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Synthesis of Nanoscale $NbSe_2$ Materials from Molecular Precursors

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This paper describes a new synthetic approach to one- (1D) and two-dimensional (2D) $NbSe_2$ nanoscale materials using soft chemical methods. Our one-pot synthesis provides a direct route to control the morphology of materials that can exhibit complex electronic properties. Studies of the properties of nanomaterials have primarily focused on relatively simple electronic and optical properties.[1] Recent synthetic progress on transition metal oxide and metallic nanowires has enabled explorations of more complicated phenomena such as ferroelectricity, themoelectricity, and superconductivity in 1D systems.[2] The controlled synthesis of nanoscale materials whose bulk counterparts show interesting behavior is critical for fundamental studies and potential devices; the simplest of these systems is binary compounds.

Transition metal dichalcogenides (ME_2) are low-dimensional, layered materials whose in-plane covalent bonds are stronger than their out-of-plane van der Waals interactions. Certain ME_2 materials (TaS_2, $TaSe_2$, and $NbSe_2$) have been studied extensively in bulk because they show interesting temperature-dependent electronic instabilities, such as metal to superconducting or charge density wave (CDW) transitions.[3] These complex properties have not been studied in nanoscale ME_2 materials primarily because of the limited availability of high-quality materials. To date, 1D $NbSe_2$ nanostructures have been prepared by the intense electron irradiation of bulk $NbSe_2$,[4] by thermal decomposition of $NbSe_3$ in a flow of argon at 700 °C,[5] and by chemical vapor transport with elemental Nb and Se in an evacuated silica ampule at 800 °C.[6] Disadvantages of these approaches to 1D $NbSe_2$ materials include low yield, low purity, and a broad size distribution of product.

Solution-based methods have several significant advantages over solid-state methods to synthesize nanomaterials including: (i) low reaction temperatures; (ii) size-selective growth; and (iii) morphological control. We and others have shown that the decomposition of molecular precursors in the presence of surfactants is a general synthetic approach to a wide variety of nanoscale metal selenides.[1,7] Other solution-based routes have been used to prepare *semiconducting* ME_2 nanostructures.[8−11] The primary drawback to these approaches is the lack of size control of the product, although reverse micelles have been used to improve the size distribution of MoS_2 nanoclusters.[8] The controlled synthesis of layered, *conducting* ME_2 nanostructures, such as $NbSe_2$, is important for uncovering how correlated electron phenomena, namely superconductivity and CDW behavior, are affected by systems of finite size. Because the characteristic length scales for superconductivity in $NbSe_2$ are less than 10 nm,[12] solution-based syntheses are a versatile approach to achieve these small sizes. Moreover, the synthesis of submicron crystals of CDW materials can facilitate investigations of new mesoscopic phenomena.

Here we report the first solution-based synthesis of 2D nanoplates and 1D nanowires of $NbSe_2$ in high yield starting from a niobium chloride precursor and elemental Se. These $NbSe_2$ nanostructures were formed in a one-pot reaction followed by thermal decomposition at high temperatures. In a typical reaction, 20 mL of degassed oleylamine (dodecylamine) were added to the mixture of $NbCl_5$ (1 mmol) and Se (2 mmol) under N_2. The reaction mixture was vigorously stirred while heating at 280 °C (250 °C) for 4 h, during which the precursors dissolved and formed a black suspension. This air-stable intermediate was extracted and washed repeatedly with hexane, dried under vacuum, and heated at 450 °C for 3 h under a N_2 atmosphere. We discovered that different morphologies of $NbSe_2$ nanostructures were formed by quenching the hot reaction mixture at different temperatures.

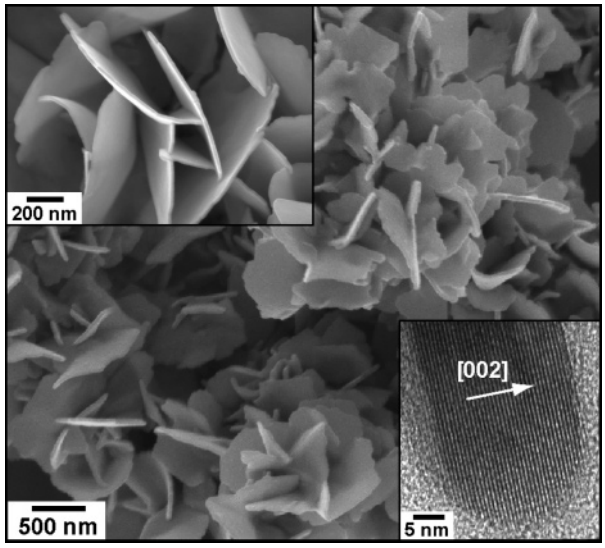

Figure 1. Scanning electron micrographs (SEM) of 2D nanoscale $NbSe_2$ plates synthesized in oleylamine. (Top inset) $NbSe_2$ nanoplates grown in dodecylamine. (Bottom inset) HRTEM of an individual nanoplate on its edge. The short axis of the nanoplate is parallel to the *c*-axis and perpendicular to the (002) planes.

Nanoscale plates with a 2D lamellar structure were grown when the reaction mixture was cooled slowly (∼5 °C/min) from 280 °C to room temperature (rt) before washing with hexane (Figure 1). Both amines resulted in a nearly 100% 2D morphological yield. The thickness of the nanoplates is between 10 and 70 nm with typical lateral dimensions between 500 and 1000 nm. The powder X-ray diffraction (PXRD) pattern (Figure S1, Supporting Information) is consistent with bulk $NbSe_2$ (PDF #19-0872) consisting of Nb atoms trigonally coordinated with Se atoms in a hexagonal sandwich arrangement with two sandwich layers per unit cell (a = 3.454 Å and c = 12.592 Å). High-resolution transmission electron microscopy (HRTEM) of a nanoplate on its edge reveals a fringe spacing of 6.3 Å (bottom inset, Figure 1B), which corresponds to the separation between (002) planes. Hence, the structure of the 2D nanoplates is a smaller version of the bulk $NbSe_2$ structure. Elemental analysis by energy-dispersive X-ray spectroscopy (EDX) indicated that individual plates exhibited Nb and Se in a 1:2 ratio.

