Vertically oriented few-layered HfS₂ nanosheets: growth mechanism and optical properties

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Abstract
For the first time, large-area, vertically oriented few-layered hafnium disulfide (V-HfS₂) nanosheets have been grown by chemical vapor deposition. The individual HfS₂ nanosheets are well [001] oriented, with highly crystalline quality. Far different from conventional van der Waals epitaxial growth mechanism for two-dimensional transition metal dichalcogenides, a novel dangling-bond-assisted self-seeding growth mechanism is proposed to describe the growth of V-HfS₂ nanosheets: difficult migration of HfS₂ adatoms on substrate surface results in HfS₂ seeds growing perpendicularly to the substrate; V-HfS₂ nanosheets inherit the growth direction of HfS₂ seeds; V-HfS₂ nanosheets further expand in the in-plane direction with time evolution. Moreover, the V-HfS₂ nanosheets show strong and broadened photons absorption from near infrared to ultraviolet; the V-HfS₂-based photodetector exhibits an ultrafast photoresponse time of 24 ms, and a high photosensitivity ca. 10³ for 405 nm laser.

1. Introduction
In contrast to graphene with zero bandgap, group-VIB layered transition metal dichalcogenides (TMDs, general formula MX₂, M = Mo, W, X = S, Se, Te) with sizable bandgaps have attracted more attention because of their unique catalytic activity [1, 2], electrical performance [3, 4] and optoelectronic properties [5, 6]. Compared with group-VIB TMDs, group-IVB TMDs (M = Hf, Zr; X = S, Se, Te) are theoretically predicted to have better electrical and optoelectronic properties [7, 8]. The calculated room-temperature mobility can be above 1800 cm² V⁻¹ s⁻¹ for HfS₂, which is much higher than that of MoS₂ (ca. 340 cm² V⁻¹ s⁻¹) [8].

In spite of their superiority in theoretic prediction, there are only limited experimental researches on HfS₂. Very recently, Kai Xu et al have demonstrated few-layer HfS₂ phototransistors, which exhibit ultra-high photoresponsivity and photogain [9]. They also have demonstrated high-performance top-gate HfS₂ field-effect transistors (FETs) with HfO₂ as dielectric and Al and Y as buffer layer [10]. Toru Kanazawa et al have fabricated few-layer HfS₂ FETs and observed high drain current and mobility [11]. Sang Hoon Chae et al have prepared few-layer AA-stacking HfS₂ FETs display excellent on/off current ratio and reasonable mobility [12]. All HfS₂ flakes used in above studies were mechanically exfoliated from HfS₂ single crystal using the scotch tape technique. The synthesis of large-area high-quality HfS₂ nanosheets still faces a great challenge.

It is noted that numerous studies of synthesis of large-area group-VIB TMD nanosheets have been reported by chemical vapor deposition (CVD) [13–16], which is more facile and efficient than mechanical exfoliation. However, it is extremely difficult to grow HfS₂ nanosheets by CVD, mainly lacking suitable Hf-based precursor compared to synthesize other TMD nanosheets, or mixed products (such as HfOₓ) existing after the reaction. Furthermore, the CVD growth of vertically oriented HfS₂ (V-HfS₂) nanosheets is much...
more difficult. But it is of great significance to grow V-HfS₂ nanosheets with high active surface areas and predominately exposed edges, which will have multifarious applications in hydrogen evolution reactions, lithium-ion batteries, sodium-ion batteries, dye-sensitized solar cells, laser pulse generation and photodetectors, similar to other vertically oriented MX₂ nanosheets [17–22]. Unfortunately, so far, there are no reports on the CVD synthesis of large-area and high-quality HfS₂ nanosheets, not to mention high-quality V-HfS₂ nanosheets; corresponding growth mechanism and applications of CVD grown HfS₂ have never been explored.

To address the issues mentioned above, herein, for the first time, few-layered V-HfS₂ nanosheets with large-area size and highly crystalline quality have been grown by CVD using HfCl₄ as Hf source instead of conventional Hf-based oxide or organic compound source. A novel dangling-bond-assisted self-seeding growth mechanism is proposed to describe the growth of V-HfS₂ nanosheets, far different from conventional van der Waals epitaxy for 2D TMDs. Furthermore, the V-HfS₂-based photodetectors exhibit excellent ultrafast photoresponse and high photosensitivity.

