Strong interlayer hybridization in the aligned SnS\textsubscript{2}/WSe\textsubscript{2} hetero-bilayer structure

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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\textsubscript{2}/WSe\textsubscript{2} hetero-bilayer structure grown by chemical vapor deposition. Surprisingly, the valence band maximum position of WSe\textsubscript{2} is moved from the \( \Gamma \) point for the single layer WSe\textsubscript{2} to the \( \Gamma \) point for the aligned SnS\textsubscript{2}/WSe\textsubscript{2} hetero-bilayer. Additionally, a significant photoluminescence quenching is observed for the SnS\textsubscript{2}/WSe\textsubscript{2} hetero-bilayer structure with respect to the WSe\textsubscript{2} monolayer. Using photoluminescence spectroscopy and nano-angle-resolved photoemission spectroscopy techniques, we demonstrate that the SnS\textsubscript{2}/WSe\textsubscript{2} 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\textsubscript{2}/WSe\textsubscript{2} hetero-bilayers for envisaging their applications in nanoelectronics.

ARTICLE

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\textsubscript{2}) possess a high carrier mobility\textsuperscript{1} and several spin properties\textsuperscript{2,–4} 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,\textsuperscript{4} photonics, and superconductivity.\textsuperscript{5} 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.\textsuperscript{6,–9}

Among the 2D materials, tin disulfide (SnS\textsubscript{2}) 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\textsubscript{2} interact with each other through vdW interactions. Note that SnS\textsubscript{2} is an earth-abundant, and a low-cost and an environmentally friendly material. In its bulk form, SnS\textsubscript{2} is extensively studied mostly for photovoltaics.\textsuperscript{6} As a 2D TMD, SnS\textsubscript{2} is interesting since it exhibits high carrier mobility\textsuperscript{10} and a strong excitonic effect (binding energy of \( \sim 0.9 \text{ eV} \) for a single layer).\textsuperscript{11} The electronic band structure of SnS\textsubscript{2} has been investigated in several DFT studies showing that in contrast to TMDs, the indirect to direct band gap transition for SnS\textsubscript{2} does not occur from bulk down to a single layer.\textsuperscript{11,–12} This has been experimentally confirmed by Huang et al.\textsuperscript{12} through layer-dependent photoluminescence (PL) and band structure measurements of bulk SnS\textsubscript{2}. However, the electronic band structure of a single layer of SnS\textsubscript{2} has not been measured yet.

The SnS\textsubscript{2}/WSe\textsubscript{2} hetero-bilayers have started to attract a great attention,\textsuperscript{13} in order to combine the various characteristics of SnS\textsubscript{2} and WSe\textsubscript{2} single layers. Different methods have been used to obtain this heterostructure. For example, mechanically exfoliated few-layer/few-layer stacked WSe\textsubscript{2}/SnS\textsubscript{2} heterostructures with an anti-ambipolar behavior have been reported by Wang et al.\textsuperscript{14} In addition, Zhang et al.\textsuperscript{15} have demonstrated the possibility of growing few layers of WSe\textsubscript{2} on micro-plates of SnS\textsubscript{2} randomly oriented. More recently, Yang et al.\textsuperscript{13} have employed a two-step vapor phase route to grow WSe\textsubscript{2}/SnS\textsubscript{2} 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\textsubscript{2}/2H-WSe\textsubscript{2} is a type II heterostructure characterized by the high efficiency of charge separation.\textsuperscript{14,16} Devices based on this type of vdW heterostructures have shown improved optoelectronic performances.\textsuperscript{16} 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.\textsuperscript{13}

In order to realize vdW heterostructures promoted by weakly bonded layered structure of these 2D materials, mechanical...
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.\textsuperscript{17,18} 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 SnS\textsubscript{2}/WSe\textsubscript{2} heterostructure, grown via the CVD technique, with microscopic Raman (\textmu{}-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 present on the same heterostructure.

**RESULTS AND DISCUSSION**

2H-SnS\textsubscript{2}/2H-WSe\textsubscript{2} heterostructures were grown via two-step CVD (see Materials and Methods and ref. \textsuperscript{13}). Single layer WSe\textsubscript{2} flakes were first grown on SiO\textsubscript{2}/Si substrates. Then, these structures were used as templates for the subsequent growth of single layers of SnS\textsubscript{2} to form the vertical hetero-bilayer structures of SnS\textsubscript{2}/WSe\textsubscript{2}. A schematic side and top views of the atomic structure of the vertically stacked SnS\textsubscript{2}/WSe\textsubscript{2} vdW heterostructure are presented in Fig. 1a, b, respectively. The large lattice mismatch between SnS\textsubscript{2} and WSe\textsubscript{2} (14.3\%) indicates that the bonding between adjacent layers is principally of the vdW type.\textsuperscript{19,20} 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 SnS\textsubscript{2}/WSe\textsubscript{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).\textsuperscript{13} 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 SiO\textsubscript{2}/Si substrate through the CVD process. These triangular flakes are only composed of one edge termination, namely, the W-zz termination.\textsuperscript{21} 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 synthetized by means of the CVD method,\textsuperscript{22,23} and is mainly due to structural differences in the edges of the flakes and to the local difference in the growth rates.\textsuperscript{24} It is noteworthy that the irregular evolution of the SnS\textsubscript{2} edge with respect to WSe\textsubscript{2} edge could be related to the presence of distinct seeding centers, which affect the growth kinetics of the CVD growth of SnS\textsubscript{2} on WSe\textsubscript{2}.\textsuperscript{24}

