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Point defects in $[\text{Ca}_2\text{Nb}_3\text{O}_{10}]^-$ monolayers and intralayer excitons in $[\text{Ca}_2\text{Nb}_3\text{O}_{10}]^-/\text{WSe}_2$ heterostructures

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Point defects in $[\text{Ca}_2\text{Nb}_3\text{O}_{10}]^-$ monolayers and intralayer excitons in $[\text{Ca}_2\text{Nb}_3\text{O}_{10}]^-/\text{WSe}_2$ heterostructures

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Supplementary material for this article is available [online](#)

Abstract

We report the fabrication and atomic-scale characterization of a novel van der Waals heterostructure composed of monolayer WSe_2 and monolayer $[\text{Ca}_2\text{Nb}_3\text{O}_{10}]^-$ (CNO). Using 60kV Cc/Cs-corrected high-resolution transmission electron microscopy, we obtain atomic-resolution images of freestanding CNO monolayers, revealing their crystalline structure and beam-induced defect formation. Structure modeling, image simulations, and first-principles calculations point at the preferential oxygen and calcium vacancy formation under electron irradiation. Spatially resolved monochromated STEM-EELS analysis reveals a small but reproducible redshift (~ 20 meV) of the D exciton of WSe_2 when covered by CNO, consistent with a weak interfacial modification of the local dielectric/electronic environment. Additional first-principles calculations indicate weak interfacial coupling and show that the electronic structure is highly sensitive to the charge-compensating environment of the CNO layer. Our findings demonstrate that functional oxide nanosheets can be integrated with transition metal dichalcogenide (TMD) monolayers to form oxide/TMD van der Waals heterostructures with locally modified excitonic properties, offering new opportunities for engineered 2D material systems.

1. Introduction

Beyond graphene [1–3], transition metal dichalcogenide (TMD) monolayers, such as WSe_2 , have attracted considerable attention over the past decade due to their remarkable optoelectronic properties [4–10]. Their optical response is predominantly governed by excitons, enabling applications in

miniaturized optoelectronic devices, including photodetectors [6, 11, 12]. A central focus of recent research has been the design of vertical heterostructures composed of two different TMDs [13–15], which enable engineering of properties via mechanisms such as interlayer excitons [16–19] or modifications in the intralayer exciton spectrum [20–23]. More recently CrI_3 [24] has also

been shown to influence the excitonic behavior in WSe₂.

In addition to TMDs [4, 25–27], other layered materials have garnered increasing attention [28–30], particularly those with perovskite structure. Among them, the Dion-Jacobson phase material KCa₂Nb₃O₁₀ [31–33] stands out. By replacing the intercalated potassium ions with tetra-n-butylammonium (TBA⁺), the layers can be separated [34] enabling the isolation of mono- to few-layer [Ca₂Nb₃O₁₀][−] (CNO) nanosheets (see figure 1). These nanosheets have already shown potential applications in various fields such as photocatalysis [35] and high- κ dielectrics [36]. Previous work by Virdi *et al* [37] explored monolayers of CNO using valence electron energy-loss spectroscopy (valence-EELS), determining the material's band structure. However, heterostructures combining TMD monolayers with CNO monolayers have rarely been investigated and may offer new opportunities for tailoring optoelectronic properties.

Low-voltage aberration-corrected high-resolution transmission electron microscopy and scanning transmission electron microscopy are crucial techniques for studying the atomic structure of two-dimensional materials [38–44]. In particular chromatic and spherical aberration-corrected high-resolution transmission electron microscopy (HRTEM) enables atomic-resolution imaging at low acceleration voltages, which is essential for beam-sensitive 2D materials [40]. When combined with high-resolution electron energy-loss spectroscopy in the low-loss regime, these techniques enable spatially resolved studies of excitonic effects [45, 46].

In this paper, we report fabrication and characterization of a van der Waals heterostructure composed of monolayer WSe₂ and monolayer CNO. Using Cc/Cs-corrected HRTEM and first-principles calculations, we aim to understand the crystalline structure and beam-induced defect formation in monolayer CNO. Cs-corrected STEM-EELS analysis is then performed to determine the electronic structure of WSe₂, focusing on weak local modifications induced by the CNO overlayer.

2. Method

2.1. Chemical vapor deposition (CVD)

Monolayers of WSe₂ were grown on 90 nm SiO₂/Si wafers via CVD. WSe₂ powder precursor (150 mg) was loaded into an alumina boat positioned at the center of a quartz tube furnace, with the substrates placed 7 cm downstream from the crucible. The furnace was first heated to 1020 °C within 40 min under 200 sccm of N₂ gas. Then the furnace was ramped to 1060 °C over 10 min, during which the carrier gas was switched to Ar/H₂ (5%) with water vapor. The water vapor was terminated for 40 s before shifting

the reaction zone 130 mm downstream, with Ar/H₂ flow remaining during the cooling process.

2.2. Calcium niobate synthesis

First, bulk KCa₂Nb₃O₁₀ was synthesized from K₂CO₃, CaCO₃ and Nb₂O₅ by heating a mixture stoichiometric ratio to 1200 °C for 60 h, following our own adapted procedure as published in Zhang *et al* [47]. In the second step, the potassium atoms were removed from the structure by treatment of the material with 6 M HCl for at least three days, forming the ion-exchanged product HCa₂Nb₃O₁₀. The product was then filtered, washed with water, and dried. Finally, Ca₂Nb₃O₁₀ nanosheets were obtained by exfoliation of the ion-exchanged product in an aqueous TBAOH-30-hydrate aqueous solution at 1:1 molar ratio for at least 7 d. Note that the negatively charged nanosheets must be balanced by either TBA⁺ or H⁺. Residual bulk solids were removed by centrifugation. Monolayers could be isolated from the supernatant.