2. Results and discussion

Unlike most of CVD synthesis of TMDs, the hafnium dioxide (HfO₂) was not considered a reactant as hafnium source since the evaporation temperature of HfO₂ is prohibitively high (ca. 2500 °C). Instead, we chose hafnium tetrchloride (HfCl₄) with a low sublimation temperature (317 °C) as precursor by reference to monolayer and few-layer MoS₂ [23] and ZrS₂ [24, 25] prepared by the reaction of chloride and sulfur under appropriate conditions. Figures 1(a)–(b) typically illustrates the low-pressure CVD setup for V-HfS₂ nanosheets synthesis in a two-zone furnace and typical growth conditions. In the growth process with argon and hydrogen flowing, the substrates were placed at the second heating zone of furnace at temperature of 950 °C. To avoid unintended reaction of sulfur evaporation and HfCl₄ powder, the quartz boats loaded with HfCl₄ powders and sulfur pieces were respectively put inside two smaller quartz tubes and placed at the first heating zone of the furnace at temperature of 160 °C. The heating temperature of source is determined by the point where the vapor pressure data lines intersect in the inset of figure 1(b), which is calculated in supporting information. By designing the same vapor pressure, the evaporation of source is more controllable, which depends only on the amount of precursor and the flow rate of carrier gas (see experimental section for optimized synthesis parameters). It is notable to point out that hydrogen is essential in the sulfurization of HfCl₄, which is different than sulfurization of WCl₆ [26], MoCl₃ [23, 26] and ZrCl₄ [24]. In our experiment, V-HfS₂ cannot be obtained if there is no hydrogen gas served as the strong additional reductant. The possible reaction formulation is as follows

$$\text{HfCl}_4(\text{g}) + 2\text{S}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{HfS}_2(\text{g}) + 4\text{HCl}(\text{g}).$$

Figure 1(c) shows an optical image of large-area V-HfS₂ nanosheets grown on a ca. 5 cm × 1 cm SiO₂/Si substrate. The as-grown V-HfS₂ appears a homogeneous yellow-green color, demonstrating its good uniformity and continuity via our CVD method.

With the purpose of investigating the morphology, crystalline structure and elemental composition of the as-grown V-HfS₂ nanosheets on SiO₂/Si substrate, a series of characterization techniques were used including scanning electron microscope (SEM), energy dispersive x-ray spectroscopy (EDX), Raman spectroscopy, x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS). As demonstrated clearly in figures 2(a)–(b), the surface structure of the as-grown HfS₂ are composed of vertically oriented nanosheets with uniform thickness (along c-axis direction) of ca. 10 nm, height (perpendicular to substrate) of ca. 400 nm and width (parallel to substrate) of ca. 1 μm. We can figure out the existence of Hf and S elements with an atom ratio of 1:2.2 from EDX shown in the inset of figure 2(b), which is very close to the ideal value for HfS₂. The Raman spectrum is shown in figure 2(c). Apparently, excepting for Si peak at 520 cm⁻¹, there are two peaks located at ca. 259 and 337 cm⁻¹, corresponding to E₂g mode which caused by the vibration of the S atoms in the basal plane, and A₁g mode which is consequence of the S atoms vibration out of the basal plane, respectively. The spectrum agrees well with the previous experimental studies of bulk [27, 28] and few-layered HfS₂ [9–12], and no additional peaks are observed. XRD was used to characterize the crystalline structure of V-HfS₂. As shown in figure 2(d), excepting diffraction peak at 2θ = 33.1° and 69.2° ascribed to the substrate of Si (200) and (400), we observed only (00l) diffraction peak of HfS₂ at 2θ = 15.1°, 30.5°, 46.6° and 63.5°, corresponding to (001), (002), (003) and (004) of HfS₂ (ICPDS card No.28-0444), respectively. It indicates that individual HfS₂ nanosheets are highly [001] oriented, as the same as reported of another 1T-structure ReS₂ nanosheets with vertically oriented structure [29]. The narrow and sharp diffraction peaks, all with <0.3° full-width-at-half-maximum (FWHM) values, indicate the highly crystalline quality of the as-grown V-HfS₂ nanosheets. The atomic model of 1T-HfS₂ is shown in the inset of figure 2(d), in which each layer consists of three atomic planes in the sequence of S–Hf–S with interlayer distance of is 0.585 nm calculated by XRD. The elemental and bond composition of V-HfS₂ was examined by the XPS measurements. Peaks are observed at 17.8 eV, 16.1 eV, 162.0 eV and 160.8 eV, corresponding to the Hf 4f₇/₂, Hf 4f₉/₂, S 2p₁/₂ and 2p₃/₂, respectively (figure 2(e)) [30]. All above
confirmed that the vertically oriented nanosheets grown via our CVD system are HfS$_2$ with highly crystalline quality. Based on previous report [31], 2D materials with thin and vertically oriented structure could serve as an ideal material for energy storage, catalysis, detector or edge emitter devices because of the
high active surface areas and predominately exposed edges. Therefore, it is reasonable that the V-HfS$_2$ nanosheets have similar potential multifarious applications in such fields.

