

Anti-Stokes Photoluminescence of van der Waals Layered Semiconductor PbI_2

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Recently, organic–inorganic lead iodide perovskite has become one of the most promising emergent materials, which exhibits great potential in photovoltaics, lasing, laser cooling, etc. The building block of such great material is PbI_2 , a van der Waals (vdW) layered semiconductor material, which arouses increased interest also owing to its potential applications for X-ray and γ -ray detection, lasing, etc. Similar and even superior to some vdW layered materials such as thin layers of transition metal dichalcogenides like MoS_2 , WS_2 , MoSe_2 , or WSe_2 , PbI_2 layers possess a direct bandgap of visible frequency with a wide range of thicknesses (>3 layers). This study reports the anti-Stokes photoluminescence (ASPL) of PbI_2 layers, which is very rarely investigated at present. Universe and robust ASPL in both 4H- and 2H- PbI_2 layers are observed and a phonon-assisted and multiphoton absorption up-conversion mechanisms are proposed through in situ temperature-dependent, incident laser-power-dependent measurements of both Stokes photoluminescence and ASPL. The successful observation and explanation of the universal anti-Stokes emission of PbI_2 layers, will certainly enrich fundamental understandings of vdW layered semiconductors and perovskite, then further benefit to developing applications based on such emerging materials.

Van der Waals (vdW) layered materials, especially semiconductors exhibit rich properties of optics, electronics, optoelectronics, etc.^[1–6] The feasibility of thinning such layers even down to a single atomic/molecular layer and transferring thin layers onto other 2D materials offers great chances to design and engineer dielectric environment of semiconductors in a 2D platform.^[3,5,7,8] Enhanced Coulomb interaction, particle–particle

coupling, spin–orbit coupling, and so on, are expected and indeed observed in these emerging vdW layer systems.^[2,9–11] Studies of light emission and light-matter interaction in such vdW layers are the unique and advancing means to explore fundamental understandings and develop practical applications of vdW layered semiconductors.^[2,5,9,11,12] Therefore, a layered semiconductor possessing a direct bandgap is highly desired for excitonic physics and technology study. Lead iodide, PbI_2 fits this criterion perfectly. PbI_2 crystals are built up by repeatedly stacking a hexagonally closed-packed layer of lead ions sandwiched between two layers of iodide ions. Superior to well-known transition metal dichalcogenides like MoS_2 , WS_2 , MoSe_2 , or WSe_2 , PbI_2 layers of even submicrometer thick show a direct bandgap of visible range (≈ 2.55 eV).^[13,14]

PbI_2 is a stable nuclear radiation detector^[15,16] and has been studied since 1970s. Moreover, PbI_2 is one of the building blocks hosting organic molecules and forming lead halide perovskite, the most promising candidate of photovoltaics recently, together with many great advances in lasers, laser cooling, etc.^[17–24] Raman scattering including resonant Raman effect. Stokes photoluminescence (SPL), stimulated emission, lasing, etc. of PbI_2 flakes have been observed and probed.^[14,25–28] However, up-conversion or anti-Stokes photoluminescence (ASPL), a critical feature of semiconductors and perovskite,^[18,29,30] is rarely investigated in PbI_2 .^[31] In this work, we prepare PbI_2 flakes of varying thicknesses by both mechanical exfoliation and chemical vapor deposition (CVD). The polytypes of the as-prepared PbI_2 flakes are identified by ultralow-frequency Raman spectroscopy to be either 4H or 2H phase. An obvious ASPL is observed for both 4H and 2H PbI_2 flakes at room temperature. The further in-situ low-temperature and power-dependent ASPL and SPL measurements clearly uncover the nature of the observed emission. The corresponding emission mechanisms are also proposed. Our findings contribute to a thorough understanding of vdW layered semiconductor PbI_2 and connecting it to studies of promising organic–inorganic perovskite, which is hosted by PbI_2 . Recently, anti-Stokes PL of lead halide perovskite was reported by Ha et al.^[18] Our studies of the anti-Stokes PL phenomenon of PbI_2 , as one of the precursors to form the lead halide perovskite, will be helpful to

