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## ARTICLE OPEN

Strong interlayer hybridization in the aligned SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer structureJihene Zribi<sup>1</sup>, Lama Khalil<sup>1</sup>, Biyuan Zheng<sup>2</sup>, José Avila<sup>3</sup>, Debora Pierucci<sup>4</sup>, Thibault Brulé<sup>5</sup>, Julien Chaste<sup>6</sup>, Emmanuel Lhuillier<sup>6</sup>, Maria C. Asensio<sup>7</sup>, Anlian Pan<sup>2</sup> and Abdelkarim Ouerghi<sup>1</sup>

The combination of monolayers of different two-dimensional (2D) materials into van der Waals hetero-bilayer structures creates unprecedented physical phenomena, acting as a powerful tool for future devices. Understanding and exploiting these phenomena hinge on knowing the electronic structure and the hybridization of hetero-bilayer structures. Here, we show strong hybridization effects arising between the constitutive single layers of a SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer structure grown by chemical vapor deposition. Surprisingly, the valence band maximum position of WSe<sub>2</sub> is moved from the K point for the single layer WSe<sub>2</sub> to the  $\Gamma$  point for the aligned SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer. Additionally, a significant photoluminescence quenching is observed for the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer structure with respect to the WSe<sub>2</sub> monolayer. Using photoluminescence spectroscopy and nano-angle-resolved photoemission spectroscopy techniques, we demonstrate that the SnS<sub>2</sub>/WSe<sub>2</sub> heterostructure present a type-II band alignment. These findings directly answer many outstanding questions about the electronic band structure and the band offset of SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayers for envisaging their applications in nanoelectronics.

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## INTRODUCTION

Two-dimensional (2D) layered semiconductors with few atomic layer thicknesses and tunable bandgaps have attracted a significant interest in the last years. Particularly, 2D transition metal dichalcogenides (TMDs) (e.g. tungsten diselenide WSe<sub>2</sub>) possess a high carrier mobility<sup>1</sup> and several spin properties,<sup>2–4</sup> and are made of an ordered stacking of building blocks. These 2D TMD materials constitute promising candidates for the study of novel physical phenomena and functionalities in electronics,<sup>4</sup> photonics, and superconductivity.<sup>5</sup> By combining individual monolayers (MLs) of different 2D layered materials in a van der Waals (vdW) heterostructure, presenting sharp interfaces at the atomic scale, one can tailor the energy band alignment. This opens up vast opportunities for fundamental investigations of novel electronic and optical properties. Therefore, most of the recent research in the field of 2D TMDs has been focused on TMDs/TMDs or TMDs/graphene heterostructures.<sup>6,7</sup>

Among the 2D materials, tin disulfide (SnS<sub>2</sub>) has an atypical band structure, being a IV–VI semiconductor in which each layer of Sn atoms is sandwiched between two layers of S atoms; the weakly coupled layers in SnS<sub>2</sub> interact with each other through vdW interactions. Note that SnS<sub>2</sub> is an earth-abundant, and a low-cost and an environmentally friendly material. In its bulk form, SnS<sub>2</sub> is extensively studied mostly for photovoltaics.<sup>8</sup> As a 2D TMD, SnS<sub>2</sub> is interesting since it exhibits high carrier mobility<sup>9,10</sup> and a strong excitonic effect (binding energy of ~0.9 eV for a single layer).<sup>11</sup> The electronic band structure of SnS<sub>2</sub> has been investigated in several DFT studies showing that in contrast to

TMDs, the indirect to direct band gap transition for SnS<sub>2</sub> does not occur from bulk down to a single layer.<sup>11,12</sup> This has been experimentally confirmed by Huang et al.<sup>12</sup> through layer-dependent photoluminescence (PL) and band structure measurements of bulk SnS<sub>2</sub>. However, the electronic band structure of a single layer of SnS<sub>2</sub> has not been measured yet.