In order to understand how and why the vertically oriented few-layered hafnium disulfide nanosheets grow, the growth evolution of V-HfS$_2$ were investigated. The time of growth was precisely controlled and set at 1, 3, 5, 10, 15 and 20 min. It is noticed that the surface color of the as-grown film on SiO$_2$/Si substrate changes from magenta, purple, cerulean, cyan, chartreuse to olive with increasing growth time from 1 to 20 min (figures 3(a)–(f), top right corner). Empirically, the blue shift of color is caused by increasing amount of V-HfS$_2$. This speculation is verified by the subsequent SEM and Raman analysis. As shown in figure 3(a), an ultrathin flat layer, instead of vertically oriented HfS$_2$ nanosheets, was observed. And a weak Raman peak located at 337 cm$^{-1}$, which belongs to A$_{1g}$ of HfS$_2$, was also noticed. That means, at the beginning of growth, HfS$_2$ indeed exists in some form rather than nanosheet perpendicular to the growth substrate. After growing for 3 min (figure 3(b)), vertically oriented nanosheets start to appear, along with the enhancement of A$_{1g}$ peak which exceed the intensity of 2TA(X) peak at 302 cm$^{-1}$ and LO(X) peak at 433 cm$^{-1}$ corresponding to Si substrate [32]. When the growth time reaches 5 min (figure 3(c)), the density of V-HfS$_2$ increases and the weak E$_g$ peak of HfS$_2$ at 259 cm$^{-1}$ emerges. Then, with the extended the growth time (figures 3(d)–(f)), V-HfS$_2$ nanosheets become larger and larger in the in-plane direction prominently, as the same of the surface coverage of V-HfS$_2$ on SiO$_2$/Si substrate. Meanwhile, the FWHM of the A$_{1g}$ peaks decrease from 14.7 to 10.3 cm$^{-1}$ (figure S1), which is attributed to a larger crystallite size and a smaller amount of defects [33, 34]. The location positions of A$_{1g}$ and E$_g$ keep unchanged and A$_{1g}$/E$_g$ intensity ratios remain approximately constant at 0.09. One can see that few HfS$_2$ nanosheets have hexagonal shape (yellow arrows in figure 3(e)), suggesting the vertical growth rate is near equilibrium but can be further optimized [35]. The sheet size evolution of V-HfS$_2$ visualizes the growth process and reveals two forms of HfS$_2$ during development.

For further studying the growth mode and explore the growth mechanism of V-HfS$_2$, the morphologies, crystalline structures and element composition of the sample, which was at intermediate stage (sample grown for 15 min) with both vertically oriented and the other form of HfS$_2$ simultaneously, were characterized. Figure 4(a), matching up with figure 3(c), shows HfS$_2$ nanosheets arrange themselves perpendicularly to the bottom layer which is invisible in the SEM images. Larger-magnification TEM (figure 4(b)) reveals that the bottom layer is consisted of nanoparticles which may be the other form of HfS$_2$. The high-resolution transmission electron microscopy (HRTEM) image in figure 4(c), corresponding to the region 1 marked in figure 4(b), shows a typical edge view of approximately 6-layer V-HfS$_2$ nanosheets with clear lattice fringes. The interlayer spacing is measured to be 0.59 nm, corresponding to (001) plane of 1T-HfS$_2$ which is consistent with the result calculated from XRD. The diffraction pattern in the fast Fourier transform (FFT) image of HfS$_2$, lying on the bottom layer