2.3. Heterostructure preparation

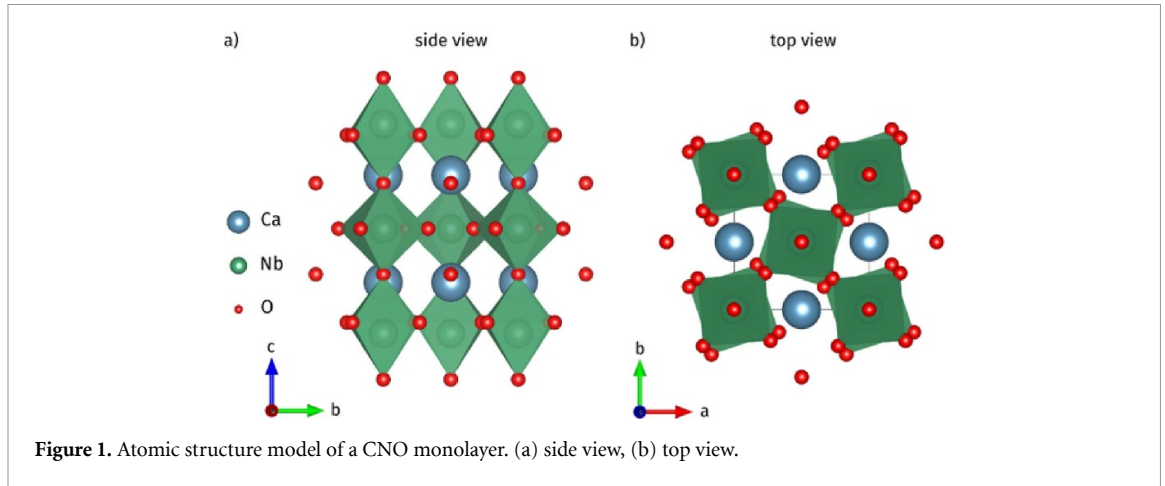
WSe₂/CNO heterostructures were prepared directly on Quantifoil TEM grids. First, suitable areas with WSe₂ monolayers on the SiO₂/Si wafer were identified using optical microscopy. The TEM grid was then placed accordingly and brought into contact with the monolayer using an evaporating drop of isopropyl alcohol (IPA). Next, the SiO₂ surface was etched with a KOH solution, releasing the grid with the attached WSe₂. The grid was subsequently washed with ultrapure water, and finally, 3 μ l of CNO solution was drop-cast onto the grid and left to dry.

2.4. HRTEM

HRTEM was carried out using the chromatic and spherical (Cc/Cs)-corrected Sub-Ångström Low-Voltage Electron microscopy (SALVE) instrument, operated at an acceleration voltage of 60 kV [48]. The SALVE microscope corrects axial geometric aberrations up to the fifth order, off-axial aberrations up to third, and chromatic aberrations at the first order, resulting in a resolution of 83 pm at 60 kV [41]. HRTEM imaging was performed under negative Cs—imaging conditions, with an optimized Cs of −13.7 μ m, chosen in accordance with a measured fifth-order spherical aberration (C₅) of 4.8 mm. A slight overfocus was applied to produce bright atom contrast and optimize the contrast transfer function. To minimize beam-induced damage, an electron dose of 0.6×10^6 e[−] nm^{−2} per image was used, and most focusing and stigmation was carried out in regions away from the area of interest.

2.5. STEM-EDX

For overview imaging and elemental characterization of the as-prepared heterostructures, STEM-EDX analysis was performed on a ThermoFisher Talos F200X microscope equipped with a SuperX



EDX detector, operated at an acceleration voltage of 80 kV. Quantitative evaluation of the EDX spectra was carried out using ThermoFisher Velox software, applying the Brown–Powell model for ionization cross-sections [49]. High-angle annular dark-field (HAADF) imaging was employed, enabling Z-contrast imaging, where the signal intensity scales approximately with the square of the atomic number [50]. This allowed clear distinction between the multilayer WSe₂ and the CNO nanosheets.

2.6. STEM-EELS

For the acquisition of spatially resolved EELS an aberration corrected Nion HERMES STEM instrument with an operating voltage of 60 kV was used [51]. The microscope is equipped with a ground-potential monochromator and an IRIS spectrometer offering a high energy resolution of down to 6 meV. A Dectris ELA direct electron detector enabled recording of spectra with a high signal-to-noise ratio [52]. The energy resolution was determined as the full width at half maximum (FWHM) of the zero-loss peak (ZLP). To reduce noise, the originally acquired data—256 by 256 pixels at a resolution of 0.5 nm/px—was first binned by a factor of four along both the x and y axes. Additionally, the data was smoothed using a Gaussian filter with a radius of 4 pixels. This smoothing was applied exclusively to the x - and y -axes and not the electron energy loss axis to preserve the energy resolution. The spectrum in each lateral position was fitted with four Lorentzian functions on a linear background in the range of 1.55–3.4 eV to extract the excitation positions.

2.7. First-principles calculations

The spin-polarized density functional theory (DFT) calculations were carried out using Perdew–Burke–Ernzerhof (PBE) [53] exchange-correlation functional as implemented in the VASP code [54, 55]. The cutoff energy of 400 eV and energy convergence threshold of 1×10^{-6} eV were used in the structure relaxation. A rectangular supercell consisting of 16 Ca, 24 Nb, and 80 O atoms was used

in the vacancy formation and dynamical calculations. Brillouin Zone sampling was performed with $4 \times 4 \times 1$ Γ -centered k -point mesh. The monolayers were separated with ~ 30 Å out-of-plane vacuum spacing and resulting structures were fully optimized with the maximum force on each atom being less than $0.01 \text{ eV } \text{\AA}^{-1}$.

The vacancy formation energy E_f^{vac} was calculated as

$$E_f^{\text{vac}} = E_{\text{defective}} - E_{\text{pristine}} + \mu_X, \quad (1)$$

where E_{pristine} and $E_{\text{defective}}$ are total energies of the pristine supercell and the supercell containing single vacancy, respectively (both after full structural relaxation). μ_X is the chemical potential of the removed species X . For atomic vacancies (Ca, Nb), μ_X was taken as the energy of the corresponding isolated atom. This choice is not governed by the thermodynamics, but rather by the response of the system to electron irradiation resulting in the sputtering of the recoil atoms into vacuum.

Simulations of the displacement process upon electron impacts were carried out using *ab initio* molecular dynamics (MD) with a time step of 0.5 fs and a single Γ point Brillouin Zone sampling. Similar to our previous calculations [56, 57], an initial velocity was assigned to the recoil atom in the bottom (with regard to the electron source) layer of the material in the direction normal to the surface, then the evolution of the system was simulated using DFT MD as a microcanonical ensemble. In the simulations, the initial velocity of the recoil atom was increased until the displacement criteria were met after the MD run (minimum 5 Å displacement, force on the atom $< 0.1 \text{ eV } \text{\AA}^{-1}$). The displacement threshold energy was defined as the minimum initial kinetic energy of the atom resulting in its sputtering. Thermal vibrations of the atoms were accounted within the framework of the ideal gas model [58] at 300 K.