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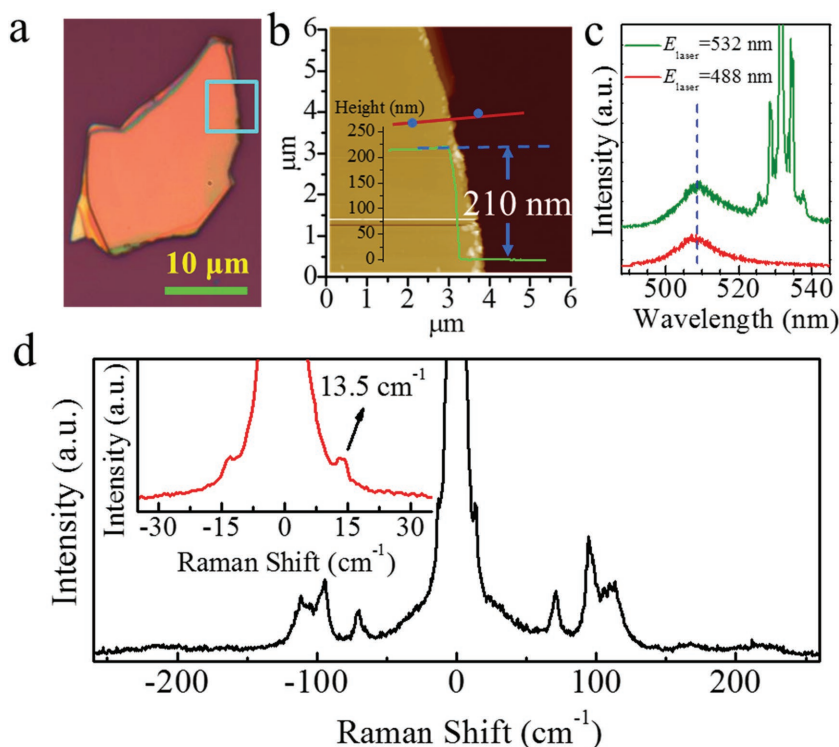


Figure 1. a) Optical image of mechanically exfoliated PbI_2 flake. b) AFM image with the height profile of the selected zone in (a). c) Stokes and anti-Stokes PL spectra and d) Raman spectrum of the PbI_2 flake. The sharp peaks near the excitation laser line (532 nm) in (c) are the Raman modes. Inset of (d) is the zoom-in view of the ultralow frequency region.

gain an insight into the anti-Stokes PL of lead halide perovskite. Using the well-developed method of obtaining thin layers/flakes from a vdW layered bulk crystal, we peeled flakes of PbI_2 with different thicknesses from a PbI_2 bulk crystal and transferred them onto 300 nm SiO_2/Si substrates. **Figure 1a** shows the optical image of a typical mechanically exfoliated PbI_2 flake with the thickness of 210 nm as determined by the atomic force microscopy (AFM) (**Figure 1b**). A direct energy bandgap structure associated with thin (more than 3 layers) and thick (even bulk) PbI_2 flakes facilitates remarkably strong PL emission.^[13,14] As clearly demonstrated in **Figure 1c**, at room temperature, a strong PL emission of 2.44 eV (508 nm) is pumped by the incident photons of 2.54 eV (488 nm) with laser power of 1 μW and integration time of 5 s. Interesting enough, in the same energy range, though comparably weaker, an obvious PL peak is observed under the excitation of 2.33 eV (532 nm) with relative higher laser power of 0.5 mW and longer integration time of 20 s. Such up-conversion anti-Stokes luminescence possesses many interests of uncovering fundamental knowledge and practical applications like laser cooling.^[18,29,30] Unfortunately, it is rarely studied for PbI_2 .

In addition to the PL emission, several ultrasharp peaks locating at the both sides of the excitation laser line (532 nm) are Raman modes of PbI_2 flake. It is well known the vdW layer PbI_2 has many polytypes.^[32,33] Among them, 2H and 4H are most frequently observed.^[32] 2H is the simplest form, which is similar to 2H- CdI_2 structure. Sharing the identical structural layers but differing in stacking orders, 4H PbI_2 is often formed

