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Isolation of inorganic molecular chains from rod-like bulk V_2Se_9 crystal by liquid exfoliation

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We studied the optimum dispersion solvent for bulk V_2Se_9 material, which can be used as a new one-dimensional (1D) material, to separate into 1D chain units. Selected twelve solvents, which have different dielectric constants and surface tensions, were tested to exfoliate bulk V_2Se_9 into nano-scale chains. The atomic level (~ 1 nm, mono-chain) exfoliation of V_2Se_9 was performed using acetone as the solvent. The dispersion concentration was high in solvents having medium dielectric constants ranging from 20 to 40 with surface tensions ranging from 25 to 35 mJ m⁻². This result is similar to the dispersion results of previous transition metal dichalcogenides (TMDCs) such as MoS_2 , WS_2 , $MoSe_2$, $MoTe_2$, $TaSe_2$, $NbSe_2$, and $NiTe_2$, indicating that the V_2Se_9 material and its dispersion to 1D units can be expected to play an important role in opening opportunities for new low-dimensional material studies.

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Low-dimensional materials enable new research directions and advanced applications. Two-dimensional (2D) materials including graphene, transition metal dichalcogenides (TMDCs), and black phosphor have attracted much attention due to their unique physical, chemical, optical, and mechanical properties. These materials have multiple interesting applications in transistors, superconductors, and optoelectronic devices.^{1–5} Unlike previous low-dimensional materials, which were obtained by simply reducing the sizes of bulk materials, 2D materials with atomic thickness are prepared by isolating single atomic layers from three-dimensional materials with strong covalent in-plane bonds and weak interlayer interactions. When one atomic unit layer or several unit layers are isolated from the bulk crystal, excellent properties that are not present in the bulk state are observed due to the quantum confinement effect and the dangling bond-free surface.

Recently, new one-dimensional (1D) materials, such as $LiMo_3Se_3$,^{6–10} $Mo_6S_3I_6$,^{11–14} and $Mo_6S_{4.5}I_{4.5}$,^{15,16} having similar originality to 2D materials, have been investigated. These 1D materials have been prepared by isolating inorganic molecular chains from bulk crystals comprising strong covalently bonded unit chains connected by weak inter-chain interactions. When isolated from the bulk crystals, these molecular chains are as small as 1 nm in diameter and have unique surface

characteristics. For example, $LiMo_3Se_3$ has a negatively charged chain surface because of ionic interactions between the chains.¹⁷ $Mo_6S_3I_6$ and $Mo_6S_{4.5}I_{4.5}$ have no dangling bonds on the chain surface, similar to graphene sheets, because of the van der Waals (vdW) forces between chains. These structural features give rise to unique physical and chemical properties including 1D quantum confinement effects, thus permitting applicability in composites, molecular connectors, transistors, sensors, and photovoltaic devices.^{11–13,18–23} In addition, new 1D inorganic materials, namely, Sb_2S_3 and Sb_2Se_3 , have been reported to exhibit excellent optoelectronic properties because the chain surfaces lack dangling bonds.^{24–26}

We have been studying the synthesis of new 1D inorganic materials and recently prepared a new semiconducting 1D bulk crystal of V_2Se_9 . Exfoliation has been previously shown to separate CNTs into individual tubes, and has been used for many useful applications.^{27–29} Therefore, exfoliation is recognized as an important first step toward applications and thus, it is an indispensable scientific goal. The isolation of inorganic chains from this bulk crystal is necessary in order to study the materials' properties or device applications. For this purpose, we have exfoliated the V_2Se_9 bulk crystal in various solvents because exfoliation in a solvent is a simple and high-yield method compared with other exfoliation methods. In this study, we determined the optimal solvent for V_2Se_9 exfoliation and verified the isolation of single chains from the obtained dispersion solutions.

