide materials are hexagonal-phase SnSe$_2$ and orthorhombic-phase SnSe. By selecting special organic Sn or Se precursors and carefully monitoring the reaction conditions, specific SnSe$_2$ and SnSe nanostructures have been synthesized,\textsuperscript{38–44} but very few 2D tin selenide nanostructures have been prepared. To the best of our knowledge, only hexagonal SnSe$_2$ nanodisks (NDs),\textsuperscript{41,45} square SnSe NSs,\textsuperscript{46} and single-layer SnSe NSs\textsuperscript{47} have been synthesized. Despite these successes, the phase-controlled synthesis of 2D tin selenide nanostructures remains a challenge, and no studies of these nanostructures in SCs have been reported. On the basis of the excellent electronic properties of 2D layered crystal structures and their unique mechanical flexibility,\textsuperscript{48,49} synthesizing 2D tin selenide nanostructures and exploring their applications in SCs are of great importance.

In this paper, we report results for the phase-controlled synthesis of 2D tin selenide nanostructures and their use in flexible, all-solid-state SCs. The synthesis is based on a simple one-pot chemical route, i.e., heating common SnCl$_2$ and trioctyl-phosphine (TOP)-Se precursors in the presence of borane-tert-butylamine complex (BTBC) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU). The significant features of our synthesis are as follows: (1) DMPU is an environmentally friendly solvent and a weak oxidant that triggers an increase in the valence of tin from +2 to +4; (2) BTBC is a reducing agent that binds with TOP to form unique surface ligands that permit lateral growth while passivating vertical growth along the $c$-axis of SnSe$_2$; (3) by simply adjusting the amount of BTBC, it is possible to selectively obtain pure SnSe$_2$ NDs, SnSe NSs, and mixed-phase SnSe$-$SnSe$_2$ NDs. Phase-dependent pseudocapacitive behaviors are observed for these 2D nanostructures. Due to their high specific capacitances, pure SnSe$_2$ NDs (168 F g$^{-1}$) and SnSe NSs (228 F g$^{-1}$) are chosen as active materials to fabricate flexible, all-solid-state SCs. The areal capacitances, cycling stabilities, rate capabilities, mechanical flexibilities, and stabilities of these fabricated solid-state devices are studied systematically. In this study, the overall performance of the SnSe$_2$ NDs device is superior to that of a device based on SnSe NSs, as well as other results for devices based on graphene\textsuperscript{9} and 3D GeSe$_2$ nanostructures,\textsuperscript{50} indicating that SnSe$_2$ NDs are promising candidate materials for use in high-performance, flexible, all-solid-state SCs.

RESULTS AND DISCUSSION

Figure 1A shows the X-ray energy dispersive spectra (EDS) patterns of as-synthesized SnSe$_2$ NDs and SnSe NSs. Except for small C and O peaks that originate from adsorbed organic capping reagents or air, only Sn and Se are detected. By integration calculation, the atomic ratios of Sn to Se are approximately 1:2 and 1:1 in the two samples, indicating that they are likely to be SnSe$_2$ and SnSe, respectively. Further evidence comes from X-ray diffraction (XRD) analysis, shown in Figure 1B. Compared with Joint Committee on Powder Diffraction Standard Cards (JCPDS-89-2939 and JCPDS-72-1460), the two samples can be assigned to hexagonal-phase SnSe$_2$ and orthorhombic-phase SnSe. The corresponding XPS fine spectra for Sn 3d and Se 3d (Supporting Information, Figure S1) confirm that the valences of Sn in the two samples are $+4$ and $+2$, and the valence of Se is $-2$ in both cases.\textsuperscript{39,41,42} The morphologies and microstructures of those two samples are examined by field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM), respectively. Figure 1C and D show the low- and high-magnification FE-SEM images of the SnSe$_2$ NDs, respectively. In Figure 1C, many 2D pancake-like nanostructures can be observed. The lateral width or diameter of those NDs is approximately 2–3 $\mu$m, and their average thickness, measured from Figure 1D, is about 8 nm. Further atomic force microscopy (AFM) characterization (Figure S2A,B) identifies that the exact thickness of the SnSe$_2$ NDs is 9 nm. The corresponding TEM image is given in Figure 1E. The selected area electron diffraction (SAED) pattern of the SnSe$_2$ NDs shows well-defined spots, indicating that they are single crystals. The related HRTEM analysis (Figure 1F) for an individual ND exhibits clear lattice fringes, and the lattice spacing is approximately 1.94 Å, corresponding to the interplanar separation of (110) facets of hexagonal-phase SnSe$_2$. As for the SnSe sample, sheet-like nanostructures with some wrinkles are observed (Figure 1G), and their thickness is estimated to be about 3 nm from their turnup edges. Further AFM measurement (Figure S2C,D) reveals that the actual thickness of the SnSe NSs is 2 nm. The corresponding HRTEM analysis (Figure 1H) shows clear lattice fringes, and the lattice spacing is approximately 3.05 Å, assigned to the interplanar separation of the (110) facets of orthorhombic-phase SnSe. As evidenced by SAED analysis, these SnSe NSs are also single crystals. In addition, Fourier transform infrared (FT-IR) spectra tests (Figure S3)
demonstrate that both the SnSe2 NDs and SnSe NSs are covered with a layer of surface ligand (the combination of TOP and BTBC).