in samples grown by vapor-phase processes. Among the various techniques such as X-ray diffraction, transmission electron microscopy, etc. which are capable of characterizing phases of PbI_2 , Raman spectroscopy is the most simple and efficient method, especially for quick and precise distinguishing micrometer/submicrometer scale PbI_2 flakes of 2H or 4H phase. 2H and 4H PbI_2 belong to the space groups of D_{3d}^3 and C_{6v}^4 , respectively. The Brillouin-Zone center vibrations are represented as $\Gamma = A_{1g} + E_g + 2A_{2u} + 2E_u$ for 2H, where A_{1g} and E_g are Raman active modes; for 4H, $\Gamma = 3A_1 + 3B_1 + 3E_1 + 3E_2$, where $2A_1, 3E_2$ are Raman active modes and $2E_1$ are active for both Raman and Infrared.^[34] Among all these Raman modes, the most distinctive feature between 2H and 4H phases is in the ultralow frequency region (less than 30 cm^{-1}). **Figure 1d** displays the room temperature Raman spectrum of the PbI_2 flake shown in **Figure 1a**. Both Stokes and anti-Stokes Raman modes are presented. The zoom-in panel shows a sharp peak at 13.5 cm^{-1} , which represents the degenerate pair of shear-motion rigid-layer mode. Such mode is uniquely observable in 4H PbI_2 as where the alternate two layers from the doubling unit cell move against each other along the in-plane direction and form a zone-center Raman active optical mode,

while the vibration is a zone-boundary acoustic (Raman inactive) mode in 2H PbI_2 .^[35] In 4H polytype, the weak interlayer coupling (vdW interaction) should be able to lift the degeneracy of the E_1 mode ($\approx 71 \text{ cm}^{-1}$) and cause the frequency splitting of this mode, the so-called Davydov or factor group splitting.^[34] However, such splitting is highly excitation energy dependent and usually observed at cryogenic temperatures.^[34,36] It is also noticed that there is a relatively weak and broad Raman peak at around 215 cm^{-1} , which represents an overtone phonon mode (2LO) from a resonant Raman effect.^[25,37] In this work, we also systematically study the PbI_2 flakes grown by chemical vapor deposition. The appearing of the shear modes indicates the CVD grown PbI_2 flakes prefer to stack layers into a 4H phase and such 4H structures could sustain in the further formation process of organic-inorganic perovskite (see **Figure S1g**, Supporting Information).^[17] The ASPL and SPL universally present in the CVD-grown 4H PbI_2 though the feature of ASPL in the thin flakes (i.e., less than 40 nm) is trivial (see **Figure S1**, Supporting Information), especially under a low laser power for avoiding laser heating induced decomposition.

To further reveal the nature of the observed ASPL, in situ temperature-dependent photoluminescence measurements are conducted and the spectra are shown in **Figure 2a**. With the decrease of the temperatures, the ASPLs exhibit obvious blueshift meanwhile the strength of the emission gradually decays. This ASPL eventually fades out near 210 K under the laser power of 0.5 mW in this measurement. We attribute this up-converted ASPL to a phonon-assisted shallow level trap state