The dispersion of the solid material in the solvent may be affected by the wetting behavior and binding energy between the solvent and the solid surface. Among the various physical properties of solvents, surface tension (surface energy) affects

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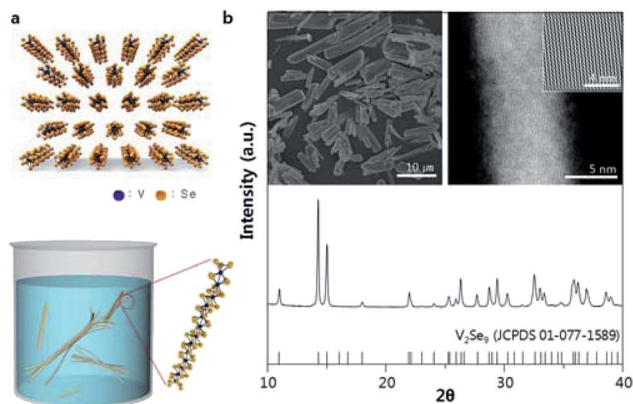


Fig. 1 (a) Schematic of crystal structure and exfoliation process of V₂Se₉. (b) Powder XRD pattern of the V₂Se₉ crystal (inset: SEM image of V₂Se₉ crystal (left) and TEM image of the exfoliated V₂Se₉ in acetone (right)).

the wetting property, and the dielectric constant affects the bonding energy between solid surface and liquid by dipole-dipole interactions. In other words, in order to be well dispersed, the solid material has to dissolve well in the solvent, and the theory explaining this phenomenon is the Hansen solubility parameter. Solids are most soluble in solvents with similar properties, such as dispersion forces, dipole intermolecular forces, and the hydrogen bonding energy between solvents and solid materials. The surface characteristics of the two-dimensional transition metal di-selenides and the 1D V₂Se₉ material used in this experiment show similar characteristics in the large frame of vdW bonding, but the detailed surface characteristics are different. In this experiment, it is meaningful

to provide basic experimental data of dispersion for a new 1D material by analyzing the dispersion characteristics of V₂Se₉ in various solvents.

The V₂Se₉ chain is a 1D molecular chain of linearly connected V atoms decorated externally with Se atoms (top of Fig. 1a). Although the chain bonding is covalent, adjacent chains are stacked *via* vdW interactions to form the 3D crystal. In dispersion, single chains can be exfoliated from the 3D crystal because of the weak interactions between chains (bottom of Fig. 1a). Single-crystalline V₂Se₉ was prepared *via* the flux method using excess molten Se as a solvent. When the V–Se liquid at 330–340 °C is cooled to room temperature, dark grey bulks are precipitated, and X-ray diffraction (XRD) analysis confirms that the obtained material has a well crystallised V₂Se₉ phase (Fig. 1b). The inset of Fig. 1b shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the as-prepared V₂Se₉ crystals. The resulting dark grey V₂Se₉ crystals have diameters of several tens of micrometres. Because of the weak attraction between V₂Se₉ chains, the V₂Se₉ crystals show axially cleaved sections. The TEM image shows that the V₂Se₉ crystal comprises 1D aligned chains with diameters < 1 nm. With the successful synthesis and structural identification of V₂Se₉, dispersion was performed in order to obtain mono- and few-chain nanowires in several solvents.

Liquid exfoliation is known to be insensitive to air and water, and is potentially scalable to yield large quantities of exfoliated materials.³⁰ In order to determine the best exfoliation solvent for the V₂Se₉ chain material, twelve solvents were considered with varied dielectric constants (Table 1).

V₂Se₉ particles were dispersed in the solvents by sonication and further centrifuged to remove sediments of large and non-exfoliated particles. Photos of the dispersed solution before and

Table 1 Molecular structure, surface tension, and dielectric constant of 12 selected solvents

| Solvent | Molecular structure | Surface tension (mJ m ⁻²) | Dielectric constant |
|---------------------------|---------------------|---------------------------------------|---------------------|
| Hexane | | 18.43 | 1.89 |
| Toulene | | 28.43 | 2.38 |
| Chloroform | | 27.5 | 4.81 |
| Dichloromethane (DCM) | | 26.5 | 8.93 |
| Isopropyl alcohol (IPA) | | 23 | 17.9 |
| Isobutyl alcohol (IBA) | | 22.98 | 18.1 |
| Acetone | | 25.2 | 20.7 |
| Acetonitrile | | 36.4 | 37.5 |
| Dimethyl sulfoxide (DMSO) | | 36 | 46.7 |
| Propylene carbonate | | 41.1 | 64 |
| Water | | 72.8 | 80.1 |
| N-Methyl formamide (NMF) | | 11 | 171 |



