This paper describes a new synthetic approach to one- (1D) and two-dimensional (2D) NbSe2 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. Recent synthetic progress on transition metal oxide and metallic nanowires has enabled explorations of more complicated phenomena such as ferroelectricity, thermoelectricity, and superconductivity in 1D systems. 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 (ME2) are low-dimensional, layered materials whose in-plane covalent bonds are stronger than their out-of-plane van der Waals interactions. Certain ME2 materials (TaS2, TaSe2, and NbSe2) 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. These complex properties have not been studied in nanoscale ME2 materials primarily because of the limited availability of high-quality materials. To date, 1D NbSe2 nanostructures have been prepared by the intense electron irradiation of bulk NbSe2, by thermal decomposition of NbSe3 in a flow of argon at 700 °C, and by chemical vapor transport with elemental Nb and Se in an evacuated silica ampule at 800 °C. Disadvantages of these approaches to 1D NbSe2 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. Other solution-based routes have been used to prepare semiconducting ME2 nanostructures. 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 MoS2 nanoclusters. The controlled synthesis of layered, conducting ME2 nanostructures, such as NbSe2, 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 NbSe2 are less than 10 nm, 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 NbSe2 in high yield starting from a niobium chloride precursor and elemental Se. These NbSe2 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 NbCl5 (1 mmol) and Se (2 mmol) under N2. 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 N2 atmosphere. We discovered that different morphologies of NbSe2 nanostructures were formed by quenching the hot reaction mixture at different temperatures.

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 NbSe2 (PDF #19-0872) consisting of Nb and Se in a 1:2 ratio. 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 NbSe2 nanowires are 2–25 nm in diameter with lengths up to tens of microns.
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 bulk NbSe₂ (6.296 Å).

We propose that the morphological control of NbSe₂ 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 Nb₂Se₇ and Se (Figure S2, Supporting Information). We also investigated other strategies to control the shape and size of the NbSe₂ 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 NbSe₂ 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., TaS₂ and NaTaO₃) 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.

References