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Atomic-layer triangular WSe$_2$ sheets: synthesis and layer-dependent photoluminescence property

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Abstract
The exotic band structures and distinctive physical properties of two-dimensional materials have exhibited great potential for fundamental research and technical applications in spintronics, electronics, photonics, optoelectronics, and so forth. Facing the challenge of effective synthesis of WSe$_2$ two-dimensional sheets, for the first time we demonstrate a straightforward catalyst-free vapor–solid (VS) growth method to synthesize ultrathin, even monolayer, WSe$_2$ sheets with high yield, regular shapes and high quality optical properties on sapphire substrates. By detailed layer-number-dependent photoluminescence measurements at a low temperature of 40 K, we find the spin–orbit splitting at the K point of the WSe$_2$ valence band with a fixed energy difference of 0.36 eV independent of layer number and the transition of indirect-to-direct gap when the thickness decreases to monolayer. These results, comparable to those of mechanically peeled WSe$_2$ sheets, further prove the high optical and crystal quality of our WSe$_2$ nanosheets via the VS growth approach. Our efforts may open up new exciting opportunities in future valley-based electronics, optoelectronics and photonics.

(Some figures may appear in colour only in the online journal)

1. Introduction
Two-dimensional (2D) layered materials, which are formed through strong in-plane covalent bonding in individual atomic layers and weak van der Waals interaction between two adjacent layers, have attracted a great deal of attention over the past decade. The exotic band structures and distinctive physical properties of 2D materials have opened up new opportunities for fundamental research and technical applications in spintronics, electronics, photonics, optoelectronics, and so forth [1–3]. As a typical representative, graphene is the most widely investigated 2D material and has displayed extremely high carrier mobility, exceeding $10^6$ cm$^2$ V$^{-1}$ s$^{-1}$ at 2 K [4]. This renders graphene accessible for fast electronic devices, for example, super-high radio frequency applications [5–7]. However, the intrinsic limitation caused by its small bandgap hinders graphene-based field-effect transistors (FETs) from being effectively switched off and obtaining high on/off ratios, even though the bandgaps can be somehow tuned via various methods, such as chemical functionalization [8], nanoribbon fabrication [9] and dual electric field gates [10].

Inspired by the success and band structure limitation of graphene, many other 2D materials, such as GaS, GaSe, SnSe, Bi$_2$Te$_3$, Bi$_2$Se$_3$, h-BN, transition metal oxides, etc have been extensively studied [11–18]. In particular, research interest in the family of transition metal dichalcogenides (TMDCs) including but not limited to MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$, has increased dramatically because they have been discovered to possess layer-dependent physical properties, for example, a transition from an indirect bandgap in bulk form to a direct bandgap in monolayer form [19–30]. In addition, TMDCs

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with desired bandgaps around 1–2 eV are suitable for FETs and optoelectronic devices rather than graphene. For instance, single layer MoS$_2$ demonstrates excellent FET performance with a relatively high channel mobility ($\sim 200$ cm$^2$ V$^{-1}$ s$^{-1}$) and high on/off switching ratio ($10^8$) [19].

Recently, both theoretical and experimental works have found a transition from indirect bandgap to direct bandgap and valley polarization in WSe$_2$ 2D material on reducing its thickness to monolayer [27, 28, 31]. In addition, monolayer WSe$_2$ has been discovered to be the first TMDC material combining p-type and n-type conducting behaviors in the same material [29, 30], which offers the possibility to design complementary logic circuits in the same monolayer. The above unique properties of WSe$_2$ provide superb potential in applications of valley-based electronics, logic circuits and optoelectronics. As one of the important compounds in the TMDC family, WSe$_2$ is composed of two-dimensional trilayer Se–W–Se sandwich structures, with a W atom plane in the middle of two hexagonal S atom planes, as shown in figure 1(A). The WSe$_2$ sheets are weakly bonded together by non-covalent bonds to form the crystal. Because of the relatively weak interlayer bonding in WSe$_2$, monolayer sheets can be easily fabricated via a micromechanical exfoliation method [27, 28]. This method can effectively fabricate WSe$_2$ monolayers with high purity and cleanliness for fundamental characterization. However, it fails to realize large-scale, uniform, regular shaped samples with high yield and controllability. A new fabrication method is highly desired. To date, we are not aware of any other methods, including epitaxy growth [14, 32], vapor transport and deposition [20], liquid exfoliation [33] and solution synthesis [13], which have been used to produce WSe$_2$ nanosheets apart from the micromechanical exfoliation method as reported recently in [27, 28]. Motivated by the success in MoS$_2$, Bi$_2$Te$_3$ and Bi$_2$Se$_3$, vapor–solid (VS) growth is chosen for our attempt at WSe$_2$ ultrathin nanosheet fabrication.