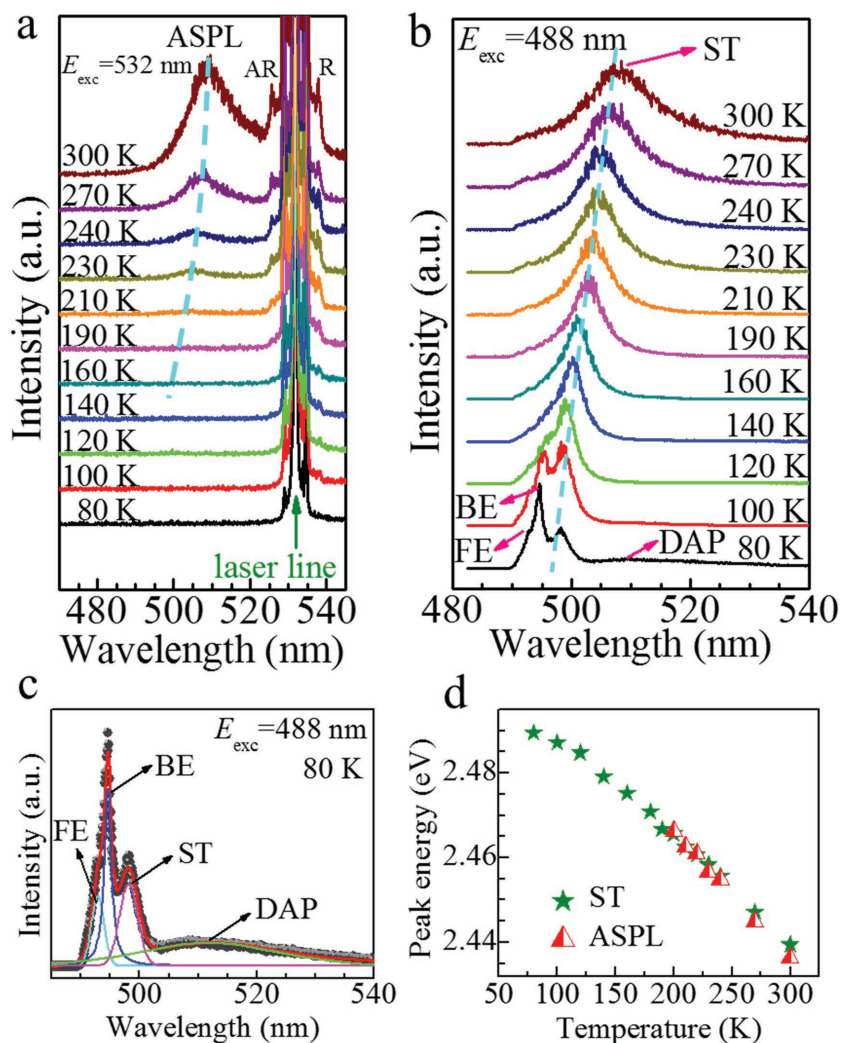


Figure 2. In situ temperature-dependent anti-Stokes a) and Stokes b) PLs of the mechanically exfoliated 4H-PbI₂ flake. c) PL spectrum with 488 nm excitation laser at 80 K with fitted curves. d) Emission peak energies of ASPL and ST as a function of temperatures. To clearly see the changes, the spectra in (a) and (b) are purposely shifted and the spectra in (b) are normalized. The original spectra of (b) is plot in Figure S2 in the Supporting Information. In (a), R represents Stokes resonant second-order Raman mode, while AR denotes anti-Stokes resonant second-order Raman mode.

emission (named as ST in this work) tentatively. The weakening of the ASPL in the cooling process is mainly due to the increment of the emission energy levels, shifting away from the incident energy and the significantly lowered absorbance of the pumping photons. Such off-resonance is also evidenced by the weakening of the resonant second order Raman mode (labeled as R). Meanwhile, the reduction of phonon population may also play a role in the drop of ASPL intensity in the cooling process. The temperature-driven band structure evolution of 4H PbI₂ is further investigated by typical SPL studies. As presented in Figure 2b,c, rich excitonic emissions are observed in the SPL spectra, in particular at liquid Nitrogen temperature (80 K). The ST corresponding to the ASPL also shows blueshift as temperatures decrease. The detailed PL peak energies at different temperatures are plotted in Figure 2d obtained by carefully fitting the spectra of ASPL and ST, respectively. A good

agreement between them is observed. On the contrary of the ASPL, the emission of ST becomes stronger when the sample is cooled down (see Figure S2, Supporting Information). This is associated with the reduction of thermally activated nonradiative decays and the enhancement of the absorption when the energy gaps of the emission enlarge and the emission energy levels are approaching the incident energy (2.54 eV), which in fact agrees with the discussion above, the decrease of absorption when the bands move away from the incident energy in the ASPL process. At 80 K, in addition to the ST, there are two more sharp peaks as shown by the fitted curves in Figure 2c. Their positions of 493 nm (2.51 eV) and 495 nm (2.50 eV) indicate they might be free exciton (FE) and bound exciton (BE) emission, respectively.^[14] The broad peak centering at 511 nm (2.43 eV) is assigned as donor-acceptor pair (DAP) emission.^[14] It is also noticed that the significant increase of the DAP accompanies with the dramatic decrease of the ST, implying the competition between these two emission species at near 80 K and the DAP, as at a relatively low energy level is more favorable. The broad DAP emission was also observed in the ASPL measurement at 4.2 K.^[31]

The observation of strong free and bound exciton emission in the SPL (Figures S2 and S3, Supporting Information) is indeed intriguing for tracing the corresponding up-conversion ASPL. By increasing laser power and selecting samples (thick flakes) which are usually stable under a relative high power illumination, we successfully observe the ASPLs of these excitonic emission near the band edge (2.55 eV) together with the ASPL of the broad DAP luminescence in both CVD and mechanically exfoliated 4H PbI₂ flakes, as shown in Figure 3a,b. The effect of the cooling process in the increase of the emission energy levels though is unambiguously demonstrated by the blueshift of the SPL peaks, the enhancement of the intensities is opposite to the response of the ASPL presented in the room temperature spectra, which therefore demands a proposal of different emission mechanism.