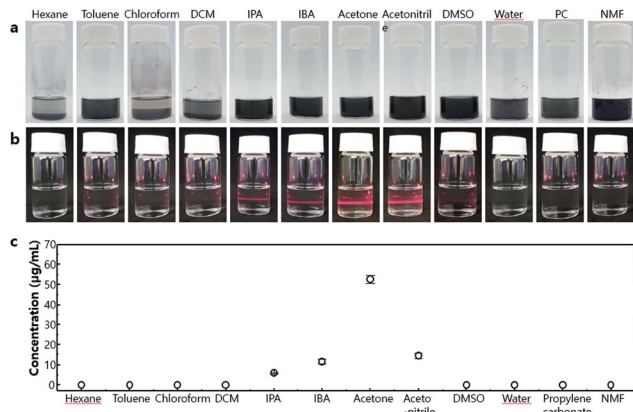


Fig. 2 Photographs of (a) dispersion solutions after ultrasonication and (b) separated supernatant after centrifugation with Tyndall effect. (c) Concentration of the V_2Se_9 dispersion solution depending on the solvents. Error bars represent standard deviations obtained from three measurements of the same sample.

after centrifugation are shown in Fig. 2a and b. The solvents isopropyl alcohol (IPA), isobutyl alcohol (IBA), acetone, and acetonitrile show a clear Tyndall effect, indicating that nano-dispersions of V_2Se_9 chains are obtained (see the inductively coupled plasma (ICP) mass spectrometry results for different solvents in Fig. 2c).

The exact concentration of V_2Se_9 in each solution was analysed by ICP mass spectrometry and plotted with the dielectric constants and the surface tensions of the solvents, as shown in Fig. 3a and b, respectively. The dispersion concentration is high in solvents having intermediate dielectric constants in the range of 20–40 and surface tensions in the range of 25–35 $mJ m^{-2}$. To understand the dispersion behaviour of a material in a solvent, the surface structure of the exfoliated material must be understood. 1D V_2Se_9 is a transition metal chalcogenide (TMC) comprising chains of Se-decorated V atoms. These structural features are similar to those of well-known 2D TMDCs, which comprise hexagonal layers of metal atoms (M) sandwiched between two layers of chalcogenide atoms (X) with the stoichiometry MX_2 . Furthermore, 1D chains and 2D sheets, which are the unit structures of V_2Se_9 and TMCs, respectively, are linked by vdW interactions. Dispersions of TMCs in solvents have been studied extensively. TMDCs including MoS_2 , $MoSe_2$,

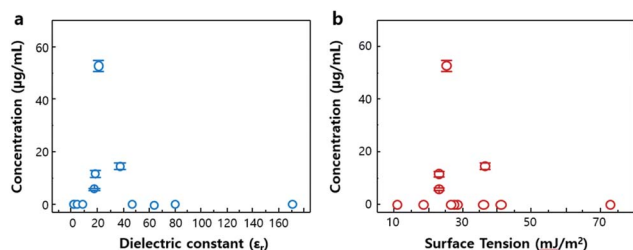


Fig. 3 Concentrations of the V_2Se_9 dispersion solutions versus (a) dielectric constant and (b) surface tension. Error bars represent standard deviations obtained from three measurements of the same sample.