To probe the details of light emission obtained from the WSe\textsubscript{2} and SnS\textsubscript{2}/WSe\textsubscript{2} domains, \textmu{}-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 WSe\textsubscript{2} regions reveal a higher PL intensity than the SnS\textsubscript{2}/WSe\textsubscript{2} hetero-bilayer domains (Fig. 2a). This is confirmed by comparing their corresponding PL spectra.
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 WSe2 ML region (blue curve) and from the SnS2/WSe2 hetero-bilayer domain (red curve). The PL intensity acquired from the SnS2/WSe2 hetero-bilayer structure has multiplied by a factor of 100 in order to visualize the signal. d, e μ-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 WSe2 (blue curve) and the SnS2/WSe2 hetero-bilayer (red curve). Inset: Raman spectrum obtained after a long time integration on the SnS2/WSe2 hetero-bilayer domain. A small peak, visible at 310 cm$^{-1}$ and attributed to the $A_{1g}$ mode of SnS2, is detected obtained from two specific points 1 and 2 representative of the distinct regions (see Fig. 2c). Actually, for the SnS2/WSe2 hetero-bilayer region, we detect a drastic PL quenching with respect to the uncovered WSe2 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 SnS2 and WSe2, which leads to a strong photo-induced electron transfer from WSe2 to SnS2, hindering the recombination of electron-hole pairs created by the photoexcitation. Another more probable scenario explaining the PL quenching is a predicted WSe2 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, a ruthless modification of the WSe2 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 SnS2/WSe2 hetero-layer structure, we have conducted a μ-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 μ-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 with a 532 nm laser excitation. These maps reveal that a downshift of the peak positions and a slight variation in the peak intensities of SnS2, is detected. The presence of this peak confirms the PL results, where a negligible intensity of the PL peak has been identified for the SnS2/WSe2 hetero-bilayer structure. Besides, for the latter structure, the main WSe2 Raman peak is redshifted by an amount of 0.3 cm$^{-1}$ 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 SnS2/WSe2 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$_2$/Si. Therefore, graphene/SiC substrates are very appropriate for XPS and ARPES investigations. Fig. 3a shows an optical image of the probed region on the sample, which contains the flakes. Wide XPS spectra, acquired on both the WSe2 single layer and the SnS2/WSe2 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 SnS2/WSe2 hetero-bilayer (red curve) with respect to the WSe2 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 the WSe2 domains. Beside the uncovered WSe2 single layer (see Fig. 2c); the intensity of the second order harmonic 2LA(M) mode at 266 cm$^{-1}$, and the third order LA(M) mode at 401 cm$^{-1}$. Additionally, we can detect Raman peaks at 352 and 378 cm$^{-1}$, which constitute combination modes between LA(M), TA(M) or ZA(M), with $E_{2g}$ ($\Gamma$) modes. From the Raman spectra of Fig. 2f, we can conclude that the Raman peak amplitude obtained from SnS2 single layer is expected to be negligible. However, after long time integration, a small peak, visible at 310 cm$^{-1}$ (inset in Fig. 2f) and attributed to the $A_{1g}$ mode of SnS2, is detected. The presence of this peak confirms the PL results, where a negligible intensity of the PL peak has been identified for the SnS2/WSe2 hetero-bilayer structure. Besides, for the latter structure, the main WSe2 Raman peak is redshifted by an amount of 0.3 cm$^{-1}$ 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.

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From the ARPES yields in Fig. 4a, b, we can clearly notice areas where the intensity is higher represent respectively at 100 eV. In order to enhance the spatial resolution the WSe$_2$/SnS$_2$ heterostructure, which allows us evidently prove that we were able to localize with a nanometric optical image of the specimen, which contains the flakes. Consequently, this strong band interaction, coming from the heterostructure formation, pulls up the energy level of the valence band located at the K point at 1.63 eV binding energy below the Fermi level. Moreover, for the 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.