Here, for the first time, we develop a straightforward, high yield method for the growth of ultrathin WSe$_2$ sheets, even monolayers, with regular shapes and high quality optical properties on sapphire (001) substrates via a catalyst-free VS growth mechanism. By detailed layer-number-dependent PL measurements at a low temperature of 40 K, we found the spin–orbit splitting at the K point of the WSe$_2$ valence band with a fixed energy difference of 0.36 eV independent of layer number and a transition of indirect-to-direct gap when the thickness was decreased to monolayer thickness, $\sim 0.8$ nm. These physical phenomena are very similar to the results in 2D WSe$_2$ sheets peeled by the mechanical exfoliation method of previous studies [27, 28], which further proves that the optical and crystal quality of our WSe$_2$ nanosheets via the VS growth approach is comparable to that by the mechanical exfoliation method.

2. Experimental details

Synthesis of triangular ultrathin WSe$_2$ nanosheets is carried out in a 2 in diameter horizontal tube furnace via a catalyst-free VS growth process (figure 1(B)), using a similar setup to our previous In$_2$Te$_3$ nanowire vapor–liquid–solid (VLS) growth [34]. In brief, WSe$_2$ powder (99.999%, Alfa Aesar) is placed in the center of the tube furnace as the source. Sapphire (001) substrates are placed downstream $\sim 6$ cm away from the source as the deposition acceptors. Before increasing the temperature, the tube is pumped to a vacuum lower than 1 Pa and flushed with Ar gas three times to remove the oxygen residue. Then, under 25 sccm Ar, the furnace temperature is raised to 950°C at a rate of 30°C min$^{-1}$ and is held for 30 min at 950°C for growth. The corresponding temperature is around 940°C at the position $\sim 6$ cm away from the hot center. Finally, the furnace is allowed to cool down to room temperature under Ar gas flow.
The resulting products are characterized by field emission scanning electron microscopy (FESEM, Hitach S-4800), atomic force microscopy (AFM, Veeco Multimode), optical microscopy (OM, Olympus BX51M) and micro-Raman spectroscopy (Renishaw InVia, 532 nm excitation laser). PL measurements of WSe$_2$ samples with various layer numbers are performed (figure 1(C)). The samples are excited using a 325 nm He–Cd laser (Kimmon, ik3301R-G). The PL signals are dispersed by a 550 mm spectrometer (HORIBA Jobin Yvon) and detected by a Si-CCD cooled by liquid nitrogen.

3. Results and discussion

Figure 2(A) shows a typical SEM image of WSe$_2$ nanosheets on a sapphire (001) substrate. Most of the samples clearly exhibit quasi-equilateral triangle shapes, which is consistent with their crystal structures (inset in figure 1(B)). From the magnified SEM image, the equilateral triangle shapes are further confirmed. A typical triangular WSe$_2$ sheet has three similar lateral lengths ($a = b = c = 2.7 \mu m$) and $\sim 60^\circ$ angles between two adjacent sides, as indicated in figure 2(B). It should be noted that the charging effect on insulating sapphire substrates during SEM scanning caused the nonuniform brightness and blurry focus of the e-beam on the sample. The shapes and thicknesses of the samples are further identified by their optical contrast in OM images, as shown in figure 2(C). Similarly to the SEM results, regular quasi-equilateral triangle shapes are observed. The optical contrast is generally dependent on the thickness or layer number of layered nanostructures, which has been used to confirm the layer numbers of graphene and other 2D materials [35]. Remarkably, uniform contrast on most of the individual nanosheets except for the samples indicated by red arrows in figure 2(C), implies they have homogeneous thickness along the entire plane. Figure 2(D) shows the size (side length of the triangle) distribution of a total of 131 pieces of WSe$_2$ 2D sheets obtained from SEM images. The red curve is the corresponding Gaussian fitting. Figure 2(D) explicitly reveals that the lateral dimensions extend from 1 to $5 \mu m$ and the most common size is around $3 \mu m$. In addition, the SEM and OM results also reflect that the VS growth method has high yield.