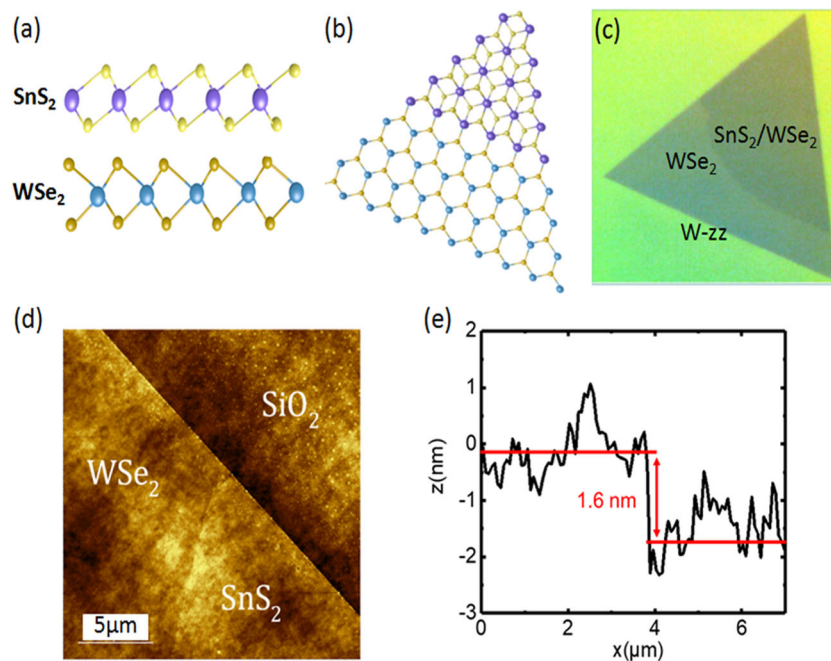
The SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayers have started to attract a great attention,<sup>13</sup> in order to combine the various characteristics of SnS<sub>2</sub> and WSe<sub>2</sub> single layers. Different methods have been used to obtain this heterostructure. For example, mechanically exfoliated few-layer/few-layer stacked WSe<sub>2</sub>/SnS<sub>2</sub> heterostructures with an anti-ambipolar behavior have been reported by Wang et al.<sup>14</sup> In addition, Zhang et al.<sup>15</sup> have demonstrated the possibility of growing few layers of WSe<sub>2</sub> on micro-plates of SnS<sub>2</sub> randomly oriented. More recently, Yang et al.<sup>13</sup> have employed a two-step vapor phase route to grow WSe<sub>2</sub>/SnS<sub>2</sub> flakes, having the largest size of atomic layered vertical heterostructures with a lateral size reaching up the millimeter scale. According to its band alignment, 2H-SnS<sub>2</sub>/2H-WSe<sub>2</sub> is a type II heterostructure characterized by the high efficiency of charge separation.<sup>14,16</sup> Devices based on this type of vdW heterostructures have shown improved optoelectronic performances.<sup>16</sup> Note that electrical transport measurements and optical characterizations have revealed that the direct growth of high-quality vdW heterostructures is promising for the obtainment of high-performance integrated optoelectronic devices.<sup>13</sup>

In order to realize vdW heterostructures promoted by weakly bonded layered structure of these 2D materials, mechanical

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**Fig. 1** Crystal structure, and optical and AFM images of  $\text{WSe}_2$  single layer and  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer: Schematic **a** side and **b** top views of the atomic structure of the vertically stacked  $\text{SnS}_2/\text{WSe}_2$  vdW heterostructure. **c** A zoomed-in optical image of one flake, in which the formation of the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer is clearly visible. **d** AFM image of the  $\text{SnS}_2/\text{WSe}_2$  heterostructure. **e** The height profile indicates that the thickness of the heterostructure is 1.6 nm (1 ML  $\text{WSe}_2$  + 1 ML  $\text{SnS}_2$ ). The AFM study shows the successful preparation of a vertical heterostructure

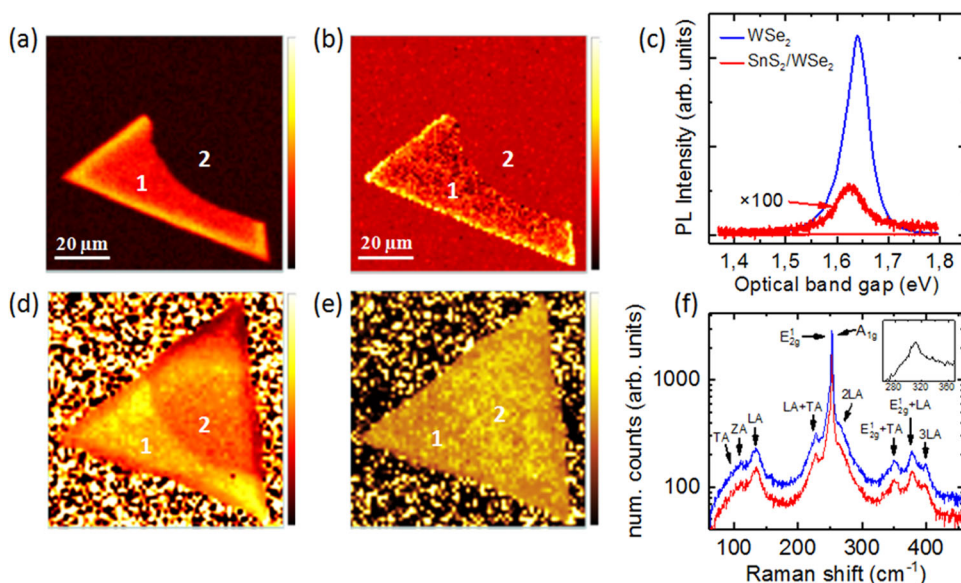
exfoliation has been largely used as one of the most appropriate fabrication techniques. However, by using this method, the stacking orientation cannot be precisely controlled and the interface is easily contaminated.<sup>17,18</sup> To avoid these limitations, chemical vapor deposition (CVD) is employed as an alternative growth method for the scalable synthesis of high-quality atomic layered vdW heterostructures with well-defined interlayer orientations and clean interfaces. In this paper, we probe the electronic structure of the hetero-bilayer  $\text{SnS}_2/\text{WSe}_2$  heterostructure, grown via the CVD technique, with microscopic Raman ( $\mu$ -Raman)/PL spectroscopy and nano angle-resolved photoemission spectroscopy (nano-ARPES). For this heterostructure, a type II band alignment was measured with an optical bandgap of about 1.65 eV. Since it is straightforward to evaluate if the constitutive single layers of the heterostructure retain their electronic properties after the layer stacking or they are strongly perturbed, we have investigated the punctual band structure of selected areas on our sample. Specifically, we have provided a precise electronic characterization for the  $\text{WSe}_2$  single layer and the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer structures, which are actually simultaneously present on the same flake after the growth. For the first time, through our nano-ARPES measurements, we provide a direct experimental evidence of a strong electronic band hybridization for the aligned  $\text{SnS}_2/\text{WSe}_2$  heterostructure. In particular, we demonstrate that the valence band maximum (VBM) of  $\text{WSe}_2$  changes its position in the Brillouin zone (BZ) from the K to the  $\Gamma$  point when moving from the single layer to the hetero-bilayer structure. A significant PL quenching was also observed for the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer structure with respect to the  $\text{WSe}_2$  monolayer.