The simulations of electronic structures and the structural properties of heterostructures were performed using FHI-aims code [59]. The details

on the heterostructure creation are given in the Supporting Information in the section “Density-functional theory simulations of heterostructures” and the references cited therein. All building blocks of the heterostructure as well as the interfaces were fully relaxed (atomic positions and in-plane lattice vectors) employing the PBE functional [53] on tight tier 1 numeric atom-centered orbitals, including the nonlocal many-body dispersion correction (MBD-nl) [60], and scalar relativistic corrections (ZORA). The γ -angle was kept fixed, while forces and stresses were minimized until below $0.01 \text{ eV } \text{\AA}^{-1}$. The SCF parameters were automatically adjusted after three steps. The electronic band structures, the Mulliken projections, and the density of states were calculated using HSE06 hybrid functional including spin-orbit coupling and considering the dipole correction.

3. Results and discussion

The as-prepared heterostructures were first characterized using overview STEM imaging to provide the general morphology and using selected-area electron diffraction (SAED) to confirm the crystal structure (figure 2). The SAED pattern of a small area of the heterostructure shows that the diffraction spots corresponding to the hexagonal lattice of the WSe_2 monolayer are clearly distinguishable from those of CNO. The latter exhibits a lattice which is in excellent agreement with the simulated diffraction pattern derived from the proposed structure model. This supports that CNO has not only retained its pristine crystalline structure but also conforms to the expected monolayer structure.

We further employ STEM-EDX to verify the elemental composition of the prepared heterostructure (see Supporting Information). The overview HAADF-STEM image in figure S1(a) displays a larger WSe_2 flake with smaller CNO nanosheets with lower grey-level contrast on its surface. The nanosheets can be distinguished from the WSe_2 growth seeds due to their lower Z-contrast. STEM-EDX mapping was performed on a flake suspended over a hole in the support, ensuring it was supported exclusively by a monolayer WSe_2 . The corresponding elemental maps confirm that the flake contains Ca, Nb, and O, consistent with CNO. Quantitative analysis of spectra summed over the flake region shows that the content of calcium and selenium are of comparable magnitude. For a monolayer WSe_2 support, this result is consistent with the presence of monolayer CNO, since the Ca/Se ratio is expected to approximately scale with the number of CNO layers in the heterostructure.

Because the CNO nanosheet constitutes the active overlayer in the CNO/ WSe_2 heterostructure and is highly sensitive to electron irradiation, understanding its atomic structure and beam-induced defect formation is essential for interpreting the

subsequent STEM-EELS measurements. In particular, the structural analysis establishes whether CNO retains its crystalline monolayer structure under the low-dose conditions used for spectroscopy, identifies the defects that may form during electron exposure, and defines the experimental stability window of the heterostructure. This information is also important for relating the measurements to first-principles calculations, which describe idealized, defect-free interface models. We therefore first analyze the atomic structure and beam response of monolayer CNO before discussing the excitonic response of WSe_2 in the CNO/ WSe_2 heterostructure. We obtained high-resolution images of CNO nanosheets, representing, to the best of our knowledge, the first atomic resolution observation of this structure. Figure 3(a) shows an overview image of a particularly informative region, where the nanosheets are suspended over a crack in the underlying WSe_2 support. The nanosheets vary in size and orientation, appearing to stack randomly rather than adopting their bulk-like arrangement. In the high-magnification image (figure 3(b)), the crystalline lattice of the monolayer is clearly resolved at atomic scale. Additionally, a second CNO layer is visible on the lower left and the upper right parts of the image, each with a different in-plane orientation. In the upper left side, a third layer can be seen, again with a different orientation relative to the layers below. The fast Fourier transform (FFT) of the monolayer region further supports that the CNO structure remains largely intact under the applied low-dose imaging conditions.

Despite the low dose rate used and the overall preservation of the lattice in the image, we already observe isolated defects after brief exposure to the beam for focusing and stigmation.

Figure 4 provides a more detailed analysis of the atomic structure of the freestanding CNO nanosheet. All experimental images shown here are magnified sections from the same acquisition, obtained with a total electron dose of approximately $10^6 \text{ e}^- \text{ nm}^{-2}$. The data reveal that the Ca columns, together with the oxygen atoms coordinated in their vicinity, are more prone to beam-induced removal than the Nb columns. This is consistent with the stronger incorporation of Nb into the Nb–O framework, likely due to the stabilization effect by the three-niobium atom column shown in figure 1(a), whereas Ca is more weakly bound and its removal is accompanied by the loss of neighboring oxygen atoms. An example of this is presented in figure 4(b), where we observe a strongly reduced image intensity in a calcium column. A structure model was built in which a stack of two Ca atoms was removed. Additional simulations including missing neighboring O atoms are shown in figure S4 and demonstrate that O vacancies produce only very small contrast changes under the present experimental conditions. Geometry optimization confirmed that

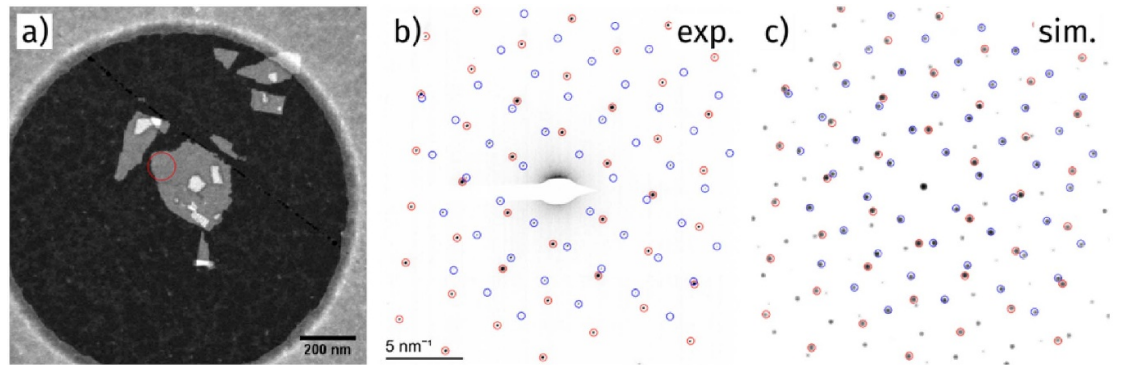


Figure 2. (a) Overview HAADF-STEM image of a CNO monolayer on WSe₂. (b) shows the SAED pattern from the area marked in red. The diffraction spots corresponding to WSe₂ are marked in red while those corresponding to CNO are marked in blue. (c) shows a simulated [001] diffraction pattern of a heterostructure of CNO and WSe₂ for comparison. In both cases, only the major spots were marked. Weaker spots in the center of the squares were omitted for clarity, but are present in both the experimental and simulated patterns.

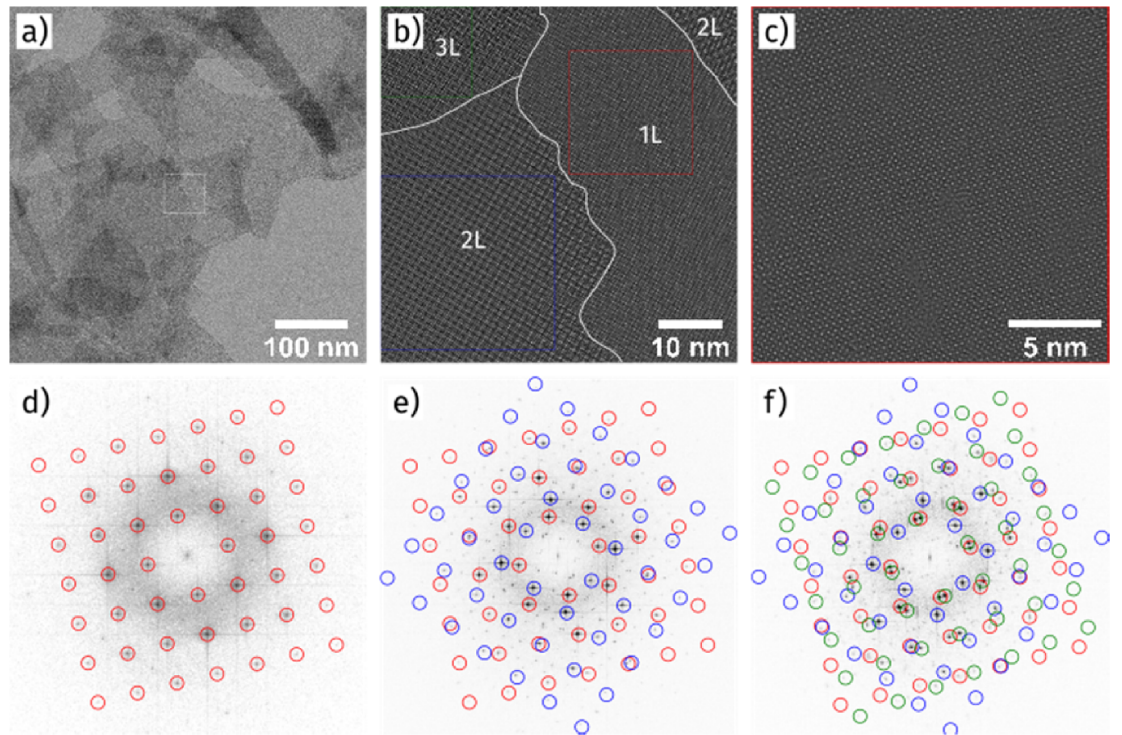


Figure 3. 60kV Cc/Cs-corrected HRTEM of freestanding CNO over a crack in the supporting WSe₂. (a) shows an overview image, revealing the randomly deposited thin sheets. (b) shows a high magnification view of the area marked in white, revealing a thin monolayer area as well as two and three sheets stacked on top of each other in other areas. (c) shows a magnified crop from the monolayer area marked red, revealing the lattice with atomic resolution. (d)–(f) show FFTs from the mono, double and triple layer areas as marked in (b) with red, blue and green boxes, respectively. The different lattice orientations are marked with their respective colors, revealing their single-crystalline lattices.

this structure is a stable configuration. Image simulations have been performed using abTEM [61], incorporating the following simulation parameters: experimental imaging conditions, residual aberrations, and noise based on the experimental electron dose and camera sensitivity. The results presented in figure 4 support the proposed defect structures, as the simulated images closely match the experimental one, which is also confirmed quantitatively by the line profiles in the lower row of figure 4. Minor

discrepancies between the image calculation and the experiment can be explained by the statistical nature of random noise. Under continued irradiation, the defects agglomerate quickly to form holes in the layer until the monolayer is ultimately destroyed after just a few image acquisitions.

To further elucidate the damage mechanism, we calculated displacement threshold energies and also assessed cross-sections for atom displacements within the framework of the McKinley-Feshbach formalism

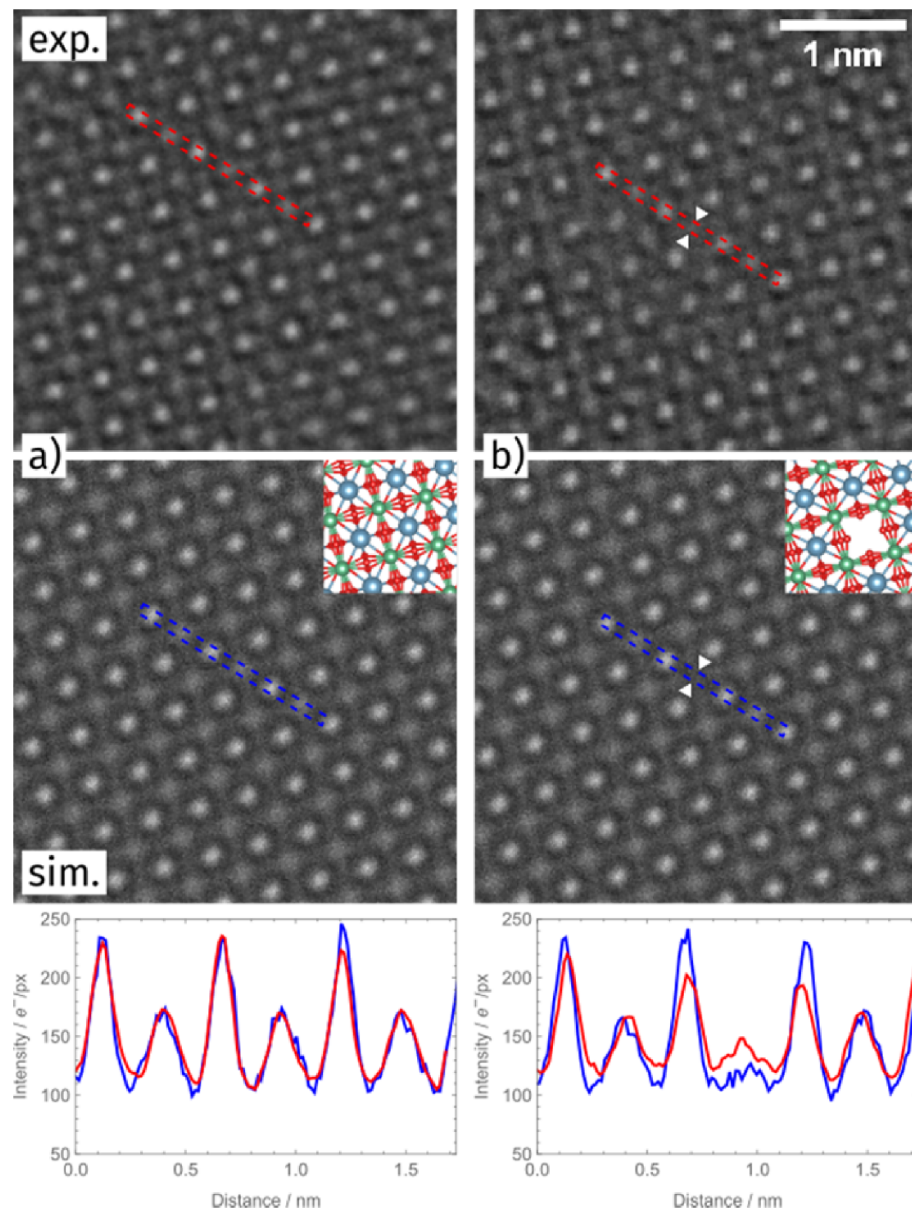


Figure 4. Defects in freestanding CNO monolayer: Top row shows experimental 60kV Cc/Cs-corrected HRTEM images, middle row the corresponding image simulations and the lower row compares line profiles from the experiment (red) and simulation (blue). (a) shows a largely pristine monolayer area without major defects. The brightest spots are the niobium columns, with the calcium in each center. The inset of the corresponding image simulation shows the structure model, with niobium green, calcium blue and oxygen red. (b) shows a calcium double vacancy defect. The simulated image is based on an MD calculation of a relaxed calcium double vacancy. Note that the models used for the simulations in figure 4 are without oxygen vacancies. Missing O atoms produce only very small contrast change (see figure S4), which is impossible to measure under our experimental conditions.

[62]. We considered both hydrogen-passivated structures (CNOH) and those without hydrogen. As shown below, H atoms are expected to be rapidly sputtered from monolayers by the electron beam, and further defect formation can be described by considering the CNO system. The results are presented in table 1 and figure 5. The displacement cross section for H atoms is rather high at electron energies below 60 keV, and the CNOH structure generally exhibits higher stability under the beam, as evidenced by higher irradiation threshold energies for various oxygen species on the surface (table 1 and figure 5) as compared to those in CNO. The situation is different,

though once most of the H atoms are displaced. It is evident that O atoms in the bottom layer (labeled as O^1) can easily be sputtered away by the electron beam already at electron energies of about 27 keV. The same is relevant to O atoms in the next layer (labeled as O^2), but the threshold electron energy is slightly higher (about 35 keV). It is worth noting that the recoil O^2 atoms normally pick up another O atom from the bottom layer (labeled $O^1 + O^2$), so that O_2 molecules leave the system. The threshold energies of the heavier Ca and Nb atoms in the pristine system are significantly higher. This is expected, as Nb bonds to four additional O atoms from the second

Table 1. Calculated displacement threshold energies and corresponding electron-beam irradiation threshold energies for selected atomic species in CNO and hydrogen-passivated CNOH monolayers. O¹, O², O³, and O⁴ denote the oxygen sites indicated in figure 5. 'O¹ + O²' refers to a correlated displacement process in which recoil of an O² atom leads to removal of a neighboring O¹ atom and emission of an O₂ molecule. 'NbO₄' denotes displacement of a Nb-centered unit rather than an isolated Nb atom.

	CNO				CNOH				
	O ¹	O ² (O ₂ =O ¹ + O ²)	Nb (NbO ₄)	Ca	H	O ¹	O ²	O ³ (OH)	O ⁴
Displacement threshold energy (eV)	3.80	5.00	13.70	15.10	7.3	10.1	12.2	6.4	19.8
Electron beam irradiation threshold energy (keV)	27	35	413	226	4	69	83	45	129

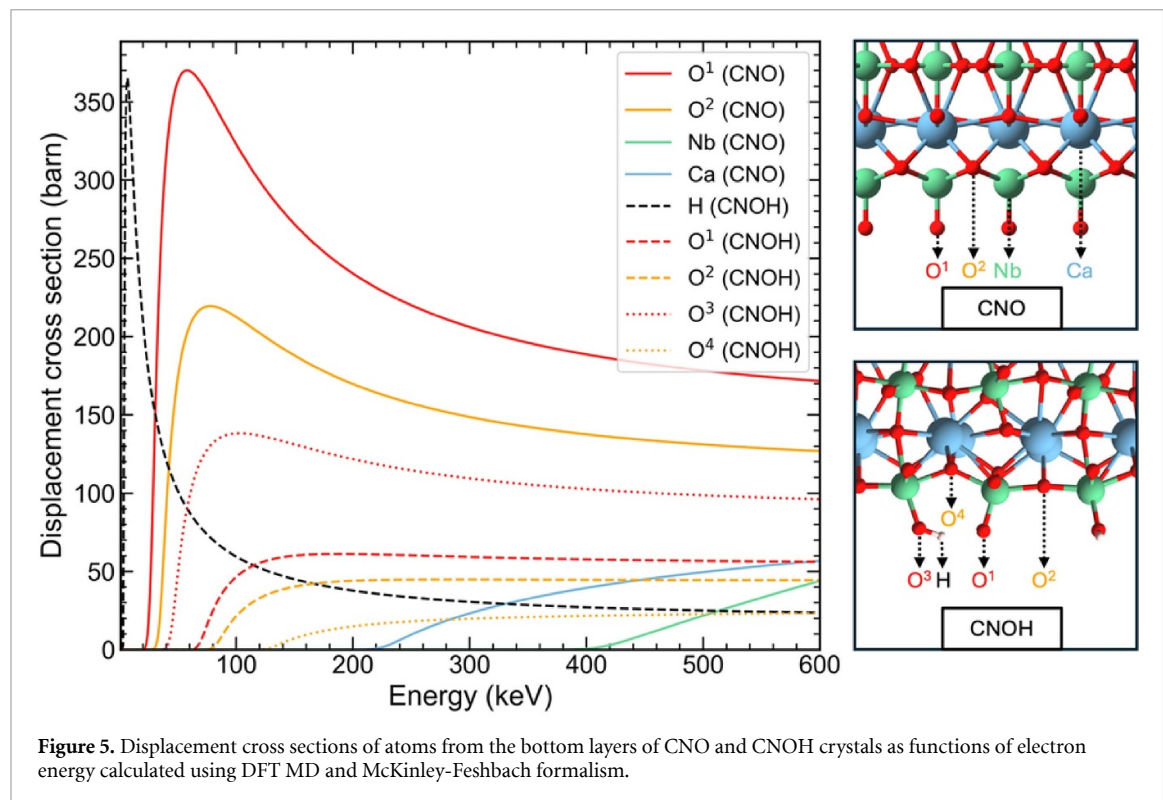


Figure 5. Displacement cross sections of atoms from the bottom layers of CNO and CNOH crystals as functions of electron energy calculated using DFT MD and McKinley-Feshbach formalism.

layer (O²), and is emitted from the monolayer as a relatively heavy NbO₄ molecule (note that O¹ beneath Nb is assumed to be already sputtered, see right panels in figure 5). The strong bonding of Nb atom to its neighbors is reflected in the formation energies of NbO₄ multivacancy (5.93 eV) and Nb single vacancy (21.54 eV): they differ by almost 16 eV, favoring the displacement of NbO₄ species rather than Nb single atom. In contrast, Ca is displaced as a single atom, although a significant Coulomb attraction to the O¹ atoms remains, exerting a force greater than 0.1 eV Å⁻¹ even at a separation of ~13 Å, explaining the much lower Ca vacancy formation energy of 4.64 eV as compared to the displacement threshold energy of 15.10 eV. Therefore, the threshold energies are expected to decrease substantially when multiple neighboring O atoms are removed. Note that although the displacement threshold energy is higher

for Ca than NbO₄, energy transfer in an elastic collision from electron to a heavy target is inversely proportional to the target mass, so more energetic electrons are required to transfer the same amount of energy to the heavier Nb atoms. Hence, the threshold electron energy for Nb is almost twice as high as that for Ca, making Ca atoms more susceptible to displacement. This is consistent with HRTEM images of defective CNO monolayers shown in figure 4. Overall, these findings suggest that the material is only marginally stable under electron beam irradiation, in agreement with the experimental observations. Note that the models shown in figure 4 are without oxygen vacancies. As shown in figure S4, missing O atoms produce only very small contrast changes that remain below the detection limit under the present experimental conditions. Therefore, the sputtering of O¹ and O² atoms predicted by our

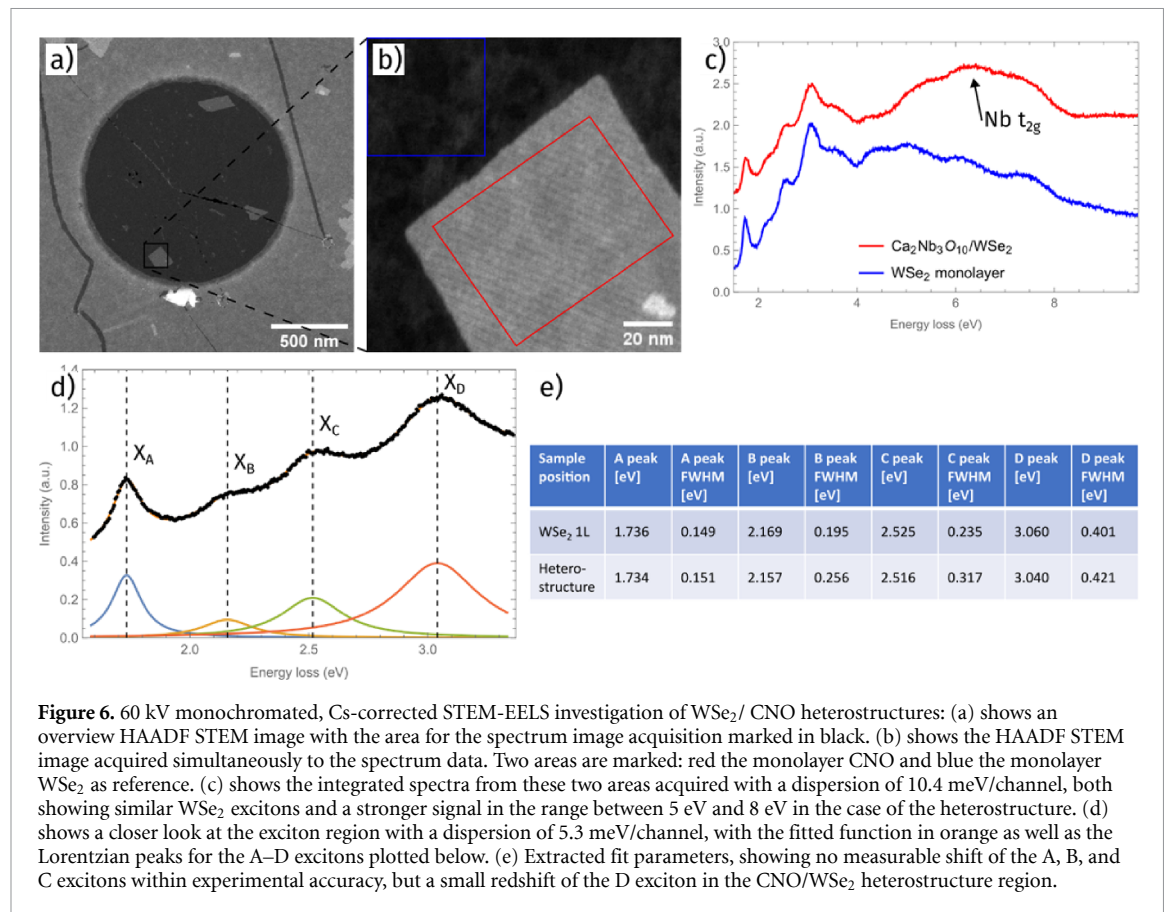


Figure 6. 60 kV monochromated, Cs-corrected STEM-EELS investigation of WSe₂/CNO heterostructures: (a) shows an overview HAADF STEM image with the area for the spectrum image acquisition marked in black. (b) shows the HAADF STEM image acquired simultaneously to the spectrum data. Two areas are marked: red the monolayer CNO and blue the monolayer WSe₂ as reference. (c) shows the integrated spectra from these two areas acquired with a dispersion of 10.4 meV/channel, both showing similar WSe₂ excitons and a stronger signal in the range between 5 eV and 8 eV in the case of the heterostructure. (d) shows a closer look at the exciton region with a dispersion of 5.3 meV/channel, with the fitted function in orange as well as the Lorentzian peaks for the A–D excitons plotted below. (e) Extracted fit parameters, showing no measurable shift of the A, B, and C excitons within experimental accuracy, but a small redshift of the D exciton in the CNO/WSe₂ heterostructure region.

calculations cannot be directly tracked experimentally; instead, we observe the subsequent Ca-related contrast loss.

Having established the atomic structure of monolayer CNO and identified the beam-induced defect formation that may occur under electron irradiation, we next investigate the electronic response of WSe₂ in the CNO/WSe₂ heterostructure. To this end, STEM-EELS investigations were performed using the monochromated, Cs-corrected Nion HERMES (STEM) instrument, operated at an acceleration voltage of 60 kV. The goal was to find out whether the CNO overlayer modifies the excitonic response of the underlying WSe₂. We performed EELS mapping in two energy ranges: first up to 5 eV with a fine dispersion of 5.3 meV per channel, focusing on the WSe₂ excitons, and second, using a higher dispersion of 10.4 meV/channel extending up to 10 eV to include the niobium t_{2g} transitions. These transitions occur when valence electrons are excited into the t_{2g} bands of niobium and are associated with energies of approximately 4.5 eV and 7 eV [63]. After completing the scans, we performed non-monochromated multi-EELS measurements at a high dispersion of 500 meV/channel to verify that the CNO remained intact. Figure 6 shows the results of such an experiment. The scan area was centered on a monolayer of CNO atop a monolayer of WSe₂ (figures 6(a) and (b)). A comparison of the integrated EELS data

up to 10 eV (figure 6(c)) reveals a stronger signal in the range of 4.5–8 eV in the heterostructure region, which can be attributed to the niobium t_{2g} transitions [64]. This signal is absent in the reference spectrum taken from the isolated WSe₂ layer during the same acquisition, while the rest of the spectrum remains virtually identical between the two areas. To investigate the WSe₂ exciton peaks in more detail, we analyze the data using the highest dispersion, i.e. 5.3 meV ch^{-1} (figure 6(d)). The fitted curve closely matches the experimental data, revealing only minor shifts in the exciton peak positions. Notably, the D exciton is redshifted by 20 meV in the heterostructure area (figure 6(e)). Given that the estimated energy resolution, based on the FWHM of the ZLP, is 10.7 meV, the shift is larger than the instrumental energy resolution estimated from the ZLP FWHM and is reproducible across the mapped heterostructure region.

To elucidate local variations in the EELS spectrum and correlate them with the spatial position of the CNO/WSe₂ heterostructure, the analyzed EELS data were mapped over the scanned area using the procedure described in the Methods section. Figure 7 shows representative maps. Integrating the spectral intensity from 4.5 eV to 8 eV (figure 7(b)) reveals a strong spatial correlation with the shape of the CNO flake observed in the simultaneously acquired HAADF-STEM image (figure 7(a)). Mapping the fitted D exciton peak (figure 7(c))

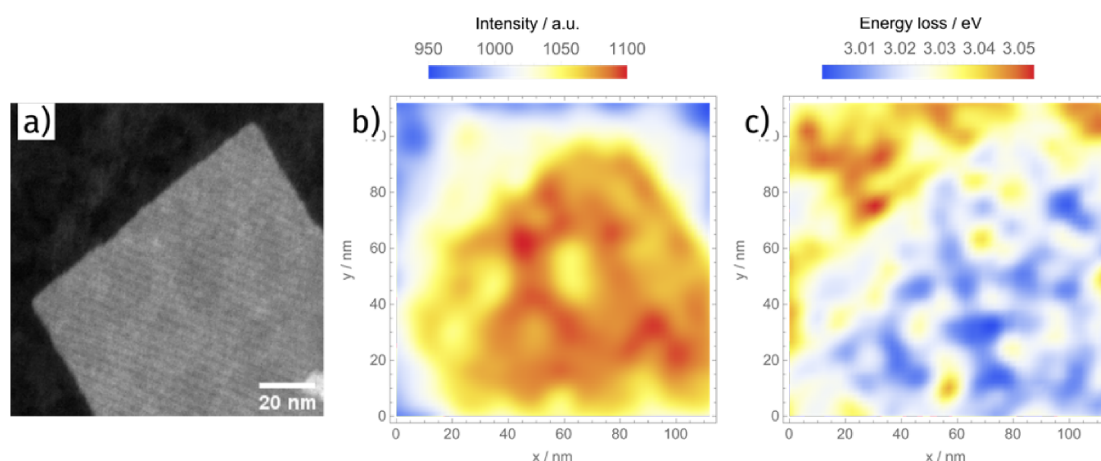


Figure 7. 60 kV monochromated STEM-EELS mapping of the WSe₂/CNO heterostructure: (a) HAADF STEM image acquired simultaneously with the EELS spectrum image. (b) maps of the integrated EELS intensity in the range of 4.5 eV to 8 eV over the scan area. (c) Map of the fitted D-exciton peak position, showing a small redshift spatially correlated with the CNO overlay.