Among the important features of 2D TMDC nanosheets, atomic thickness layers and pristine surfaces free of dangling bonds make them attractive for high performance electronic devices. This is because intrinsic surfaces can effectively reduce trapping states and roughness scattering, and hence achieve high mobility, and monolayer thickness allows effective charge control by gating the electric field [29]. In order to investigate the thickness distribution and surface roughness, a large number of AFM profile scans were performed; some of them are shown in figures 3(A)–(E). Most of the synthesized WSe$_2$ ultrathin sheets show very flat surfaces and uniform thickness across the lateral plane. Typically, a WSe$_2$ monolayer is $\sim 0.77$ nm thick, as shown in figure 3(A), consistent with previous measurements of monolayers [29, 30]. In addition, thicknesses of 1.67, 2.20, 3.03 and 9.51 nm for 2-, 3-, 4- and 12-layer WSe$_2$ sheets were observed. The histogram of ultrathin WSe$_2$ sheets obtained from a total of 102 AFM measurements reveals that the thickness is mainly distributed in the range below 6 nm (figure 3(F)). In addition, some particles are found to grow at the edges of the WSe$_2$ sheets in figures 3(A)–(E), which is most likely because the active dangling bonds of the boundary atoms can absorb more WSe$_2$ molecules. Recently,
an anisotropic bonding mechanism to grow 2D thin layered materials was proposed [15]. For WSe$_2$ VS growth, the source vapor is initially transported to the sapphire substrate and random nucleation occurs. After nucleation, the source will tend to diffuse to the edges of the nuclei and the crystal will prefer to grow along the lateral dimension. The reason
Figure 5. PL spectra of triangular WSe$_2$ nanosheets. (A) The thickness dependence of normalized PL spectra for WSe$_2$ nanosheets consisting of 1–4-layers and 12-layers. I labels the indirect band gap emission, and A and B label the direct band gap emission. Two weak peaks B and A’ are multiplied by a factor and magnified. PL measurement is performed at 40 K. (B) The peak energy between the A and B transitions as a function of the layer number. (C) The temperature dependence of PL spectra from 70 to 280 K of 2-layer sheets.

for the high growth anisotropy originates from the chemical anisotropy of the atoms at the edges and on the top surface. That is, the edge atoms have active dangling bonds; however, the top surface is passivated with chemically saturated Se atoms.

Raman spectroscopy is a powerful tool to characterize layered nanomaterials. We use a normal unpolarized incident laser to irradiate the WSe$_2$ nanosheets along the ‘c’ axis, as indicated in figures 1(A) and (C). A typical Raman spectrum for one monolayer WSe$_2$ is presented in figure 4(A). Two strong peaks at 160 cm$^{-1}$ and 264 cm$^{-1}$ correspond to the in-plane vibrational E$_{2g}^1$ and out-of-plane vibrational A$_{1g}$ modes, respectively [27]. Intensity Raman maps for the E$_{2g}^1$ and A$_{1g}$ modes on the same monolayer WSe$_2$ are shown in figures 4(B) and (C), respectively. Obviously, the intensity of the A$_{1g}$ mode is greater than that of the E$_{2g}^1$ mode, which is in agreement with the Raman spectrum in figure 4(A). In addition, the uniform distribution of Raman intensity demonstrates that the monolayer surface is homogeneous.