To gain insight into the formation mechanism of these 2D tin selenide nanostructures, a series of control experiments were performed. The valence of tin in our raw material is $+2$, which does not explain why SnSe2 is obtained in our synthesis. Is tin oxidized by O2 present in air? To investigate this question, a control experiment was performed by introducing high-purity Ar gas to purge air from the reaction vessel, after which the same SnSe2 ND synthesis procedure was followed.

Figure 1. (A) EDS and (B) XRD patterns of SnSe2 NDs (top) and SnSe NSs (bottom). (C) Low- and (D) high-magnification FE-SEM images of SnSe2 NDs. (E) TEM and (F) HRTEM images of SnSe2 NDs. The SAED pattern and magnified lattice fringes are shown in the upper right and lower left corners of (F), respectively. (G) TEM and (H) HRTEM images of SnSe NSs. The SAED pattern and magnified lattice fringes are shown in the upper right and lower left corners of (G), respectively.
Under this circumstance, the product is still SnSe\(_2\) NDs. Thus, the influence of O\(_2\) in air can be excluded. Considering that the solvent (DMPU) contains a ketone group and has some oxidative capacity, while SnCl\(_2\) is a strong reducing agent, we attribute the increase in the valence of tin to the redox reaction between SnCl\(_2\) and DMPU. Further evidence comes from another control experiment in which 1-octadecene (no oxidative ability) was used in place of DMPU and the other conditions were kept unchanged. Only quasi-1D ribbon-like SnSe nanocrystals were generated in this case (Figure S4), confirming the above deduction. These results reveal that DMPU is not only a solvent but also a weak oxidizing agent in the synthesis of SnSe\(_2\) NDs. Additionally, the TOP and BTBC also have significant impacts on the microstructure and phase of the final product. For example, without TOP and using only BTBC (100 mg) as the capping reagent, large and thick SnSe\(_2\) disks with a diameter of 8–9 \(\mu\)m were formed (Figure S5A,B), while without BTBC and using only TOP (0.5 mL) as the capping reagent, the product was identified to be small-sized SnSe nanoparticle assemblies (Figure S5 C-D). Keeping the amount of TOP and increasing BTBC from 100 to 200 mg yielded a mixed-phase, SnSe–SnSe\(_2\) hexagonal ND (Figure S6). Further increasing BTBC to 500 mg generated pure SnSe NSs. The phenomena that led to the formation of these different products may have resulted from the use of TOP and BTBC. In combination, TOP and BTBC can form donor–acceptor-type complexes due to rich electrons on P and deficient electrons on B. Excess TOP leads to the extraction of Se\(^{2-}\) from SnSe\(_2\) to generate SnSe\(_2\).