**Figure 3.** Sheet size evolution of V-HfS$_2$ during the growth process. SEM images of V-HfS$_2$ nanosheets synthesized on SiO$_2$/Si substrate with growth time of (a) 1 min, (b) 3 min, (c) 5 min, (d) 10 min, (e) 15 min, and (f) 20 min. The insets in the top right corner are corresponding color optical images, in the bottom right corner are corresponding Raman spectra, respectively.
(yellow square in figure 4(c)), is shown in the top right of figure 4(d) with the (100), (010) and (−110) planes labeled in the reciprocal lattice. It indicates that the HfS₂ nanosheet is of hexagonal structure and high crystallinity. The inverse FFT reconstruction from FFT pattern is given in the top left of figure 4(d). It clearly shows a hexagonally symmetric lattice structure, and corresponding 1T-HfS₂ structure model is well overlapped. The distance between the two peaks in the line intensity profile shown in the bottom of figure 4(d) is ca. 0.362 nm, which matches well with the value of the unit cell parameter of HfS₂. Figure 4(e) is HRTEM of the nanoparticles which compose the bottom layer, corresponding to the region 2 marked in figure 4(b). The lattice figures located at the edge of nanoparticles demonstrate a structure consisting of bent planes with lattice spacing of 0.59 nm, which correspond to HfS₂ (001) planes. Lager-magnification HRTEM image of the denoted red window in figure 4(e) is given in figure 4(f). It distinctly indicates the nanoparticle is edge-oriented HfS₂ as demonstrated by the schematic structure model overlapped. Combining edge-oriented structure with approximate circle shape, two conceivable models of the nanoparticles, the other HfS₂ form, are illustrated in the inset of figure 4(f): edge-oriented closed and not-yet-closed polygonal nanoplates. The model of fullerene-like sphere is not suitable due to taking consideration of that the layer consisted of nanoparticles should have observable thickness of ca. 60 nm if the nanoparticles are near-spherical, but the fact is that the layer has hardly any thickness in the SEM image comparing with 300 nm SiO₂ layer. EDX compositional mappings of Hf, S, Cl and O distributions within HfS₂ nanoparticle are shown in figure 4(g). Referencing HRTEM image of HfS₂ nanoparticle, Hf and S elements distributions are essentially homogeneous, Cl element is hardly to observe, and very little O element is distributed to the whole area due to absorption of oxygen and slight oxidization of HfS₂, which is reflected in ratio of Hf/S (1:1.8) from EDX spectrum and caused by transfer process to TEM gird. This result of EDX analysis is different from the growth mechanism of TMD monolayers (self-seeding fullerene nuclei) reported recently [36], the nanoparticle is not composed of a partially sulfurized hafnium tetrachloride, HfS₄Cl₄−x, or partially sulfurized hafnium dioxide, HfO₂−x, wrapped in a fullerene-like shell of HfS₂. But the mechanism in our experiment can also be deduced as ‘self-seeding’, in which HfS₂ nanoparticles act as the seed or buffer layer for the growth of vertically oriented HfS₂ nanosheets. It is noticed that the gaps between nanoparticles, bright area in figure 4(g), are not distributed any Hf or S elements. It means no horizontal HfS₂ film grown on the seed or buffer layer, consequently, the vertical growth mechanisms of TMDs based on horizontally aligned layers, such as the hierarchical growth [21], bending-growth resulted from fracturing of layers [37], collision and up-curving between two islands [38] are not suitable for our synthesis process.

To better understand the growth mechanism, the schematic illustration for the growth of V-HfS₂ nanosheets is shown in figure 5. Firstly, at the original
reaction stage (i), the vapor of HfCl₄, sulfur and hydrogen reacted to form HfS₂ species, which diffuse onto substrates simultaneously. Then, the HfS₂ species adsorbed on substrate try to migrate to form HfS₂ nanostructure. However, the existence of dangling bonds at the surface of SiO₂/Si substrate increase the energy barrier for migration of HfS₂ adatoms along the substrate surface [39]. In addition, the surface migration strongly depends on the interaction of the adatoms with substrate and the concentration gradient of the adatoms [40]. Thereby, the large interlayer interaction energy of 1T-HfS₂ (1.33 eV/primitive cell), which is much larger than MoS₂ (ca. 0.46 eV/primitive cell) [12], and low diffusion flux of gaseous HfS₂ species form the vapor phase at the beginning of reaction seriously shorten the migration length, leading to vertical growth. Subsequently, at the self-seeding state (ii), in the absence of strong interaction forces, the individual HfS₂ layers prefer to bend to form closed structures in order to decrease the number of marginal dangling bonds and the total energy of the system. The height of HfS₂ nanoparticles is restricted in limited nucleation time before the nanoparticles cover the whole surface of SiO₂/Si substrate. At the preliminary vertical growth stage (iii), the exposed dangling bonds at the top surface edges of HfS₂ nanoparticles act as growth sites for growing of vertically oriented HfS₂ nanosheets, which inherit the growth direction from HfS₂ seeds. The growth kinetics changes from on-substrate migration to on-nanoplate migration [40], the HfS₂ adatoms on surface of HfS₂ nanoparticles migrate to the growth sites and are incorporated into crystal lattice of HfS₂ nanosheets. Afterwards, with abundant flux of HfS₂ species, the HfS₂ nanosheets expand prominently in in-plane direction at the extension stage (iv). Distinguishing from conventional two-dimensional TMD materials growth, which is parallel to substrate and based on van der Waals epitaxy, the novel growth of HfS₂ perpendicular to substrate is based on dangling bonds at the surface of substrate and the edges of self-seeding layer. In-depth experimental work will be needed to further elucidate this mechanism.

