Supplementary Information

Growth of single-crystal InSe

Single crystalline ingot of InSe was grown from melt by the vertical Bridgman−Stockbarger method [1]. In and Se starting elements of a high purity grade (not less than 99.999%) were sealed in quartz ampoule, which was annealed at 950 °C under a vacuum of 10^{-6} mbar for 15 hours in a furnace. The temperature of quartz ampoule was decreased to room temperature in 24 hours. The crucible was then suspended in the middle of the vertical furnace with two zone designed. The temperature of furnace was increased to 950 °C and stayed at that temperature for 40 hours and then decreased to 750 °C. Temperature was kept at 750°C for 15 hours. The temperature of lower zone of furnace was reduced to 250 °C at a rate of 1.54 °C/h. Both of the furnace zones cooled to 250 °C in 75 hours. The solidified ingot was cooled to room temperature in 50 hours.

The grown InSe samples are 10 mm in diameter and about 60 mm in length. Samples were exfoliated into perpendicular planes of naturally cleaved (0001) planes by micromechanical cleavage.

The grown crystal was checked by X-ray diffraction (XRD) using a Bruker diffractometer with Cu−Kα radiation.

Nanofabrication of devices

The exfoliated InSe layers typically had a thickness of few atomic layers. In order to fabricate the devices capped with a thin h-BN layer we used thin viscoelastic materials adhered to glass slides, which were used as transparent stamps for h-BN layer transfer onto the selected site. The h-BN layers have also been exfoliated mechanically from bulk crystals. The details of our h-BN transfer

procedure have been reported elsewhere [2, 3]. Following this method we were able to cap and protect the sections of the InSe channel from exposure to the atmosphere.

Theoretical methods

We have used the QUANTUM-ESPRESSO code [4] and the GGA–PBE + vdW approximation, which is feasible for description of adsorption of molecules on the surfaces [5, 6] with employment of ultrasoft pseudopotentials. [7] We have used energy cutoffs of 25 Ry and 400 Ry for the plane-wave expansion of the wave functions and the charge density, respectively, and the 6×6×1 Monkhorst-Pack *k*-point grid for the Brillouin sampling [8].

For the modeling of the surface of InSe we use $In_{32}Se_{32}$ monolayer.

Vibrational experiments

HREELS experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS) at University of Calabria, Rende (CS), Italy. The energy resolution of the spectrometer is 5 meV. The primary electron beam energy is 4 eV. Each spectrum was normalized to the intensity of the elastic peak. HREELS spectra were acquired in specular conditions, with incident and scattering angles of 55° with respect to the surface normal.

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