As mentioned above, there should be a transition in WSe$_2$ from indirect bandgap in multilayer to direct bandgap in monolayer [31]. In the Brillouin zone, the indirect bandgap exists between the minimum of the conduction band between the $\Gamma$ and K points and the maximum of the valence band at the $\Gamma$ point, while the direct bandgap is displayed at the K point. Our PL results clearly show the transition in figure 5(A). For the monolayer triangular WSe$_2$ nanosheets, we could see an intense peak A at 750 nm wavelength, which is in agreement with the magnitude of the direct bandgap. As the number of layers increases, peak I appears in the 2-, 3-, 4- and 12-layer triangular nanosheets originating from indirect band gap emission. Meanwhile, peak I actually does not appear in the monolayer PL spectra, demonstrating that the WSe$_2$ bandgap undergoes an evolution from indirect bandgap in multilayer to direct bandgap in monolayer. The emerging peak I would compete with peak A deriving from direct bandgap emission, leading to a decay of the PL quantum efficiency. It should also be noted that peak I reveals a gradual red-shift from 810 to 911 nm with the number of layers increasing. The PL spectra exhibit a prominent dependence on the number of layers and can be comparable with the PL spectra of mechanically exfoliated WSe$_2$ [28], which illustrates the high optical quality of our WSe$_2$ triangular nanosheets. The monolayer triangular WSe$_2$ nanosheets manifest intense emission, whereas the emission intensity decreases strikingly with increase of the number of layers. Meanwhile, the PL spectrum of the monolayer displays a narrow full width at half maximum, of approximately 37 nm, further indicating the high optical quality of the WSe$_2$ triangular nanosheets which are prepared by our VS growth method.
Apart from direct transition peak A and indirect transition peak I, another relatively weak PL peak B (figure 5(A)) with higher emission energy is observed for all of the five sheets. According to the previous reports [28, 31, 36], peak B can be ascribed to the direct transition emission. We find that the energy difference between A and B in all five samples keeps almost a constant level of ∼0.36 eV, as shown in figure 5(B), which suggests that the energy difference is independent of the sample thickness. Recently, Ramasubramaniam et al reported that the spin–orbit coupling interaction in the Brillouin zone leads to the spin–orbit splitting at the K point in the valence band, whose energy separation is about 0.4 eV, reasonably consistent with our results [36]. These results strongly reflect the high optical quality of the WSe₂ triangular nanosheets synthesized by the VS growth method, which is comparable to that by micromechanical exfoliation. Another weak peak A′ is also observed in figure 5(A) and we believe this is caused by the splitting of the ground and excited states of the A transition [37, 38]. The temperature dependence of PL on a 2-layer triangular WSe₂ nanosheet is shown in figure 5(C). Like in most semiconductors, the PL of our WSe₂ sheets decreases in intensity and broadens in peak width, caused by the electron–hole nonradiative recombination and the temperature dependence of the bandgap [39].

4. Conclusion

In summary, for the first time we have demonstrated a facile catalyst-free VS growth method for the synthesis of ultrathin, even monolayer, WSe₂ sheets with high yield, regular shapes and high quality optical properties on sapphire substrates. AFM measurements reveal that the WSe₂ monolayer thickness is ∼0.77 nm and the ultrathin sheets have uniform smooth surfaces, further confirmed by Raman mapping. In addition, by combining a large number of AFM and SEM measurements, we find that the distribution of size and thickness is mainly around 3 µm and below ∼6 nm, respectively. Importantly, we discover the spin–orbit splitting at the K point of the WSe₂ valence band with a fixed energy difference of 0.36 eV independent of layer number and the transition of indirect-to-direct gap when the thickness decreases to monolayer by detailed layer-number-dependent PL measurements at a low temperature of 40 K. These physical phenomena are very similar to the results in 2D WSe₂ sheets peeled by the mechanical exfoliation method, which further proves that the optical and crystal quality of our WSe₂ nanosheets via the VS growth approach is comparable to that by the mechanical exfoliation method. Our efforts may open up new exciting opportunities in future valley-based electronics, optoelectronics and photonics.

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