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Synthesis of ultrathin wurtzite ZnSe nanosheets

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ABSTRACT

We demonstrate a facile chemical synthesis of 1.4-nm-thick zinc selenide (ZnSe) nanosheets with wurtzite structure. Owing to the quantum confinement arising from the ultra-thinness, absorption peaks are significantly blue-shifted compared to those of bulk materials. The narrow width of the peaks (<10 nm) indicates that thickness of the nanosheets is highly uniform. Successful synthesis of ZnSe nanosheets implies that the same chemical route may be further extended to synthesize various other non-layered materials in the form of two-dimensional nanosheet.

1. Introduction

Two-dimensional (2D) nanosheets with several-atom thickness have attracted great attention due to their unique physical and chemical properties arising from ultra-thinness and high surface-to-volume ratio. These characteristics are potentially important for various applications such as electronics, photonics, sensors, energy storage devices, and catalysis [1–6].

The 2D nanosheets can be produced by a few different techniques such as chemical synthetic routes and exfoliation of layer-structured materials [5,7,8]. Chemical synthetic routes such as lateral extension, oriented attachment of nanocrystals, and soft template method can be applied to non-layered materials [7–9], while the exfoliation technique can intrinsically be applied only to the layered materials having strong in-plane bonds and weak coupling between layers [3–5]. However, synthesis of ultrathin nanosheets has been demonstrated for only a few non-layered materials including PbS, ZnS, In_2S_3, CdSe, and Co_9Se_8 [6–11], and it is important to explore this synthetic approach for various other non-layered materials. For example, zinc selenide (ZnSe) is an attractive material because it can be used for a variety of applications such as biomedical, optical, and optoelectronic applications, and also does not contain toxic elements such as Cd, Pb, and Hg [12]. Very recently, it was reported that ZnSe nanosheets with zinc blende structure can be synthesized via soft template method [13].

In this letter, we demonstrate the synthesis of wurtzite ZnSe nanosheets with a thickness of 1.4 nm. The nanosheets have an average length and width of 82.0 ± 27.1 nm (average $\pm$ one standard deviation) and 22.0 ± 3.6 nm, respectively. Crystallographic orientation of the nanosheets was determined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). We conjecture that the ultrathin single crystalline nanosheets were formed via oriented attachment of ZnSe nanocrystals. Our results suggest that many other non-layered materials with various phases may also be chemically synthesized.

2. Experimental section

Single-layered ZnSe nanosheets were synthesized as follows. 0.3 mmol (89 mg) of zinc nitrate hexahydrate ($Zn(NO_3)_2$ $6H_2O$, Sigma-Aldrich) and 0.9 mmol (71 mg) of selenium (powder, Sigma-Aldrich) were dissolved in the mixture of 5 ml octylamine (99%, Sigma-Aldrich) and 10 ml oleylamine (70%, Sigma-Aldrich). The solution was bubbled with nitrogen at 100 °C for 30 min and heated at 170 °C for 6 h under nitrogen flow while magnetically stirred. After the reaction, the solution was cooled down to room temperature naturally. Subsequently, 1 ml of trioctylphosphine (90%, Sigma-Aldrich) was injected to the solution to eliminate excess selenium. The product was precipitated by centrifugation and rinsed with toluene and ethanol (vol% 1:1) three times. The final product was dispersed in toluene.

The structure and morphology of the nanosheets were characterized by XRD (Rigaku, D/max-2500 V/PC), TEM (FEI, Tecnai 20), and atomic force microscopy (AFM, Park Systems, Xe-100). The composition of the nanosheets was analyzed by energy-dispersive X-ray spectroscopy (EDX). Optical properties were measured by