## RESULTS AND DISCUSSION

2H- $\text{SnS}_2/2\text{H-WSe}_2$  heterostructures were grown via two-step CVD (see Materials and Methods and ref. <sup>13</sup>). Single layer  $\text{WSe}_2$  flakes were first grown on  $\text{SiO}_2/\text{Si}$  substrates. Then, these structures were used as templates for the subsequent growth of single layers of

$\text{SnS}_2$  to form the vertical hetero-bilayer structures of  $\text{SnS}_2/\text{WSe}_2$ . A schematic side and top views of the atomic structure of the flakes are presented in Fig. 1a, b, respectively. The large lattice mismatch between  $\text{SnS}_2$  and  $\text{WSe}_2$  (14.3%) indicates that the bonding between adjacent layers is principally of the vdW type.<sup>19,20</sup> This lattice mismatch leads to a periodic variation of atomic registry between individual van der Waals layers, exhibiting a Moiré pattern with a well-defined periodicity. Figure 1c illustrates a typical zoomed-in optical image of one flake, in which the formation of the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer is clearly visible. The thickness of the triangular crystals was determined by the height profiles obtained from atomic force microscopy (AFM) (see Fig. 1d, e).<sup>13</sup> Based on the optical image, we can clearly conclude that atomically thin flakes, possessing triangular shapes and sharp edges, are formed on top of the  $\text{SiO}_2/\text{Si}$  substrate through the CVD process. These triangular flakes are only composed of one edge termination, namely, the W-zz termination.<sup>21</sup> It should be pointed out that truncated triangular flakes can also be readily detected on the edges of our specimens. This modification in the shape of the flakes is a common phenomenon for the single layer of 2D materials synthesized by means of the CVD method,<sup>22,23</sup> and is mainly due to structural differences in the edges of the flakes and to the local difference in the growth rates.<sup>22</sup> It is noteworthy that the irregular evolution of the  $\text{SnS}_2$  edge with respect to  $\text{WSe}_2$  edge could be related to the presence of distinct seeding centers, which affect the growth kinetics of the CVD growth of  $\text{SnS}_2$  on  $\text{WSe}_2$ .<sup>24</sup>

To probe the details of light emission obtained from the  $\text{WSe}_2$  and  $\text{SnS}_2/\text{WSe}_2$  domains,  $\mu$ -PL spectroscopy was carried out on the microscopic flake of Fig. 1c, using a 532 nm laser excitation. The measured PL maps and spectra are reported in Fig. 2. In Fig. 2a, b, we present PL intensity and peak position mapping images obtained from the triangular flake with their corresponding intensity and energy scales on the right, respectively. At first sight, we clearly remark that the  $\text{WSe}_2$  regions reveal a higher PL intensity than the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer domains (Fig. 2a). This is confirmed by comparing their corresponding PL spectra