To explore the potential applications for V-HfS₂, the optical properties of V-HfS₂ have been further studied. Figure 6(a) shows the UV–vis absorption spectrum of V-HfS₂ nanosheets transferred on optical quartz by fast dry-transfer process. Compared to quartz substrate, two peaks located at 3.2, and 6.2 eV and two slight shoulders located at 2.9, and 5.2 eV are observed, corresponding to E₂, E₄, E₁, E₃ optical gaps of HfS₂, respectively [41]. The optical transitions in the absorption edges are contributed to the indirect allowed transitions with strongly excitonic effects [42]. The photons absorption of V-HfS₂ nanosheets from near infrared to ultraviolet makes them potential.

Figure 5. Schematics for the growth of V-HfS₂ nanosheets. (i) Original reaction stage. (ii) Self-seeding stage. (iii) Preliminary vertical growth stage. (iv) Extension stage.
candidates for solar cell applications. Figure 6(b) shows the top of valence band and bottom of conduction band of mono-, bi-, tri-, quad-layer and bulk HfS$_2$ data extracted from calculated band structures (figure S2), respectively. The direct excitonic transitions occur at $\Gamma$ point and the indirect from $\Gamma$ point to M point. With reduced layer thickness, both direct and indirect bandgap become larger, from 2.71 to 3.01 eV and 1.74 to 2.27 eV, respectively. That means different thickness distribution of few-layered HfS$_2$ nanosheets broadens the absorption range, which is consistent with our absorbance spectrum. The strong optical absorption based on direct and indirect transitions suggests that V-HfS$_2$ has potential applications in optoelectronic devices.

As a typical application example, here the V-HfS$_2$ photodetectors was fabricated. Unlike MoS$_2$ or WS$_2$, HfS$_2$ thin film is easily oxidized under ambient conditions [12]. To prevent HfS$_2$ from oxidation, the fast dry-transfer approach is more appropriate than the traditional PMMA-assisted wet-transfer method. Figure S3 illustrates the schematics of the dry-transfer process using thermal release tape. In brief, firstly, the tape was stuck on the surface of as-grown V-HfS$_2$, then the tape was peeled off with V-HfS$_2$ from the growth substrate and pressed onto the target substrate, i.e. gold interdigitated electrode on SiO$_2$/Si substrate. After that, the target substrate was placed on a hotplate at 120 °C. The tape lost the adhesion and automatically degummed, leaving the V-HfS$_2$ on the target substrate. The total time spend in try-transfer approach is less than 5 min so that to keep the sample from being oxidized during fabrication as possible.

Figure 6(c) shows the long-term stability and repeatability of V-HfS$_2$ photodetector with periodically turning on and off of a commercial laser pointer (wavelength 405 nm, power 5 mW, spot size 0.2 cm$^2$, power density ca. 250 W m$^{-2}$) at the voltage of 1 V. The enlarged portion of one single photoresponse cycle is given in figure 6(d), which demonstrates a low off state current of ca. 1.5 pA and a high on state current of ca. 1.2 nA. The device exhibits high photosensitivity to 405 nm laser with a large on/off ratio of ca. 10$^3$, a comparable value to the reported HfS$_2$ phototransistor without gate voltage [9]. As expected, In figure S4, the on/off ratio of device illuminated by 405 nm (3.1 eV) is larger than 532 nm (2.3 eV) and 650 nm (1.9 eV) laser, matching with the UV–vis absorption spectrum. More uplifting is the rise and fall times are both as short as 24 ms, limited by the precisions of measurement, demonstrating an ultrafast response and recovery performance. It is noticed that the rise time is shorter than photodetector based on mechanically exfoliated HfS$_2$ nanosheets without gate
3. Conclusions

In summary, we have successfully synthesized large-area, vertically oriented few-layered HfS$_2$ nanosheets with well [001] textured and highly crystalline quality by CVD. The dangling-bond-assisted self-seeding growth mechanism was presented. UV–vis absorption spectrum indicates that the V-HfS$_2$ has strong optical absorption based on direct and indirect transitions, suggesting that it has potential applications in optoelectronic devices. The photodetectors based on V-HfS$_2$ nanosheets exhibited high photosensitivity to 405 nm laser with a large on/off ratio of ca. 10$^3$ and ultrafast response performance with rise and fall times of 24 ms. The high active surface areas and predominately exposed edges may make V-HfS$_2$ nanosheets potential multifarious applications in the field of energy storage, catalysis, detector or edge emitter.

4. Methods

4.1. Synthesis of V-HfS$_2$ nanosheets

Typically, Single crystal silicon substrates with a thermally deposited 300 nm thick silicon oxide layer (SiO$_2$/Si) were ultrasonically cleaned for 5 min with acetone, ethyl alcohol and deionized water, respectively. After drying with compressed nitrogen gas, the substrates were put inside 1 inch quartz tube and placed at the first heating zone of the furnace. Two quartz boats loaded with 100 mg hafnium chloride (HfCl$_4$) powders (99.9%, Alfa Aesar) and 200 mg sulfur pieces (99.999%, Alfa Aesar) were respectively put inside two small quartz tubes and placed at the second heating zone of the furnace. The pressure in the chamber was reduced to 4 × 10$^{-3}$ Pa, and then, argon (10 sccm) and hydrogen (10 sccm) were pumped into the tube, reaching a pressure of 18 Pa, which keeps unchanged during the growth of V-HfS$_2$ nanosheets. The first heating zone was kept at room temperature before the second heating zone getting close to 950 °C and then heated to a temperature of 160 °C with heating rate of 25 °C min$^{-1}$ as fast as the second heating zone. After growing for 20 min, all heating was stopped and the furnace was opened immediately, then the quartz tube was taken out to rapidly cool down.

4.2. Calculation details

The calculations were performed mainly with pseudo-potential code PWscf [44], with the van der Waals density functional module to treat van der Waals interaction between layers [45]. The generalized gradient approximation functional was parameterized by Perdew, Burke, and Ernzerhof [46]. The plane-wave kinetic energy cutoff was set to 70 Ry with the density cutoff 700 Ry, and shifted 15 × 15 × 1 Monkhorst–Pack meshes for the layered structures and 15 × 15 × 13 for the bulk were used to perform Brillouin zone integration in order to ensure the convergence of the results. The convergence of the total energy was set to be better than 10$^{-9}$ Hartree. A vacuum layer with thickness of 30 Å was used to model the 2D-nature of the compounds.

4.3. Device fabrication

To fabricate the HfS$_2$ photodetector, a Gold interdigitated electrode with a finger width and an inter-finger spacing of ca. 200 μm was firstly patterned on SiO$_2$/Si substrate by electron beam evaporation using metal hard mask, and then HfS$_2$ nanosheets were transferred to Au interdigitated electrode using dry transfer assisted by thermal release tape (Notto Denko No. 3193MS, 7.3 N mm$^{-1}$).

4.4. Characterizations

The morphology and composition investigations were examined by SEM (JEOL JSM-7000F) with an EDX and TEM (FEI Tecnai F20 at 200 kV). TEM samples were prepared by scraping the as-grown V-HfS$_2$ off the substrate, then sending them to ethanol and drop-drying onto TEM grids. The crystalline structure of the obtained samples was characterized by XRD (Jordan Valley D1 Evolution) using Cu Kα radiation and HRTEM. Raman spectra were acquired at room temperature with an excitation laser line of 514.5 nm (Renishaw inVia Reflex). The electronic structure was performed by XPS (Kratos AXIS-Ultra). The UV–vis absorption was measured with spectrophotometer (Shimadzu UV-2550). The data of photocurrent were recorded using a semiconductor parameter analyzer (Agilent 4155B) at room temperature and atmospheric pressure.

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