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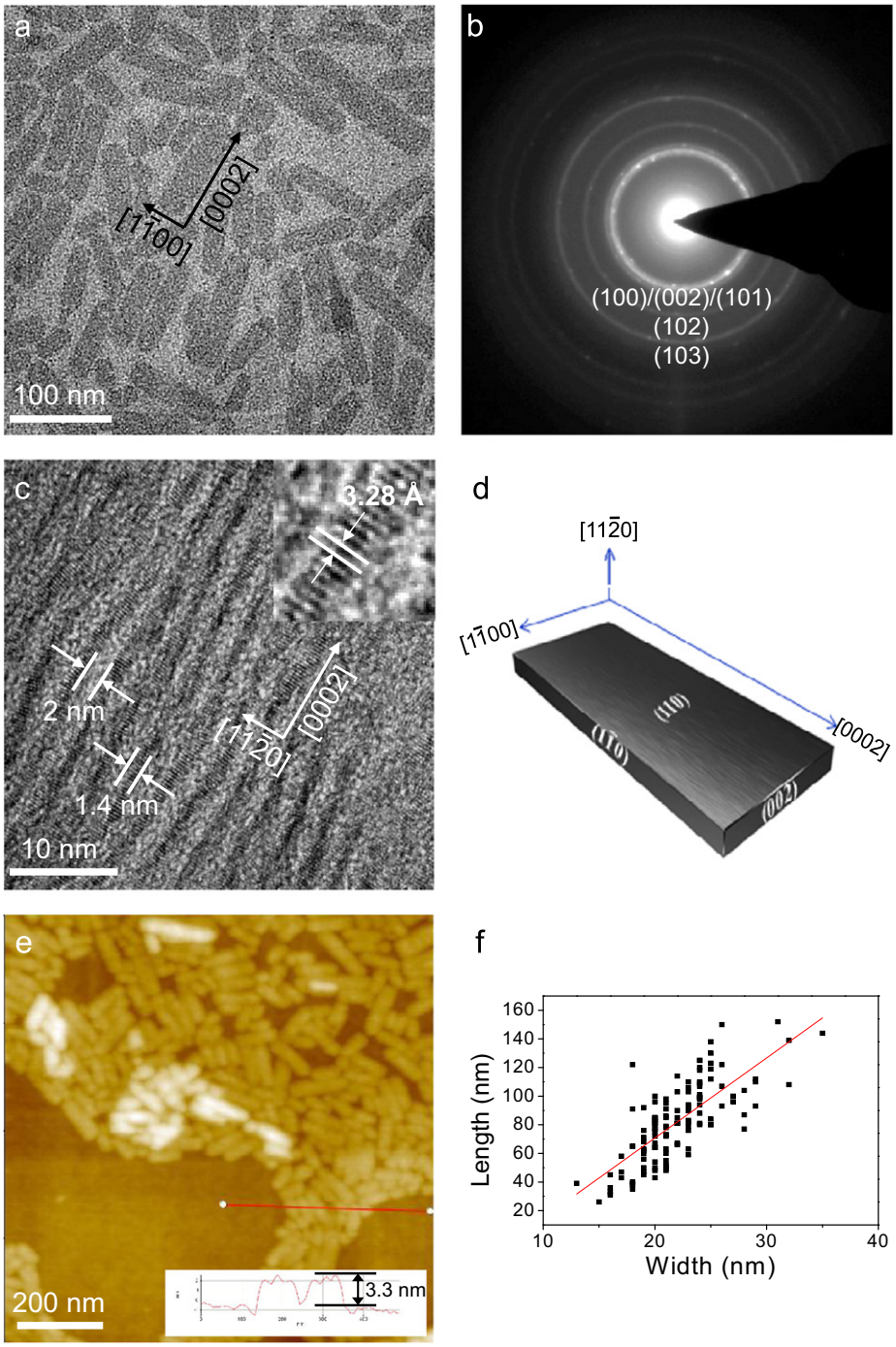

Fig. 1. (a) TEM image of single-layered ZnSe nanosheets; (b) SAED pattern; (c) TEM image of lateral side of stacked ZnSe nanosheets, inset image shows (002) lattice fringe; (d) crystallographic orientation of a ZnSe nanosheet; (e) AFM image and (f) size distribution of ZnSe nanosheets.

UV–vis absorption (Varian, Cary 50) and Raman spectroscopy (Horiba, HR 800, λ=514.5 nm).

3. Results and discussion

The ZnSe nanosheets were crystalline as shown by the XRD pattern (Fig. S1). The peak positions exactly matched with those of hexagonal ZnSe with lattice parameters of a=3.974 Å and c=6.506 Å (JCPDS # 80-0008). Interestingly, relative peak intensities of the nanosheets were different from those of bulk ZnSe. More specifically, (002) peak was significantly pronounced while (110) and (112) peaks were suppressed. This implies that ZnSe has a preferential crystallographic orientation and is not spherical.

TEM indeed shows that ZnSe has a sheet-like structure (Fig. 1(a)). Selected area electron diffraction (SAED) pattern, consistently with the XRD pattern, clearly indicates that ZnSe nanosheets are crystalline (Fig. 1(b)). To measure the nanosheet-thickness, we induced the aggregation of the nanosheets by dispersing them in ethanol. Since the surface of the nanosheet is capped with hydrophobic ligands, they aggregate and stack on top of each other in hydrophilic ethanol. This leads to the formation of lamellar structure, which allowed us to observe and study the lateral side of the nanosheets (Fig. 1(c)). The lamellar structure consists of alternating layers of ZnSe nanosheet