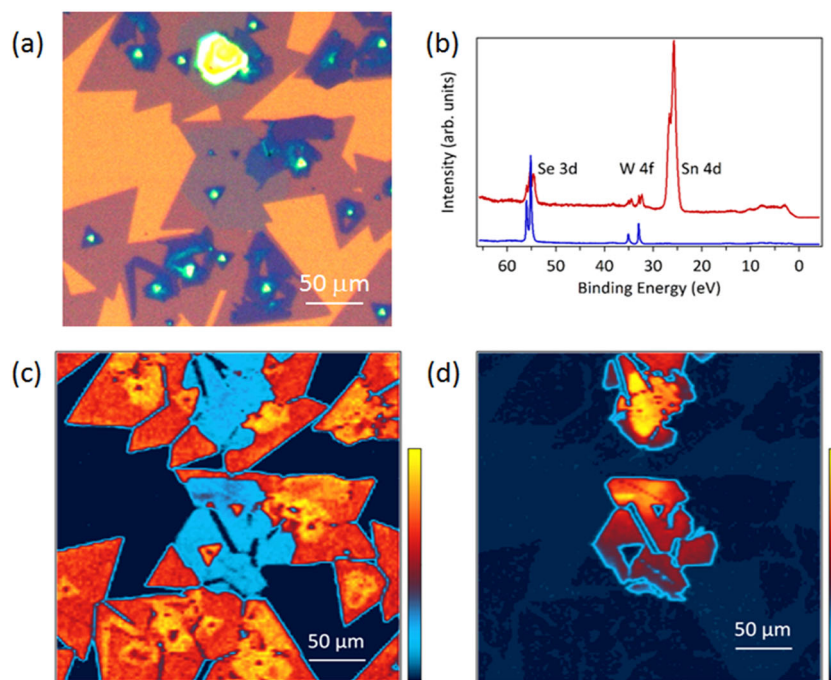
**Fig. 2** Photoluminescence and Raman spectroscopy on the heterostructure: **a, b** PL intensity and peak position mapping images obtained from the as-grown triangular flake in Fig. 1c and acquired with a 532 nm laser excitation. **c** Typical PL spectra, obtained from the WSe<sub>2</sub> ML region (blue curve) and from the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer domain (red curve). The PL intensity acquired from the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer structure has multiplied by a factor of 100 in order to visualize the signal. **d, e**  $\mu$ -Raman peak position and intensity maps of the same flake, acquired at room temperature with a laser beam generating 532 nm photons. **f** Typical Raman spectra taken from WSe<sub>2</sub> (blue curve) and the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer (red curve). Inset: Raman spectrum obtained after a long time integration on the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer domain. A small peak, visible at 310 cm<sup>-1</sup> and attributed to the A<sub>1g</sub> mode of SnS<sub>2</sub>, is detected

obtained from two specific points 1 and 2 representative of the distinct regions (see Fig. 2c). Actually, for the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer region, we detect a drastic PL quenching with respect to the uncovered WSe<sub>2</sub> single layer (see Fig. 2c); the intensity of the peaks differs at least by a factor of 200. This significant PL quenching could be related to an interlayer interaction between SnS<sub>2</sub> and WSe<sub>2</sub>, which leads to a strong photo-induced electron transfer from WSe<sub>2</sub> to SnS<sub>2</sub>,<sup>25,26</sup> hindering the recombination of electron-hole pairs created by the photoexcitation. Another more probable scenario explaining the PL quenching is a predicted WSe<sub>2</sub> bandgap transition from a direct to an indirect gap after the increase of the number of layers. This strongly affects the PL emission, as in our case. Since the interlayer coupling in our clean heterostructure is very strong due to the perfect crystalline orientation,<sup>4</sup> a ruthless modification of the WSe<sub>2</sub> electronic band structure could lead to the appearance of an indirect bandgap, providing this PL intensity drop (this will be further discussed in the next paragraphs).

To learn more about the electronic properties of the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-layer structure, we have conducted a  $\mu$ -Raman spectroscopy study. This technique has been widely used to study 2D materials, in order to determine the number and the stacking sequence of layers, as well as the external field, the molecular doping and the strain effects. Figure 2d, e show the respective  $\mu$ -Raman peak position and intensity mapping images of the as-grown triangular flake of Fig. 2a, acquired at room temperature with a 532 nm laser excitation. These maps reveal that a downshift of the peak positions and a slight variation in the peak intensities are observed when moving to the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer region. Moreover, in Fig. 2f, we present Raman spectra taken from two different points labeled 1 and 2 on the WSe<sub>2</sub> and the SnS<sub>2</sub>/WSe<sub>2</sub> domains. Beside the first order modes in the center of the BZ: the in-plane phonon mode E<sub>2g</sub><sup>1</sup>, expected at 206 cm<sup>-1</sup> for SnS<sub>2</sub><sup>11</sup> and at 249.5 cm<sup>-1</sup> for WSe<sub>2</sub>, and the out-of-plane phonon mode A<sub>1g</sub>, expected at 305 cm<sup>-1</sup> for SnS<sub>2</sub> and at 249.5 cm<sup>-1</sup> for WSe<sub>2</sub> (E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> are degenerated modes for WSe<sub>2</sub> single layer), the Raman spectra present a series of overtone and combination peaks.<sup>27</sup> In particular, we notice in our measurements the ZA(M) at

109 cm<sup>-1</sup> or the TA(M) expected at 100 cm<sup>-1</sup>, the LA(M) at 133 cm<sup>-1</sup>, a Raman mode due to LA phonons at the M point of the BZ zone, the combination of LA(M) and TA(M) at 227 cm<sup>-1</sup>, the second order harmonic 2LA (M) mode at 266 cm<sup>-1</sup>, and the third order LA(M) mode at 401 cm<sup>-1</sup>. Additionally, we can detect Raman peaks at 352 and 378 cm<sup>-1</sup>, which constitute combination modes between LA(M), TA(M) or ZA(M), with E<sub>2g</sub><sup>1</sup> ( $\Gamma$ ) modes. From the Raman spectra of Fig. 2f, we can conclude that the Raman peak amplitude obtained from SnS<sub>2</sub> single layer is expected to be negligible. However, after long time integration, a small peak, visible at 310 cm<sup>-1</sup> (inset in Fig. 2f) and attributed to the A<sub>1g</sub> mode of SnS<sub>2</sub>, is detected. The presence of this peak confirms the PL results, where a negligible intensity of the PL peak has been identified for the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer structure. Besides, for the latter structure, the main WSe<sub>2</sub> Raman peak is redshifted by an amount of 0.3 cm<sup>-1</sup> toward lower frequencies with respect to the peak of ML structure, similarly to the PL peak, which also exhibits a downshift of almost 20 meV for the optical band gap. It should be pointed out that we were not able to provide any clear evidence of an efficient charge transfer through Raman spectroscopy.