Analyzing excitation laser power dependence of light emissions is one widely adopted method to explore origins of emission centers in a semiconductor. Here, we perform the power dependence ASPL and SPL measurements on mechanically exfoliated 4H PbI₂ flakes by using the excitation laser line of 532 and 488 nm, respectively. The results are plotted in Figure 4a–c. As shown in Figure 4a, the nearly linear response of the room temperature favored ASPL, as a typical behavior of the phonon-assisted up-conversion luminescence, further supports our previous argument. As suspected, the ASPLs of FE and BE show super linear response to the incident laser power

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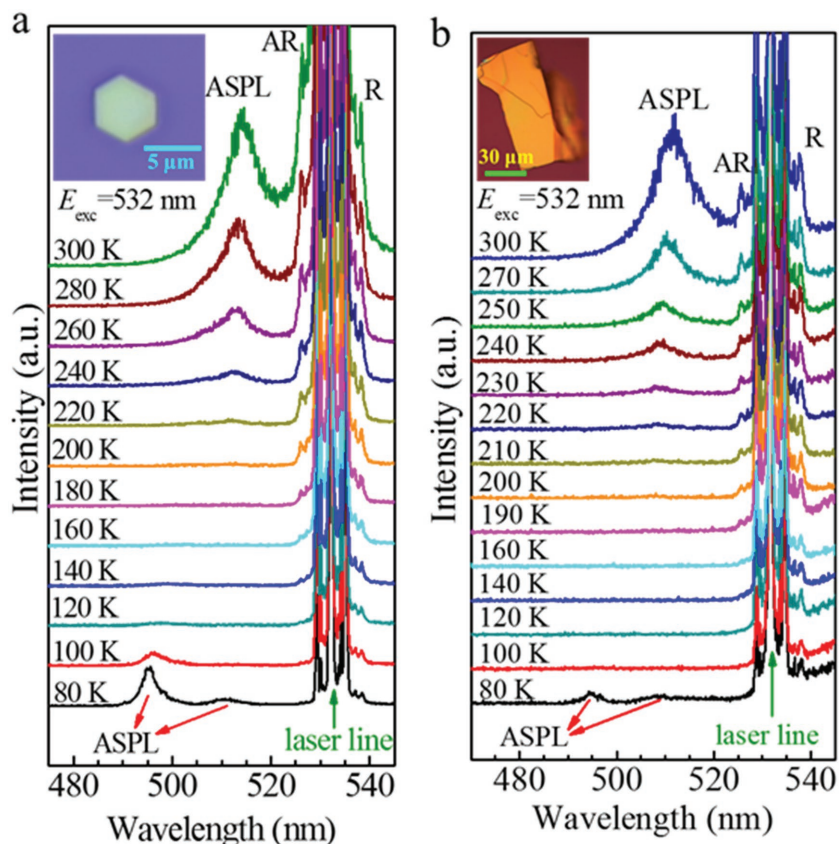


Figure 3. Temperature-dependent ASPL of a) CVD-grown and b) mechanically exfoliated 4H PbI₂ flakes. Insets are optical images.

(see Figure 4b). Hence, we propose that the up-conversion luminescence is resulted from the multiphoton absorption process. The linear dependence of SPL (Figure 4c) agrees with our assignments of FE, BE, ST, and DAP. The entire set of ASPL emission in 4H PbI₂ is schematically illustrated in Figure 4d. At room temperature, with the assistant of phonons, a photon of 2.33 eV (532 nm) pumps the emission from a shallow level trap states. When the sample is cooled down to 80 K, the multiphoton absorption pumping process is dominant. The excited electrons induce the strong emission from the FE and BE near the band edge after some nonradiative relaxation processes. Meanwhile, at relatively low energy levels, both ST and DAP emission, also pumped by the multiphoton absorption take place. Taking the advantage of Raman spectroscopy in identifying the phases of PbI₂ flakes, we also investigate the ASPL and SPL of 2H phase PbI₂ (Figure S4, Supporting Information). Our findings reveal the universal and robust ASPL exist in both 4H and 2H PbI₂ flakes.