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fabricated using SnSe2 NDs and SnSe NSs as active materials, which were identified as SnSe2 NDs-SSCs and SnSe NSs-SSCs. The polymer gel (polyvinyl alcohol-H2SO4) served as both the separator and the solid electrolyte. The detailed configurations of those two solid-state devices are shown in Figure 4A,B. For both devices, the working area was 1.0 cm2. The CV plots of SnSe2 NDs-SSCs in the potential range from −0.4 to 0.4 V (Figure 4C) are symmetric and almost rectangular because of the surface electrosorption of H⁺ and the consecutive reversible surface redox reactions of SnSe2 NDs by means of H⁺ intercalation/detercalation. The absence of redox peaks implies that the SSCs charged and discharged at a pseudoconstant rate during the voltammetric cycles.56,57 Similar CV features are observed in the potential window from −0.6 to 0.6 V for SnSe NSs-SSCs, where the peak shapes are even closer to rectangular (Figure 4D).

Moreover, the galvanostatic charge–discharge measurements of those solid-state devices were performed at current densities ranging from 20 to 150 mA m⁻² (Figure S10A,B). Their specific capacitance (normalized by area) versus current density curves are given in Figure 4E,F. For SnSe2 NDs-SSCs, the areal capacitance at 100 mA m⁻² is calculated to be 250 μF cm⁻², which is 62% of its initial capacitance (406 μF cm⁻²) at 20 mA m⁻². This decrease in capacitance may be attributed to the discrepancy that results from the insertion/deinsertion behavior of ions from the electrolyte to the electrodes.58 The results for SnSe2 NDs-SSCs show excellent electrochemical stability, and no capacitance loss is observed after 1000 cycles at constant current densities (Figure S10C). For SnSe NSs-SSCs, its areal capacitance at 100 mA m⁻² is 442 μF cm⁻², which is much higher than that of SnSe2 NDs-SSCs, graphene-based SSCs (394 μF cm⁻²),9 and 3D GeSe2 nanostructured SSCs (200 μF cm⁻²).50 At constant current densities, almost no capacitive decrease occurs, even for 1000 charge–discharge cycles (Figure S10 D), indicating good electrochemical stability and capacitance retention ability under static conditions. However, compared with its initial capacitance
(1176 μF cm\(^{-2}\)) at 45 mA m\(^{-2}\), only 38% of the capacitance is reserved at the current density of 100 mA m\(^{-2}\), implying that the rate capability of SnSe NSs-SCCs is weaker than that of SnSe\(_2\) NDs-SCCs. Further evidence comes from cycling and rate capability tests with progressively varying current densities.

Figure 5 shows the areal capacitance versus cycle number curves for the two solid-state devices under gradually increasing current densities. After 200 continuous cycles at various current densities followed by a return to the initial current density, the initial capacitances of both solid-state devices could be recovered and maintained for another 200 cycles without a noticeable decrease. These data demonstrate that the constructed solid-state SCs can meet the requirements of long cycle life and good rate capability, which are important criteria for practical energy storage devices. The performance of SnSe\(_2\) NDs-SCCs (Figure 5A) is comparable to or better than that of 3D GeSe\(_2\) nanostructured SCs.\(^{50}\) For SnSe NSs-SCCs (Figure 5B), the capacitances decrease more rapidly with progressively increasing current densities from 45 to 100 mA m\(^{-2}\) than in the cases of SnSe\(_2\) NDs-SCCs and 3D GeSe\(_2\) nanostructured SCs.\(^{50}\) That is to say, the rate capability of SnSe NSs-SCCs is less than that of the other materials. On the basis of this result, the overall performance of SnSe\(_2\) NDs-SCCs is better than that of SnSe NSs-SCCs.

Furthermore, to verify the flexibility and mechanical stability of the fabricated solid-state devices, they are folded or bent at various angles, and their electrochemical responses are recorded accordingly. Figure 6 shows the CV response signals of SnSe\(_2\) NDs-SCCs at different bending angles. Compared with the CV signal recorded at a scan rate of 200 mV S\(^{-1}\) without bending (Figure 6A), the CV curve is nearly unchanged when bent to 60° (Figure 6B). At greater bending curvatures of 90° (Figure 6C) and 120° (Figure 6D), there are no changes, and the CV plots are identical. Similar electrochemical response features were observed for SnSe NSs-SCCs at different bending angles, as illustrated in Figure S11. These results demonstrate that both of the fabricated devices possess excellent flexibility and mechanical stability.