Further information on the electronic structure of the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer could be carried out by performing nano X-ray photoemission spectroscopy (nano-XPS) measurements. It is worth noting that the CVD-grown flakes are transferred onto graphene/SiC substrates, in order to avoid problems related to charging effect that could occur when using other substrates like SiO<sub>2</sub>/Si.<sup>28</sup> Therefore, graphene/SiC substrates are very appropriate for XPS and ARPES investigations.<sup>29,30</sup> Fig. 3a shows an optical image of the probed region on the sample, which contains the flakes. Wide XPS spectra, acquired on both the WSe<sub>2</sub> single layer and the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer by means of photons with an energy of 100 eV, are presented in Fig. 3b. By comparing the core level photoemission yields of both regions, we can clearly detect the presence of an additional peak, namely, the Sn 4d shallow core level for the SnS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayer (red curve) with respect to the WSe<sub>2</sub> single layer (blue curve). By integrating the photoemission intensity within two selected energy windows around the W 4f and Sn 4d peaks, while scanning the sample along two in-plane



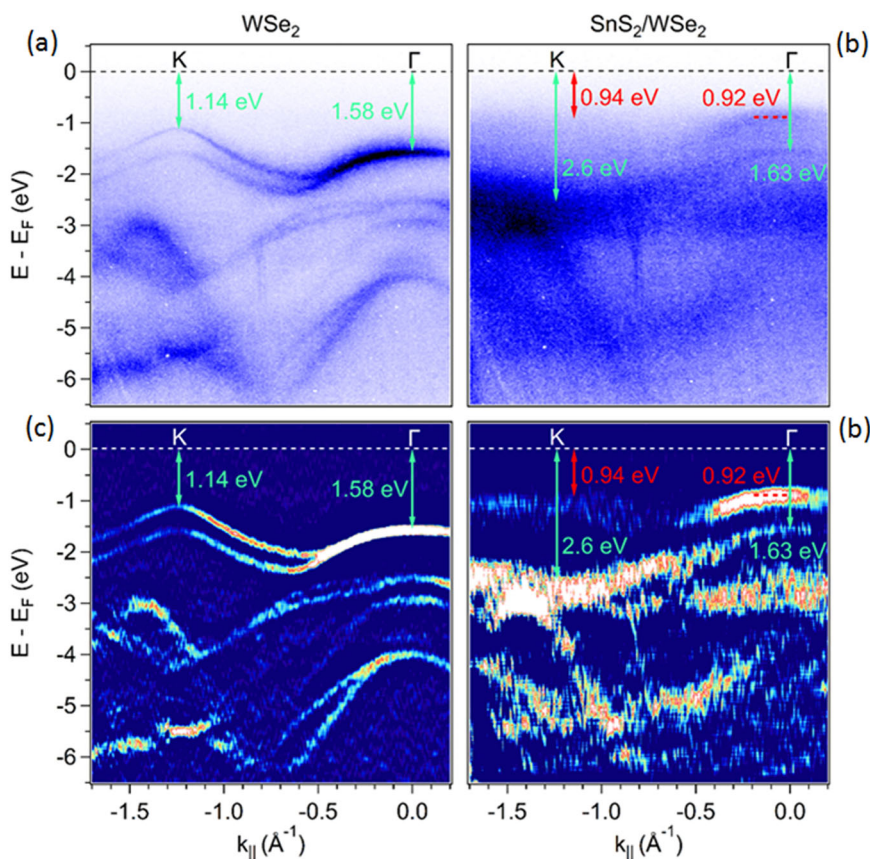
**Fig. 3** Nano-XPS maps of the  $\text{SnS}_2/\text{WSe}_2$  heterostructure: **a** Optical image of a probed region on the specimen, which contains the flakes. **b** XPS survey spectra, acquired on both the  $\text{WSe}_2$  single layer (blue curve) and the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer (red curve) with a photon energy of 100 eV. **c** Typical  $\text{W } 4f$  integrated intensity map, revealing the  $\text{WSe}_2$  ML domains marked in orange intensity color scale. **d**  $\text{Sn } 4d$  integrated intensity image, presenting a reversed intensity contrast with respect to the map of Fig. 3c; the  $\text{SnS}_2$  regions that partially cover the  $\text{WSe}_2$  flakes appear as orange in the image