In summary, ASPL of both 4H and 2H van der Waals layered semiconductor PbI₂ has been systematically studied. The nature of the emission is clearly revealed through the in-situ low-temperature and excitation-laser-power dependent PL measurements. Phonon-assisted and multiphoton absorption

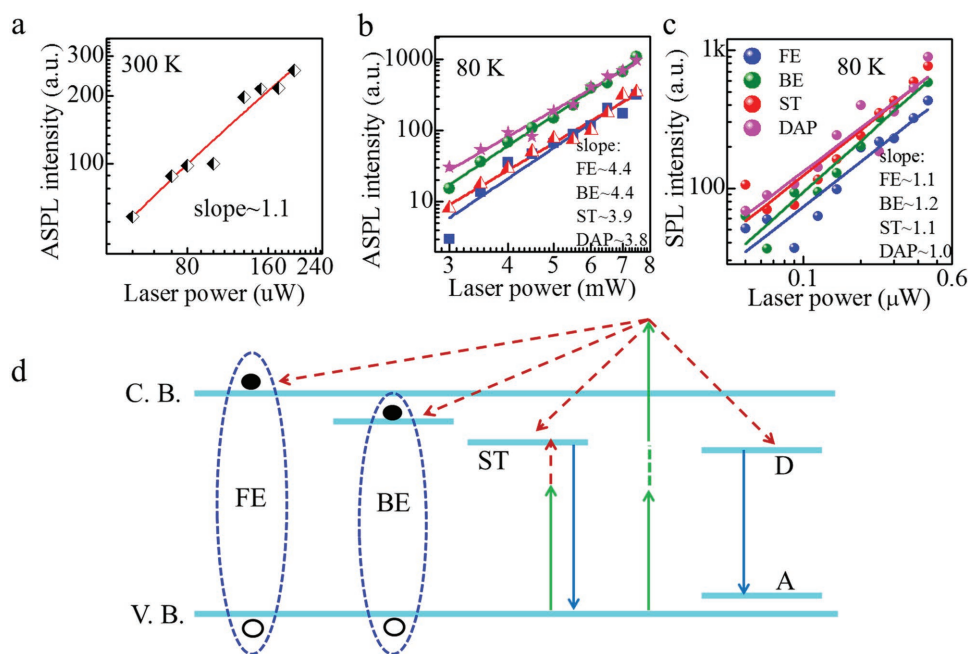


Figure 4. a) Power dependence of ASPLs in 4H PbI₂ flakes at 300 K and b) 80 K. c) Power dependence of SPLs in 4H PbI₂ flakes at 80 K. d) Schematic presentation of the emission processes in PbI₂ flakes.

up-conversion processes are proposed to be responsible for the room temperature favored emission from the shallow trap state and low temperature favored emission from the FE, BE, and DAP, respectively. The successful observation and explanation of the universal anti-Stokes emission of Pbl₂ layers, a traditional direct bandgap semiconductor and a building block of organic–inorganic perovskite will certainly enrich fundamental understandings of vdW layered semiconductors and perovskite, then further benefit to developing applications based on such emerging materials.

Experimental Section

Sample Preparation: Two kinds of lead halide platelets were used in this work. One was mechanically exfoliated from a synthesized Pbl₂ crystal (2D semiconductors Inc.) onto 300 nm SiO₂/Si substrates. The other was directly grown on the same kind of 300 nm SiO₂/Si substrates by chemical vapor deposition as described in the previous work.^[17]

Optical Measurement: The SPL/ASPL/Raman spectroscopies presented in this work were obtained by using a WITec alpha300 RAS Raman/PL system. A long-working distance 50× objective lens with numerical aperture of 0.55 and a temperature controlled stage HFS600E from Linkam Scientific Instruments were used for all SPL/ASPL/Raman measurement. The ASPL and Raman spectra were taken under excitation laser of 532 nm ($E_{\text{laser}} = 2.33$ eV) with a Rayshield low-wavenumber coupler. The SPL spectra were obtained by excitation laser of 488 nm ($E_{\text{laser}} = 2.54$ eV). A 2400 lines mm⁻¹ grating and a 600 lines mm⁻¹ were used for Raman and PL/SPL measurements, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

anti-Stokes photoluminescence, layered semiconductors, optical properties, Pbl₂, van der Waals solids

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