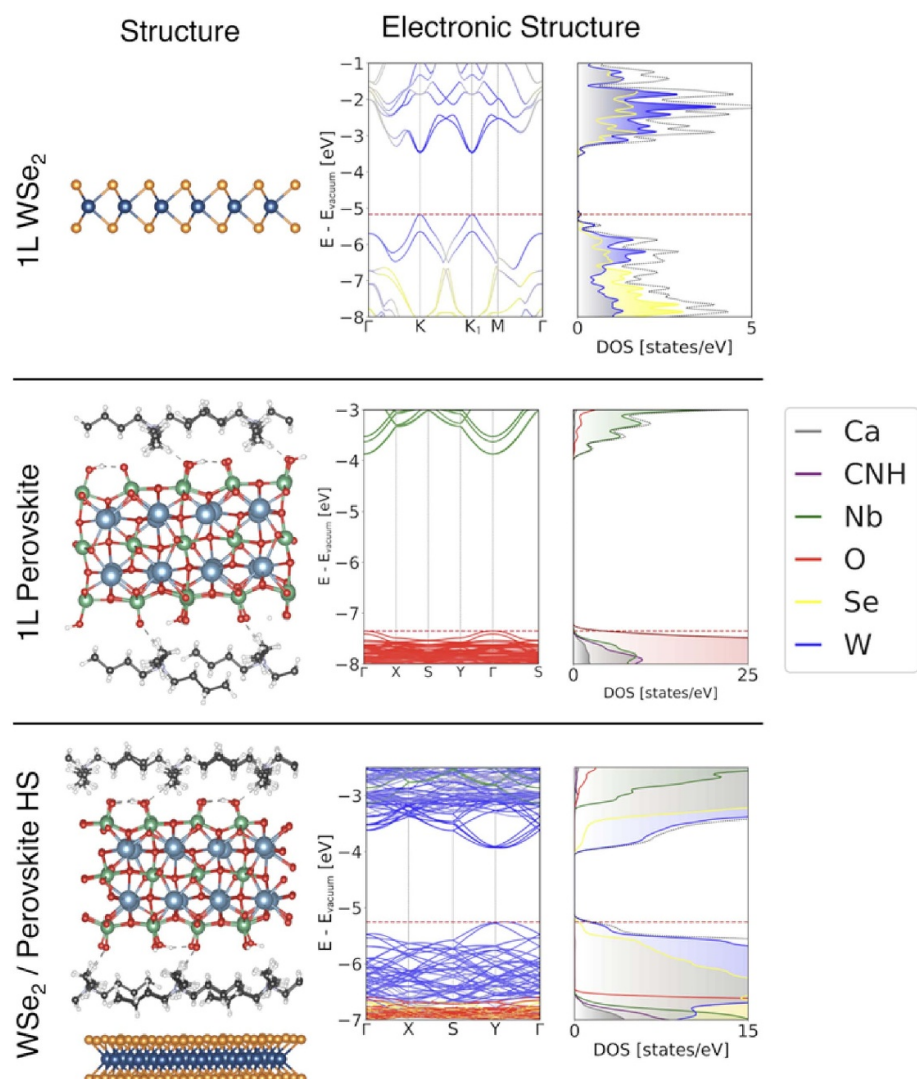


Figure 8. Atomic structures (side views) and the corresponding electronic structures (projected band structure and density of states on atoms or atom groups) of 1L WSe₂, 1L perovskite with mixed three H⁺ and one TBA⁺ counterion, and the corresponding heterostructure. The HS is a type-I semiconductor with band edges formed by WSe₂ monolayer. Other combinations of counterions may result in type-II HS (see supplemental information for details).

shows a corresponding correlation between the CNO-covered region and the redshift of the D exciton. In contrast, the A, B, and C excitons do not show a systematic peak shift in the CNO-covered region compared with uncovered monolayer WSe₂. Within the fitting uncertainty, we also do not observe a systematic linewidth change between the WSe₂-only and CNO/WSe₂ regions.

The observation that only the D exciton shows a measurable energy shift in the CNO/WSe₂ heterostructure, whereas the A, B, and C excitons remain unchanged within experimental accuracy, can be rationalized by the different k-space origins and screening sensitivities of these resonances. The A and B excitons originate from the K point, where environmental screening can affect both the quasiparticle band gap and the exciton binding energy in a partially compensating manner. In contrast, higher-energy band-nesting excitons, such as the D exciton, are more sensitive to changes in the local dielectric environment and to weak interfacial perturbations [65–68]. Other possible mechanisms, such as strain or charge transfer, are unlikely to be the dominant origin of the observed effect, because they would be expected to also affect the A and B excitons, which is not observed here. [69, 70]. Moreover, the HRTEM/FFT analysis shown in figure S2 reveals no measurable lattice distortion or atomic reconstruction of the WSe₂ lattice in the heterostructure region. Similarly, beam-induced defects could in principle introduce additional low-energy states or modify the linewidths. However, we do not observe additional low-energy features, peak splitting, or systematic linewidth broadening attributable to defect-related states [71]. We therefore attribute the selective D-exciton redshift primarily to a weak local modification of the dielectric/electronic environment induced by the CNO overlayer.

Finally, we simulated several models of CNO/WSe₂ heterostructures using DFT. All the models result in weakly bound heterostructures, however, the electronic properties strongly depend on the counterions used around the perovskite monolayer. As a baseline, we first used K⁺ ions, although they are expected to be washed out during heterostructure formation. We then examined H⁺, NH₄⁺, NC₄H₁₂⁺, and larger organic cations (see supplemental information for details). Our calculations show that K⁺ and NH₄⁺ lead to semiconducting material, whereas the other environments yield metallic behavior due to strong shifts of the perovskite band edges. Because of the weak interlayer interaction, the heterostructure band structure largely resembles a superposition of the individual WSe₂ and perovskite bands. These results suggest that reproducing the experimentally relevant semiconducting state likely requires a mixed H⁺ environment. Since the exact ratio is unknown, we selected the smallest DFT-feasible model containing three H⁺ and one TBA⁺ molecule on each side of

the perovskite layer (see figure 8). The corresponding band structure exhibits a type-I semiconductor with band edges originating from WSe₂. We emphasize that other H⁺/TBA⁺ ratios may also result in type-II alignment, as individual ions shift band edge of the perovskite in opposite directions. Owing to the complexity of the model, the presence of strain, and the fact that the present ground-state DFT calculations do not directly describe excitonic shifts, we do not attempt a quantitative calculation of the experimentally observed D-exciton redshift. Nevertheless, the calculations support weak interfacial coupling and show that the electronic structure is highly sensitive to the charge-compensating environment of the CNO layer. The presence of higher-energy perovskite-derived states may qualitatively contribute to weak perturbations of higher-energy WSe₂ excitonic resonances, consistent with the experimentally observed selectivity of the D exciton.

4. Conclusion

In this study, we prepared van der Waals heterostructures consisting of monolayers of CNO, partially suspended on monolayers of WSe₂, and analyzed the atomic structure of the freestanding CNO regions. Despite its high sensitivity to electron beam irradiation, Cc/Cs-corrected high-resolution TEM at 60 kV enabled atomic-resolution imaging of largely intact CNO monolayers. Upon continued electron irradiation, atomic defects formed. Their atomic structures were analyzed by comparison with TEM image simulations and first-principles calculations, showing that oxygen and calcium atoms are preferentially ejected from the lattice.

We further investigated the excitonic response of WSe₂ in the CNO/WSe₂ heterostructure using 60 kV atomic-resolution STEM-EELS with an energy resolution of 10.7 meV. By mapping the exciton peak positions of WSe₂ in the low-loss EELS region, we observed a small but reproducible redshift of the D exciton in regions covered by CNO, whereas the A, B, and C excitons remained unchanged within the experimental accuracy. This selective shift is consistent with a weak interfacial modification of the local dielectric/electronic environment rather than the formation of interlayer excitons.

Overall, our results demonstrate that functional oxide nanosheets can be integrated with TMD monolayers to form oxide/TMD van der Waals heterostructures with locally modified excitonic properties. This provides a promising strategy for engineering the optical and electronic response of two-dimensional materials through heterostructure formation.

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Data availability statement

The data cannot be made publicly available upon publication because they are not available in a format that is sufficiently accessible or reusable by other researchers. The data that support the findings of this study are available upon reasonable request from the authors.

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