directions, we generate the element-specified core level intensity distribution images (see Fig. 3c, d, respectively). Hence, Fig. 3c shows a spatially resolved map of  $\text{W } 4f$ , revealing the presence of triangular flakes corresponding to the  $\text{WSe}_2$  ML domains: as can be clearly noticed, areas where the intensity is higher represent the MLs of  $\text{WSe}_2$  that have not been covered with  $\text{SnS}_2$ , while areas where the intensity is lower correspond to regions rich in  $\text{SnS}_2$ . On the contrary, the spatially resolved map of  $\text{Sn } 4d$ , shown in Fig. 3d, presents a reversed intensity contrast with respect to the map of Fig. 3c, revealing  $\text{SnS}_2$  regions that partially cover the  $\text{WSe}_2$  flakes. This confirms what was already observed in the optical image of in Fig. 1c. Therefore, these core level images evidently prove that we were able to localize with a nanometric spatial resolution the  $\text{WSe}_2/\text{SnS}_2$  heterostructure, which allows us to study the electronic band structure of the system.

To study the correlation between the layer structure of the flakes (i.e.  $\text{WSe}_2$  single layer or  $\text{WSe}_2/\text{SnS}_2$  hetero-bilayer) and the electronic band structure, we have employed the nano-ARPES technique. Figure 4a, b present the photoelectron intensity maps acquired on  $\text{WSe}_2$  single layers and on  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayers, respectively at 100 eV. In order to enhance fine spectral features and get better clarity of the band structure presented in Fig. 4a, b, the second derivatives of the photoelectron intensity as a function of binding energy and parallel wave vector were also provided in Fig. 4c, d. Note that previous transmission electron microscope measurements have shown that  $\text{SnS}_2$  and  $\text{WSe}_2$  domains present the same orientation.<sup>13</sup> The alignment within this type of heterostructures is an important factor for nano-ARPES studies since it allows performing measurements along the same high-symmetry direction, i.e. along  $\Gamma$ -K, in the hexagonal BZ for both  $\text{WSe}_2$  and  $\text{SnS}_2/\text{WSe}_2$  layers. From the ARPES yields in Fig. 4a, b, we clearly detect the layer-dependent band structure evolution: in particular, moving from the  $\text{WSe}_2$  ML film to the  $\text{WSe}_2/\text{SnS}_2$  hetero-bilayer structure, we can see that the VBM located at the K point (1.14 eV binding energy) for the  $\text{WSe}_2$  single layer switches to the  $\Gamma$  point (1.63 eV binding energy) for the  $\text{WSe}_2/\text{SnS}_2$  hetero-

bilayer. In addition, the nano-ARPES measurements also reveal features related to the band structure of  $\text{SnS}_2$  single layer (see Fig. 4b), which are located at 0.92 and 0.94 eV binding energy below the Fermi level at the  $\Gamma$  and K points, respectively. One should note that the  $\text{SnS}_2$  band structure obtained from our nano-ARPES data is in a good agreement with the one calculated for  $\text{SnS}_2$  single layer by Huang et al.<sup>12</sup>

For the  $\text{WSe}_2$  single layer films, we remark that the VBM is significantly higher than the maximum of the band located at the  $\Gamma$  point (the difference between these maxima has an amount of 0.44 eV), and that the bands are remarkably sharp, indicating the high quality of the flakes. Moreover, for the  $\text{WSe}_2$  ML case, the strong spin orbit coupling (SOC) of the d-orbitals leads to an energy splitting of the valence band at the K point in the BZ, and thus the spin degeneracy is lifted by the inversion symmetry breaking. This induces a spin-polarization of the bands. Based on the ARPES data, the directly extracted value of the SOC energy splitting is equivalent to 480 meV, consistent with previous values experimentally measured in previous studies.<sup>31,32</sup> In the hetero-bilayer structure (Fig. 4b, d), the main feature indicating the band structure variation of  $\text{WSe}_2$  is the change in the VBM position from K to  $\Gamma$  point in the BZ with respect to the ML of  $\text{WSe}_2$ . In fact, the bands near the K point are extremely different from the bands of the single layer, thereby implying a strong interlayer hybridization effect between  $\text{SnS}_2$  and  $\text{WSe}_2$ ; this was previously observed also for the  $\text{WSe}_2$  homo-bilayer structure. Consequently, this strong band interaction, coming from the heterostructure formation, pulls up the energy level of the valence band located at the  $\Gamma$  point at 1.63 eV binding energy below the Fermi level) and pushes down the conduction band energy level positioned at the K point. This may later explain the type II band alignment in the aligned hetero-bilayer. Although  $\text{SnS}_2$  is covering the  $\text{WSe}_2$  layer, the employed photon energy of 100 eV allows to detect photoelectrons from  $\text{WSe}_2$  after constructing the heterostructure. This is due to the penetration depth of the beam that allows to probe more than a bilayer structure.<sup>33</sup> Consequently, the strong