CONCLUSIONS

In summary, a facile method to synthesize 2D pure SnSe\(_2\) NDs, SnSe NSs, and mixed-phase SnSe–SnSe\(_2\) NDs has been developed by combining BTBC and TOP with DMPU as a solvent and weak oxidant. Taking advantage of the interaction between TOP and BTBC and simply adjusting the amount of BTBC, a phase-controlled synthesis of 2D tin selenide nanostructures has been performed easily for the first time. Phase-dependent pseudocapactive behaviors are observed in those 2D tin selenide nanostructures. Among them, the specific capacitances (normalized by mass) of pure SnSe\(_2\) NDs (168 F g\(^{-1}\)) and SnSe NSs (228 F g\(^{-1}\)) are much higher than that of the mixed-phase product...
(31 F g^-1) and other electrode materials (graphene-Mn3O4 or CoS2 nanocomposites, activated nanoporous graphene, TiN mesoporous spheres, crumpled N-doped graphene, etc.). Thus, by using them as active materials, two stacked all-solid-state flexible devices, SnSe2 NDs-SSCs and SnSe NSs-SSCs, are fabricated by

Figure 4. (A, B) Schematic diagrams (top) and photographs (bottom) of the stacked (A) SnSe2 ND-SSC and (B) SnSe NS-SSC devices. (C, D) CV curves of devices based on (C) SnSe2 NDs-SSCs and (D) SnSe NSs-SSCs, measured at different scan rates. (E, F) Specific capacitances of devices based on (E) SnSe2 NDs-SSCs and (F) SnSe NSs-SSCs at various current densities.

Figure 5. Cycling performance of (A) SnSe2 ND-SSC and (B) SnSe NS-SSC devices, measured by progressively varying the current density.
using PVA-H2SO4 gel as the separator and solid electrolyte. The SnSe2 NDs-SSCs exhibit better performance compared with that of SnSe NSs-SSCs as well as recently reported graphene and 3D GeSe2 nanostructured devices, showing promise as a flexible power supply for driving small nanoelectronic devices in integrated nanosystems. Although the areal capacitance of our SnSe2 ND-SSC device needs to be improved relative to previously reported VS2 NS in-plane SCs, it confirms that SnSe2 NDs are another promising candidate in the LMC family for use in high-performance flexible SCs. Hybridizing them with other materials and optimizing their spatial arrangement as well as device configuration may greatly improve the capacitance or energy density of SnSe2 ND based electrode materials. Further work on this is under way.

**METHODS**

Reagents and Materials. Anhydrous SnCl2 (>99%) and Se powder (>99.8%) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). The borane-tert-butylamine complex (97%), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (98%), tri-octylphosphine (>90%), and 1-octadecene (>90%) were purchased from Aldrich. The acetylene black (ATB), polytetrafluoroethylene (PTFE) dispersion (60%), polyvinyl alcohol (PVA), and poly(ethylene terephthalate) (PET) pieces were purchased from Alfa Aesar.

Synthesis of SnSe2 NDs. In a typical synthesis, 40 mg of anhydrous SnCl2, 100 mg of BTBC, and 10 mL of DMPU were added to a clean 250 mL flask at room temperature. Then, 0.5 mL of TOP-Se stock solution, obtained by dissolving 0.316 g of Se powder in 10 mL of TOP, was added immediately to the flask. Next, the flask was placed in a reactor and heated to 240 °C at a rate of 5 °C min⁻¹ and maintained at that temperature for 30 min. Finally, the reactor was allowed to cool to room temperature. The raw product was separated by centrifugation and washed with heptane and absolute alcohol 3 or 4 times to remove byproducts. The product was dried under vacuum at 40 °C for 4 h and used for characterization and analysis.

Synthesis of SnSe–SnSe2 NDs and SnSe NSs. The synthetic procedures for SnSe–SnSe2 NDs and SnSe NSs were similar to the above procedure for SnSe2 NDs. The only difference in these procedures was the amount of BTBC. The mixed-phase SnSe–SnSe2 NDs and the pure SnSe NSs were obtained by increasing the level of BTBC to 200 and 500 mg, respectively.