When the hot reaction mixture was quenched rapidly in rt hexane, 1D nanostructures were formed (Figure 2A). The $NbSe_2$ nanowires are 2−25 nm in diameter with lengths up to tens of microns.

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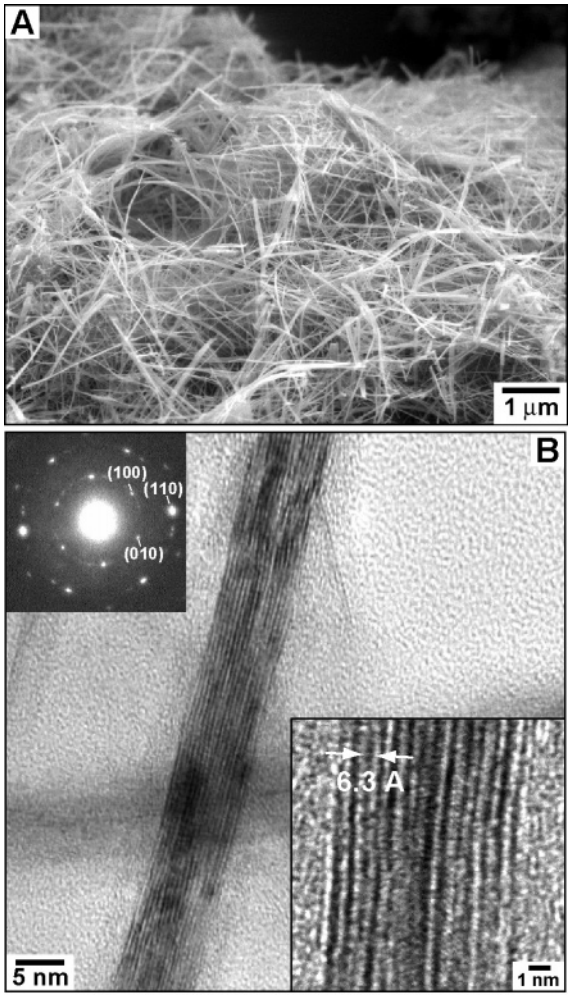

Figure 2. (A) SEM of 1D nanoscale $NbSe_2$ wires synthesized in oleylamine. (B) TEM of an 8.8-nm nanowire overlapping two other wires (faint gray areas in image). (Top inset) SAED of a small number (3−5) of $NbSe_2$ nanowires that show hexagonal symmetry. (Bottom inset) HRTEM of an individual nanowire that exhibits lattice fringes [(002) planes] parallel to the long axis of the nanowire.

HRTEM indicates that individual nanowires are polycrystalline, and the longitudinal axis of the nanowires is perpendicular to the [002] direction (Figure 2B). The selected area electron diffraction (SAED) pattern of small numbers (3−5) of nanowires exhibits slightly broadened diffraction spots because occasionally the stacked (002) sheets composing the nanowires were not uniformly spaced along the length of the wire. Also, the SAED patterns are in agreement with the PXRD patterns (not shown), which are similar to those of the 2D nanoplates.

We propose that the morphological control of $NbSe_2$ nanoscale materials results primarily from the ratio of surfactant to intermediate present after washing in hexane and before heating at elevated (450 °C) temperatures. PXRD and EDX confirmed that both extraction methods led to a mixture of Nb_2Se_9 and Se (Figure S2, Supporting Information). Quenching of the hot (250−280 °C) intermediate in rt hexane removed more surfactant (confirmed by CHN Analysis) compared with the rt intermediate washed with rt hexane. The hot quenching led to 1D nanowires, while the rt washing resulted in 2D nanoplates, whose thickness was similar in size to that of the 1D nanostructures. If the quenching in hexane was incomplete or performed while the reaction mixture was warm (100 °C) but not hot (280 °C), a mixture of 1D nanowires and 2D lamellar structures was formed, with the 2D nanoplates comprising a higher percentage of the product. Although these types of layered compounds can be intercalated with small molecules,[13] we do not observe any intercalation of the surfactant-amine based on the measured lattice spacing (6.3 Å) between (002) planes, which is similar to bulk $NbSe_2$ (6.296 Å).

We also investigated other strategies to control the shape and size of the $NbSe_2$ nanostructures by varying the ratio between the Nb and Se precursors (1:3 and 1:5), the one-pot reaction temperature (220−300 °C), and the length of reaction time (1, 2, 2.5, 3, 3.5, 5, and 6 h). No change in the size or shape was observed.

This communication describes the synthesis of two different morphologies of nanoscale $NbSe_2$ materials formed in solution by the decomposition of molecular precursors. These materials are an important first step for studies of the fundamental properties of complex electronic materials with reduced size and dimension; the measurements of these properties are in progress. Also, the synthetic approach presented here may be extended to grow nanoscale versions of other materials (e.g., TaS_2 and $NaTaO_3$) that exhibit interesting electronic and optical phenomena.

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Supporting Information Available: PXRD of nanoplates and reaction intermediate; SEM images of reaction intermediate. This material is available free of charge via the Internet at http://pubs.acs.org.

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