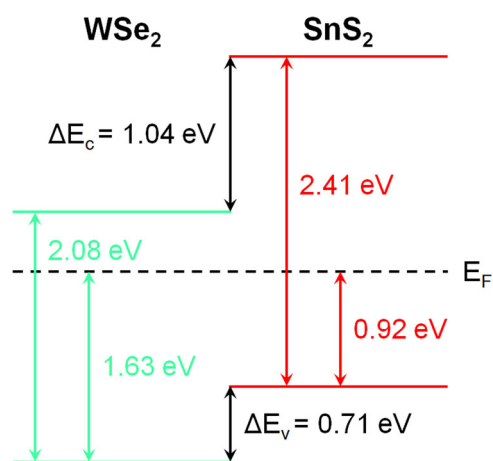
**Fig. 4** Comparison of the electronic band structure between the  $\text{WSe}_2$  single layer and the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer: **a, b** nano-ARPES images acquired on  $\text{WSe}_2$  single layers and on  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayers, and taken at a photon energy of 100 eV along the  $\Gamma\text{K}$  high-symmetry direction. **c, d** The second-derivative spectra of the maps in **a, b**, respectively, exhibiting better visibility of the bands. The Fermi level, located at 0 eV binding energy, was determined by fitting the leading edge of the graphene layer

signal attenuation observed in our ARPES intensity maps at the K point is not due to screening effects, which make the electronic structure less visible, but to a strong hybridization effect between  $\text{SnS}_2$  and  $\text{WSe}_2$ . Besides, it is instructive to compare our ARPES results with the projected band structure of the  $2\text{H-WSe}_2/2\text{H-SnS}_2$  heterostructure, obtained theoretically via first-principle calculations by Wang et al.<sup>14</sup> Even though  $\text{SnS}_2$  is lying on the bottom and  $\text{WSe}_2$  above in the latter study, we observe an electronic band structure of  $\text{WSe}_2$  similar to the one shown in our photoelectron intensity maps in Fig. 4b: the VBM of the heterostructure, located at the  $\Gamma$  point, is higher than the maximum of the valence band at the K point. Nevertheless, in contrast to our results,  $\text{SnS}_2$  is behaving more *n*-type as compared to  $\text{WSe}_2$ . This can be attributed to the choice of the substrate: in fact, in our experiment, we have used a graphene/ $\text{SiC}(0001)$  substrate, which is different from the one employed by Wang et al. By changing the substrate, one can tune the position of the Fermi level in the heterostructure. Thus, the substrate has not a direct effect on the scenario of hybridization of the atop materials, but rather participates in the charge transfer process, which affects the doping of the atop layers. Additionally, one should note that, even though the CVD process introduces considerable defects density in 2D materials, the growth of a second layer with a different chalcogen atom would not have healing effect on the first layer. To the best of our knowledge, when the deposition temperature in the second CVD process is above 750 °C, the reaction between S atoms in atmosphere and Se atoms in  $\text{WSe}_2$  will actually occur.<sup>34</sup> However, in our second CVD process, the growth temperature was deliberately chosen to be 600 °C, and thus the  $\text{WSe}_2$  layer is stable. Besides, a previous study conducted by Li et al.<sup>35</sup> on  $\text{WSe}_2$ -

$\text{MoS}_2$  lateral heterostructures has showed that the order for material growth, that is,  $\text{WSe}_2$  first and  $\text{MoS}_2$  second, is important to avoid the ionic exchange of Se-S occurring above 800 °C. The STEM measurements performed on  $\text{WSe}_2$ - $\text{MoS}_2$  confirmed that the lateral interface is atomically sharp and that there is no signature of Mo-W and Se-S bond formation in a micrometer range in parallel to the junction. Consequently, the optical signals as well as the electronic structure obtained in the present study are not affected by the growth of a layered material with two distinct chalcogen atoms.

Based on our nano-ARPES results and on literature, we have determined the band alignment of the  $\text{SnS}_2/\text{WSe}_2$  system (see Fig. 5), in which the electronic band gaps of  $\text{WSe}_2$  and  $\text{SnS}_2$  are 2.08<sup>36</sup> and 2.41 eV,<sup>11</sup> respectively. The valence band and conduction band offset values are determined to be 0.71 and 1.04 eV, respectively, with type II band alignment having the advantage of electron-hole pair separation. This efficient charge separation in the  $\text{SnS}_2/\text{WSe}_2$  heterostructure can clarify the quenching observed in the PL peak of Fig. 2c. Consequently, these observations, revealing that the band alignment is of type II, are significant for future technological electronic and opto-electronic applications since type II heterostructures facilitate the efficient electron-hole separation for light detection.

Therefore, our nano-ARPES results on the  $\text{SnS}_2/\text{WSe}_2$  heterostructure report a strong hybridization between  $\text{WSe}_2$  and  $\text{SnS}_2$ , which is evident from the change of the VBM position of  $\text{WSe}_2$  from the K point in the pristine sample to the  $\Gamma$  point in the hetero-bilayer structure due to the strong interlayer coupling. Even though not all the aspects related to the genuine determination of the conduction band minimum (CBM) of  $\text{WSe}_2$



**Fig. 5** Schematic of band alignment diagram of the  $\text{SnS}_2/\text{WSe}_2$  heterostructure, obtained from nano-ARPES measurements. The valence band maximum and conduction band minimum offset values are determined to be 0.71 and 1.04 eV, respectively, with type II band alignment

in the hetero-bilayer system are clear, we suggest that  $\text{WSe}_2$  may probably exhibit a band gap transition from a direct to an indirect gap, confirmed by the PL quenching observed for the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer. This expected band gap transition to an indirect gap was observed by Wang et al.<sup>14</sup> in their first-principle calculations of the electronic band structure of the 2H- $\text{WSe}_2/2\text{H-SnS}_2$  heterostructure. In addition, a probable photo-induced charge transfer, involving electrons from the CBM of  $\text{WSe}_2$  and holes from the VBM of  $\text{SnS}_2$ , could also contribute to the quenching observed in the PL measurements.