Synthesis of SnSe2 Control Sample. In the control experiment, that without TOP and using only BTBC as the capping reagent, the Se powder was selected as the selenium source. The detailed synthetic and post-treatment procedures were similar to those for SnSe2 NDs. The only difference was that no TOP was used in this case.

Characterizations. The X-ray energy dispersive spectra were taken on a JSM-5610LV-Vantage type energy spectrometer. X-ray diffraction patterns were recorded on a powder sample using a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite-monochromatized Cu Kα radiation in 2θ ranging from 10° to 90°. Related work voltage and current were 40 kV and 100 mA, respectively. The XPS data were acquired on a scanning X-ray microprobe (PHI 5000 Verasa, ULAC-PHI, Inc.) using Al Kα radiation. Binding energies of Sn 3d and Se 3d were calibrated using the C 1s peak (BE = 284.6 eV) as standard. FE-SEM images were taken on a field-emission scanning electron microscope (JSM-7600F, Japan), operating at an accelerating voltage of 10 kV. The atomic force microscope studies were performed by means of a Nanoscope IIIa scanning probe microscope (Agilent, USA) under tapping mode. The transmission

![Figure 6. Flexibility and stability of a SnSe2 ND-SSC device upon flexing evaluated by measuring CV curves at different bending angles: (A) 0°, (B) 60°, (C) 90°, and (D) 120°.](image-url)
Electrochemical Tests for the Three-Electrode SC System. The electrochemical performances were first carried out in a three-electrode system with a KOH electrolyte solution (6 M). The as-prepared SnSe2 NDs or mixed-phase SnSe–SnSe2 NDs or SnSe NSs on nickel foam, a platinum wire, and a saturated calomel electrode (SCE) were used as the working electrode, counter electrode, and reference electrode, respectively. The working electrode was composed of active SnSe2 NDs or SnSe NSs or mixed-phase SnSe–SnSe2 ND material (70 wt %), conductive material (ATB, 20 wt %), and binder (PTFE, 10 wt %). The mixture was first coated onto the surface of a piece of nickel foil sheet (1 cm × 1 cm) and then dried at 50 °C under vacuum for 12 h. The cyclic voltammograms and galvanostatic charge–discharge tests were performed at 25 °C on a CHI 660D electrochemical workstation (Shanghai, Chenghua Co.).

Fabrication and Electrochemical Tests for All-Solid-State Flexible SCs. The PET substrates were first deposited with a layer of Pt film (∼3–5 nm thick) and then coated with the slurry containing the active materials via a similar process to that in the three-electrode system and were used as the working electrode after drying. Subsequently, two pieces of such electrodes were immersed in the PVA/H2SO4 gel solution for 5–10 min to adsorb a layer of solid electrolyte. After the excess water was vaporized, two pieces of such electrodes coated with electrolyte were pressed together on a sheeting-out roller. Thus, the stacked all-solid-state SCs were fabricated, which were then evaluated for their supercapacitive performance on an Autolab (The Netherlands) electrochemical workstation in a two-electrode system. The CVs at different scan rates and bending angles were recorded at the potential from −0.40 to 0.40 V for SnSe2 ND- and −0.55 to 0.55 V for SnSe NS-based solid-state devices, respectively. The galvanostatic charge–discharge curves were tested at various current densities. The PVA/H2SO4 gel electrolyte was prepared as follows: 6 g of H2SO4 was added into 60 mL of a layer of solid electrolyte. After the excess water was vaporized, 3 g of PVA powder was added. The whole mixture was heated to 85 °C under stirring until the solution became clear.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: XPS spectra, AFM images, and FT-IR spectra of pure SnSe2 NDs and SnSe NSs, control experimental results, microstructural and electrochemical data for mixed-phase SnSe–SnSe2 NDs, structural characterization of pure SnSe2 NDs and SnSe NSs after stability tests, and additional electrochemical data for SnSe2 ND- and SnSe NS-based solid-state devices. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES