Two-dimensional covalent crystals by chemical conversion of thin van der Waals materials

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Exfoliation of van der Waals materials has been the go-to approach to obtain 2D nanosheets. But recent efforts in expanding the 2D library has resulted in fabricating synthetic 2D crystals which have no layered bulk analogues [1,2]. These efforts have been focused mainly on the surface growth of molecules in high vacuum or using template assisted growth techniques. Here, we report an alternate approach to making 2D crystals of covalent solids by chemical conversion of van der Waals layers [1]. As an example, we used 2D indium selenide (InSe) obtained by exfoliation and converted it by direct fluorination into indium fluoride (InF_3), which cannot be obtained by direct exfoliation (Fig. 1). The conversion of InSe into InF_3 is found to be feasible for thicknesses down to three layers of InSe, and the obtained stable InF_3 layers are doped with selenium. We study this new 2D material by optical, electron transport, and Raman measurements and show that it is a semiconductor with a direct bandgap of 2.2 eV, exhibiting high optical transparency across the visible and infrared spectral ranges. We also demonstrate the scalability of our approach by chemical conversion of large-area, thin InSe laminates obtained by liquid exfoliation, into InF_3 films. The concept of chemical conversion of cleavable thin van der Waals crystals into covalently bonded non-cleavable ones opens exciting prospects for synthesizing a wide variety of novel atomically thin covalent crystals. The method can be extended to other materials. I will discuss our most recent results in this area of research.

References

[1] Vishnu Sreepal, et. al "*Two-dimensional covalent crystals by chemical conversion of thin van der Waals materials*" *Nano letters*, 19, 9, 6475-6481 (2019)

[2] R. R. Nair et. al,"*Fluorographene: A two-dimensional counterpart of Teflon*" *Small* 6, 2877 (2010).

Figures

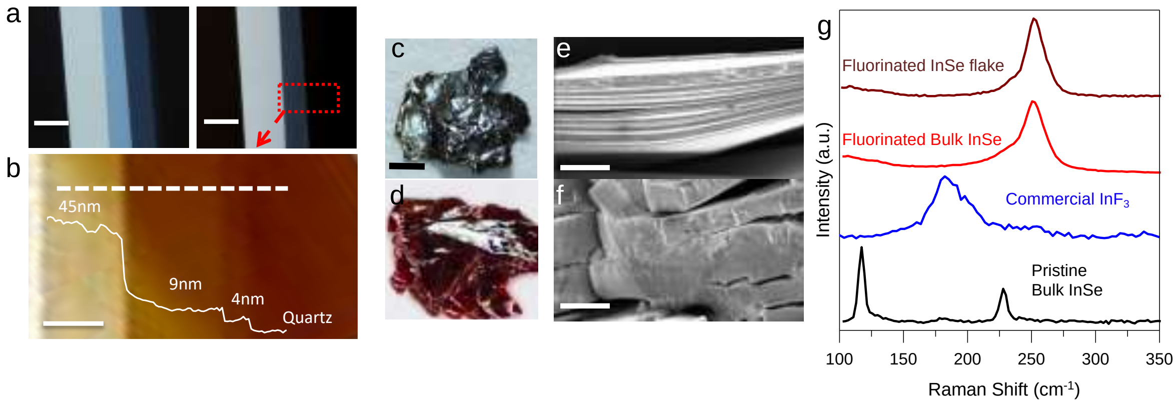

Figure 1: Characterization of fluorinated InSe. (a) Optical microscope images of InSe flakes on quartz substrate before (top left) and after (top right) fluorination. Scale bars, 7 µm. (b) An AFM image of the area marked with the red rectangle in Figure 1a. Scale bar, 5 µm. White curve: height profile along the dashed line. (c,d) Photographs of bulk InSe before and after the fluorination, respectively. Scale bars, 1 mm. (e,f) Cross-sectional SEM images of bulk pristine InSe and fluorinated InSe, respectively. Scale bars, 5 µm. (g) Raman spectra of a fluorinated InSe flake (~10 nm thick), fluorinated bulk InSe, commercial InF_3, and pristine bulk InSe