In summary, we have studied the electronic structure of the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer structure. A detailed investigation by means of  $\mu\text{-PL}$  and nano-ARPES allowed us to extract the band alignment of this heterostructure, revealing that it has a type II configuration with an optical gap of 1.65 eV. A significant PL quenching was observed for the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer structure with respect to the  $\text{WSe}_2$  ML, suggesting that  $\text{WSe}_2$  may probably present a band transition from a direct to an indirect gap or/and a possible photo-induced charge transfer. In perspective, further time-resolved ARPES experiments and doping strategies, like for instance with potassium<sup>37</sup> are required to study in detail the unoccupied states of the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer structure in order to verify the probable band gap transition. Our findings demonstrate the possibility of band structure engineering of TMDs, by taking advantage of the strong hybridization effects occurring between the constitutive single layers of the heterostructure, as in the case of the  $\text{SnS}_2/\text{WSe}_2$  hetero-bilayer structure.

## METHODS

### Growth and transfer of $\text{SnS}_2/\text{WSe}_2$

The  $\text{SnS}_2/\text{WSe}_2$  heterostructures were grown through a two-step chemical vapor deposition process. Firstly, to grow  $\text{WSe}_2$  monolayers, tungsten diselenide powder was placed at the center of a furnace and  $\text{SiO}_2/\text{Si}$  substrate was placed at the downstream of a quartz tube. Then, the argon carrier gas flow rate was fixed at 50 sccm and the temperature was increased to 1100 °C and maintained stable for 10 min. The as-synthesized  $\text{WSe}_2$  monolayers were, subsequently, used as templates for the growth of  $\text{SnS}_2$ .  $\text{S}$  powder,  $\text{SnO}_2$  powder and as-grown  $\text{WSe}_2$  monolayers on  $\text{SiO}_2/\text{Si}$  substrate were placed at the upstream, center, and downstream of the quartz tube, respectively. Thereafter, the argon carrier gas flow rate was fixed at 50 sccm at a pressure of 8 Torr and the temperature was increased to 600 °C and kept stable for 8 min. After the growth, the furnace was cooled down to room temperature. The  $\text{SnS}_2/\text{WSe}_2$  flakes transferred onto graphene,<sup>38,39</sup> retain their triangular shapes with unchanged lateral sizes. Before any measurement, the sample was annealed at 250 °C for 60 min in

ultrahigh vacuum, in order to remove the residual surface contaminations induced by the wet transfer.

### Single layer Graphene on $\text{SiC}(0001)$

Single layer graphene was produced following a two-step thermal heating growth process of  $\text{SiC}(0001)$  substrate. Before the graphitization, the substrate was etched with hydrogen (100%  $\text{H}_2$ ) at 1550 °C to produce well-ordered atomic terraces of  $\text{SiC}$ . Afterwards, the  $\text{SiC}$  substrate was heated to 1000 °C and then further heated to 1550 °C in an argon atmosphere.

### Micro-Raman and photoluminescence spectroscopy

The micro-Raman and photoluminescence measurements were conducted using a commercial confocal HORIBA LabRAM HR Evolution micro-Raman microscope operating at 532 and 633 nm. The incident photon beam was focused down to a submicrometric spot ( $\sim 0.5 \mu\text{m}$  in diameter) on the sample. The incident power was  $\sim 0.1$  mW. All measurements were performed at room temperature with the same microscope using a  $\times 100$  objective and a CCD detector (detection range between 1.2 and 6.2 eV).

### Angle-resolved photoemission spectroscopy

The nano-ARPES experiments were performed at the ANTARES beamline of the SOLEIL synchrotron light source (Saint-Aubin, France). The ARPES data were taken at a photon energy of 100 eV, using linearly polarized light. All measurements were carried out at a base pressure of  $5 \times 10^{-11}$  mbar and a base temperature of 70 K.

## DATA AVAILABILITY

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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## AUTHOR CONTRIBUTIONS

B.Z. and A.P. fabricated the samples. J.Z., D.P., A.O., J.A. and M.C.A. carried out the nano-XPS/nano-ARPES experiments. J.C., A.O. and T.B. characterized the samples by means of  $\mu\text{-Raman/PL}$  spectroscopy and analyzed the Raman/PL data. J.Z., T.B., J.C., L.K., J.A., D.P. and E.L. analyzed the data. J.Z. and L.K. wrote the paper under the supervision of A.O. All the authors discussed the results and commented on the paper.

## ADDITIONAL INFORMATION

**Competing interests:** The authors declare no competing interests.

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