Layered Ultrathin PbI$_2$ Single Crystal for High Sensitivity Photodetector

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Designing of mineralizer:

Considering that the (001) plane of PbI$_2$ tends to be terminated by I$^-$, in order to restrict the growth rate along the [001] direction and enhance the two dimensional growth of the single crystals, the basic growth units should be negatively charged. KI was usually used as mineralizer for growing iodide single crystals, which can generate negative charged complex ions. However, for our system, excessive KI may lead to the formation of KPbI$_3$. Therefore, we choose KNO$_3$ (1 M) as the mineralizer. The schematic illustration of the growth habit of PbI$_2$ in presence of KNO$_3$ mineralizer is shown in Figure S1. As shown in Figure S1, adding high-concentration NO$_3^-$ ions to the solution may lead to the formation of the intermediate complex [PbI$_2$(NO$_3$)]$_2^-$ and thus increased the solubility of PbI$_2$. More importantly, the basic growth units in such a growth environment should be the negatively charged [PbI$_2$(NO$_3$)]$_2^-$-ions, which are less likely to be absorbed on the I-terminated (001) plane. Therefore, the growth rate along the [001] direction is restricted, and the continuous two-dimensional growth can be achieved.

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Electric characteristics of PbI₂ with different metal contacts:

To evaluate the influence of different metal contacts on the electric characteristics of PbI₂, we have deposited different metals (Au, Cu, Ag, 50 nm thick) on the ultrathin PbI₂ single crystals (300 nm thick using mechanical exfoliation from the thin PbI₂ single crystals) through a Cu grid shadow mask to form two electrodes with a gap of 20 μm. The current-voltage (I-V) characteristics of the devices were measured in dark and under the illumination of a 407 nm laser diode. The dark current and light current of the devices using different metal contacts at 5 V bias were shown in Figure S2. It can be seen that under our experimental conditions, with the increasing of the work function of metal contacts, the dark current of the devices decreased dramatically, while the light current were not significantly changed. Thus, Au contacts can effectively improve the ON/OFF ratio of the PbI₂ photodetectors. Here, it should be noted that decreasing the thickness of PbI₂ single crystal is also an effective way to reduce the dark current of the lateral M-S-M photodetectors.
Figure S2. Dark current vs. light current of the devices using different metal contacts at 5 V bias.

Furthermore, to exhibit the contact behavior of Au on PbI$_2$, we also fabricate a device on a 2 μm thick PbI$_2$ single crystal with one 2 × 2 mm Au contact on the top and another on its back. The $I$-$V$ measurements (shown in Figure S3) showed that the Au contacts exhibit a non-Ohmic rectifying behavior, which may be responsible for the suppressed dark current.

Figure S3. $I$-$V$ curves of Au metal contacts on 2 μm thick PbI$_2$ single crystal in a vertical configuration.