For the WSe$_2$ single layer films, we remark that the VBM is significantly higher than the maximum of the band located at the Γ 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, the 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. In the heterobilayer structure (Fig. 4b, d), the main feature indicating the band structure variation of WSe$_2$ is the change in the VBM position from K to Γ point in the BZ with respect to the ML of 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 SnS$_2$ and WSe$_2$, which was previously observed also for the 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 Γ 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 heterobilayer. Although SnS$_2$ is covering the WSe$_2$ layer, the employed photon energy of 100 eV allows to detect photoelectrons from 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. Consequently, the strong

Fig. 3  Nano-XPS maps of the SnS$_2$/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 WSe$_2$ single layer (blue curve) and the SnS$_2$/WSe$_2$ hetero-bilayer (red curve) with a photon energy of 100 eV. c Typical W 4f integrated intensity map, revealing the WSe$_2$ ML domains marked in orange intensity color scale. d Sn 4d integrated intensity image, presenting a reversed intensity contrast with respect to the map of Fig. 3c; the SnS$_2$ regions that partially cover the WSe$_2$ flakes appear as orange in the image.
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 SnS2 and WSe2. Besides, it is instructive to compare our ARPES results with the projected band structure of the 2H-WSe2/2H-SnS2 heterostructure, obtained theoretically via first-principle calculations by Wang et al.14 Even though SnS2 is lying on the bottom and WSe2 above in the latter study, we observe an electronic band structure of WSe2 similar to the one shown in our photoelectron intensity maps in Fig. 4b: the VBM of the heterostructure, located at the Γ point, is higher than the maximum of the valence band at the K point. Nevertheless, in contrast to our results, SnS2 is behaving more n-type as compared to WSe2. This can be attributed to the choice of the substrate: in fact, in our experiment, we have used a graphene/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 WSe2 will actually occur.34 However, in our second CVD process, the growth temperature was deliberately chosen to be 600 °C, and thus the WSe2 layer is stable. Besides, a previous study conducted by Li et al.35 on WSe2-MoS2 lateral heterostructures has showed that the order for material growth, that is, WSe2 first and MoS2 second, is important to avoid the ionic exchange of Se-S occurring above 800 °C. The STEM measurements performed on WSe2-MoS2 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 SnS2/WSe2 system (see Fig. 5), in which the electronic band gaps of WSe2 and SnS2 are 2.08,e11 and 2.41 eV, 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 SnS2/WSe2 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 SnS2/WSe2 heterostructure report a strong hybridization between WSe2 and SnS2, which is evident from the change of the VBM position of WSe2 from the K point in the pristine sample to the Γ 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 WSe2...
in the hetero-bilayer system are clear, we suggest that WSe₂ may probably exhibit a band gap transition from a direct to an indirect gap, confirmed by the PL quenching observed for the SnS₂/WSe₂ hetero-bilayer. This expected band gap transition to an indirect gap was observed by Wang et al. in their first-principle calculations of the electronic band structure of the 2H-WSe₂/2H-SnS₂ heterostructure. In addition, a probable photo-induced charge transfer, involving electrons from the CBM of WSe₂ and holes from the VBM of SnS₂, could also contribute to the quenching observed in the PL measurements.

In summary, we have studied the electronic structure of the SnS₂/WSe₂ hetero-bilayer structure. A detailed investigation by means of μ-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 SnS₂/WSe₂ hetero-bilayer structure with respect to the WSe₂ ML, suggesting that WSe₂ 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, are required to study in detail the unoccupied states of the SnS₂/WSe₂ 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 SnS₂/WSe₂ hetero-bilayer structure.

METHODS

Growth and transfer of SnS₂/WSe₂

The SnS₂/WSe₂ heterostructures were grown through a two-step chemical vapor deposition process. Firstly, to grow WSe₂ monolayers, tungsten diselenide powder was placed at the center of a furnace and SiO₂/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 WSe₂ monolayers were, subsequently, used as templates for the growth of SnS₂. S powder, SnO₂ powder and as-grown WSe₂ monolayers on SiO₂/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 SnS₂/WSe₂ flakes transferred onto graphene 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 SiC(0001)

Single layer graphene was produced following a two-step thermal heating growth process of SiC(0001) substrate. Before the graphitization, the substrate was etched with hydrogen (100% H₂) at 1550 °C to produce well-ordered atomic terraces of SiC. Afterwards, the 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 (~0.5 µm in diameter) on the sample. The incident power was ~0.1 mW. All measurements were performed at room temperature with the same microscope using a x100 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 × 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 measurements. J.C., A.O. and T.B. characterized the samples by nano-XPS/nano-ARPES experiments. J.Z., D.P., A.O., J.A. and M.C.A. carried out the nano-ARPES experiments at the ANTARES beamline of SOLEIL. Angle-resolved photoemission spectroscopy performed at room temperature with the same microscope using a x100 objective and a CCD detector. A.M., A.O., J.A. and M.C.A. carried out the angle-resolved photoemission spectroscopy measurements. The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

ADDITIONAL INFORMATION

Competing interests: The authors declare no competing interests.

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