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A novel Pd_2Se_3 two-dimensional phase driven by interlayer fusion in layered $PdSe_2$

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Many novel physical phenomena and fascinating properties emerge when materials are thinned down to two dimension (2D) [1, 2]. Therefore, in the last decade of the 2D materials research, the search for new 2D materials with fascinating physical properties became the scientific mainstream. So far, all known 2D materials have essentially the same atomic structure as a single layer of the corresponding layered bulk form [3, 4].

Here we report the first example of a 2D material whose stoichiometry and structure is different from the corresponding layers in the bulk form. In the mechanically exfoliated $PdSe_2$ sample (schematic shown in Fig. 1), we found that the monolayer form of layered $PdSe_2$ differs from what one expects from its bulk counterpart. The monolayer is in a completely new Pd_2Se_3 phase with unique structure and beautiful symmetry, that has never been reported even as a bulk phase (Fig. 2).

Combining the atomic imaging in a scanning transmission electron microscope (STEM) and density functional calculations, we discovered that this new monolayer phase is reconstructed directly from a $PdSe_2$ *bilayer* through a vertical-interlayer fusion mechanism. We further demonstrate that the interlayer fusion process is triggered by Se deficient conditions in $PdSe_2$ layers, where a substantial reconstruction of the residual under-coordinated Pd atoms pulls the layers towards each other, fusing them into a new Pd_2Se_3 layer, which inherits the lattice parameters from its parent $PdSe_2$ phase. As evidence, we used electron irradiation to create artificial Se-deficient conditionsion few-layer $PdSe_2$. The new Pd_2Se_3 is observed to grow along the $PdSe_2$ matrix by in-situ sequential imaging, which verifies our DFT predictions.

Our work reveals that the $PdSe_2$ phase expected from bulk $PdSe_2$ is not the intrinsic monolayer phase in the monolayer limit of $PdSe_2$. This is due to the substantial interlayer interaction which leads to the unexpected interlayer fusion. Instead, the as-fused Pd_2Se_3 phase reported in this work serves as an alternative and the most stable monolayer phase derived from the bulk $PdSe_2$. Our findings represent a breakthrough in understanding another fascinating property in monolayer materials and opens the way for more complex engineering of 2D phases [5].

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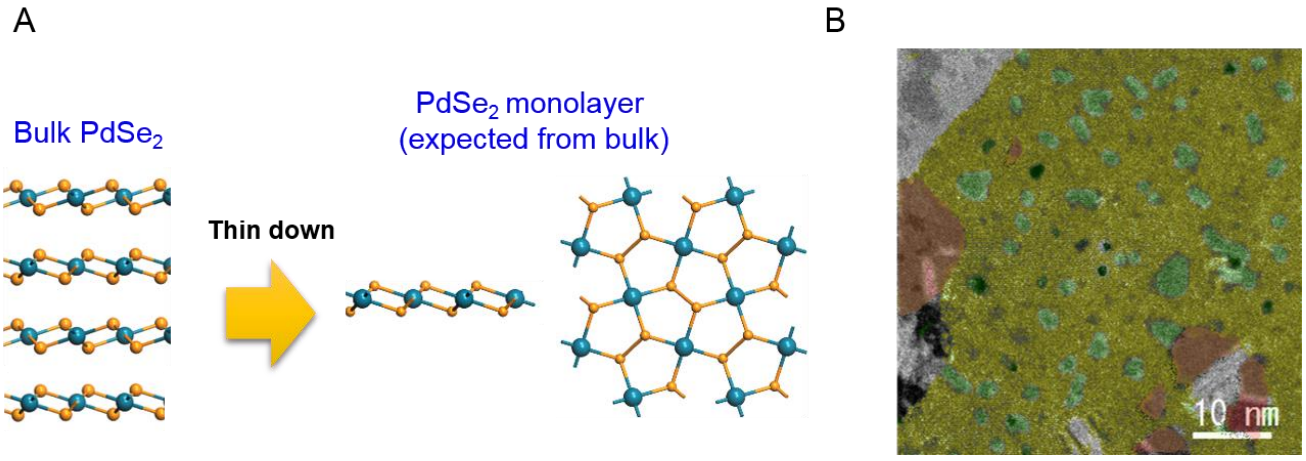

Figure 1: Exfoliation of layered $PdSe_2$ sample. (A) Schematic of the expected exfoliation of monolayer $PdSe_2$ from its bulk form. (B) ADF STEM image of a large area of few-layer $PdSe_2$. The image intensity indicates a layer-by-layer thinning as highlighted by different colors, where the yellow corresponds to tri-layer, green as bilayer and red as monolayer.

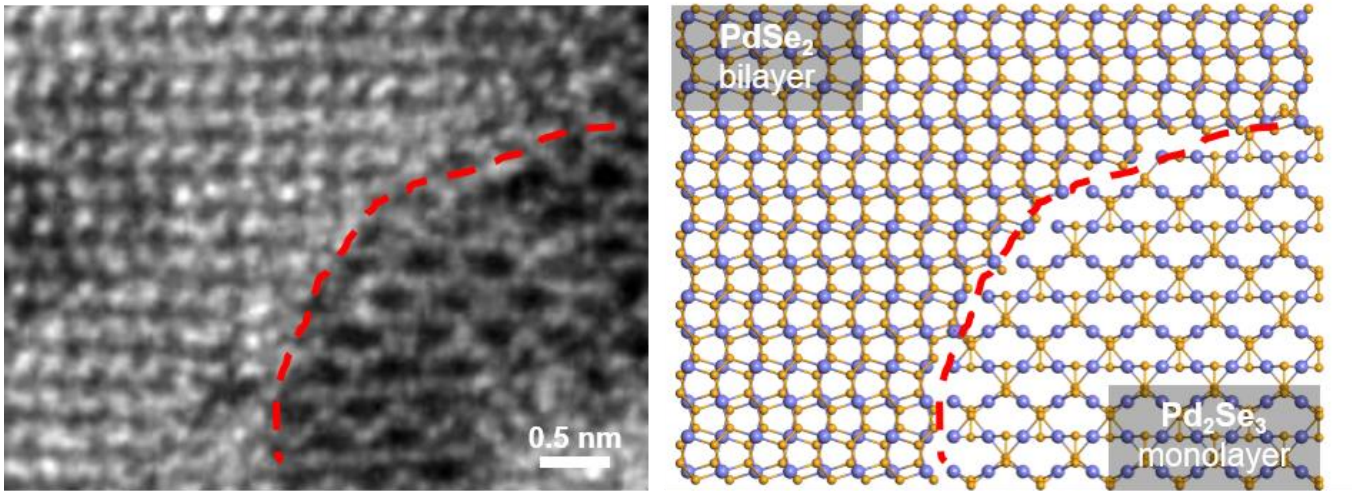

Figure 2: High resolution image of the exfoliated layered $PdSe_2$ sample. High resolution ADF STEM images showing a thin few-layer exfoliated region. The monolayer is in Pd_2Se_3 other than $PdSe_2$ phase.

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