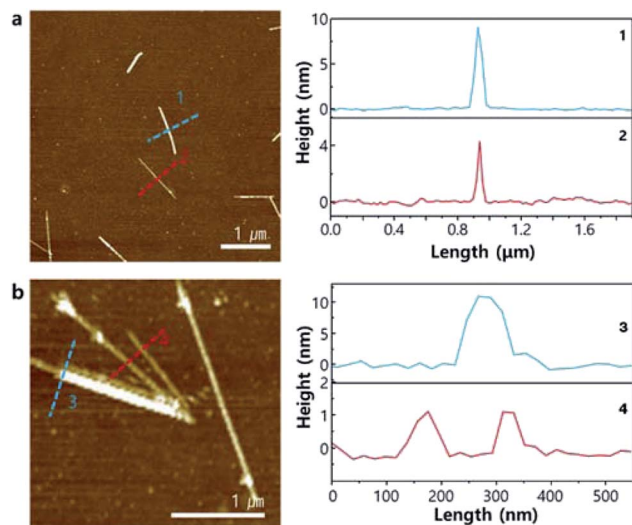


Fig. 4 (a) AFM image of the exfoliated V_2Se_9 nanowires on Si/SiO_2 wafer, the height profiles along each dashed line and histograms of the diameter distributions. (b) AFM image of the exfoliated V_2Se_9 nanowire with a diameter of 1 nm.

$MoTe_2$, and $NbSe_2$ are effectively dispersed in solvents with surface tensions between 30 and 40 $mJ m^{-2}$.³⁰ This result is similar to that obtained in this study because both V_2Se_9 and TMDCs have surface structures in which chalcogenide atoms encapsulate transition metals and vdW interactions between these unit material surfaces. The highest concentration of 52.8 $\mu g mL^{-1}$ was obtained in acetone.

V_2Se_9 dispersed in acetone was spin-coated onto SiO_2/Si substrates to analyse the size of the nanochain using an atomic force microscope (AFM); the results are shown in Fig. 4a and b. It is evident that the V_2Se_9 chains with 1D structure of and size < 10 nm are well dispersed. This confirms that monochains of size ≤ 1 nm can be obtained in a specific dispersion region (Fig. 4b). More details on the separation of 1D V_2Se_9 chains into atomic units will require the optimisation of the dispersion solvent and the dispersion process.

In summary, in this study, a novel 1D inorganic molecular chain material (V_2Se_9) was synthesised through a chemical reaction between V and Se. 1D nanoscale (≤ 10 nm) and mono-chain scale (~ 1 nm) of V_2Se_9 chains were successfully obtained by the dispersion process, and the best solvent for V_2Se_9 dispersion was acetone. The covalently bonded V_2Se_9 chain, when isolated from its 3D bulk material, may have unique physical properties based on the confinement of electrons in the 1D chain structure and the absence of dangling bonds on the chain surface. Therefore, this 1D material may inspire the development of new nanoelectronic devices, similar to the various 2D materials currently under investigation.

Experimental section

Synthesis

V_2Se_9 was synthesised by a flux method using V (–325 mesh, 99.5%, Aldrich) and Se (>99%, Alfa Aesar) elemental powders.



First, 1 g of mixed V and Se with the molar ratio of 3 : 97 was pelletized. Then, the pellets were sealed in a 10 cm-long evacuated quartz tube. The evacuated quartz tube was heated to 330 °C for 120 h, and then cooled at 10 °C h⁻¹. The product was a dark grey powder. The unreacted Se was sublimated in a low-pressure tube furnace at 250 °C under Ar flow (100 sccm) for 24 h.

Dispersion

V₂Se₉ powder (10 mg) was immersed in 10 mL of each solvent. The initial large powder particles were crushed using ultrasonication by a probe sonicator (VC 505, Sonics & Materials, Inc.), operated for 5 min at a 2 s on/2 s off interval. Subsequently, bath sonication (B2005S-68K, 68 kHz, 200 W, KODO Technical) was performed for 3 h. After ultrasonication, the solution was centrifuged at 6000 rpm for 10 min to remove the insufficiently exfoliated chains. For further analysis, 5 mL of the supernatant solution was used.

Characterization

To examine the morphology of the as-synthesised V₂Se₉ powder, field-emission SEM (FE-SEM) was employed. An aberration-corrected scanning transmission electron microscope (STEM, JEM ARM 200F, JEOL) was operated at an acceleration voltage of 80 kV. The sample for STEM observation was prepared by drop-casting on a graphene-coated Quantifoil TEM grid. The concentrations of the dispersion solutions were confirmed by ICP-mass spectrometry (Agilent 7500, Agilent Technologies Inc.). To evaluate the morphology of the exfoliated V₂Se₉, AFM (Park Systems, NX10) was employed in non-contact mode, for which the samples were prepared by spin-coating on SiO₂/Si wafers.

Conflicts of interest

There are no conflicts to declare.

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