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<td>Author(s)</td>
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Optical signature of symmetry variations and spin-valley coupling in atomically thin tungsten dichalcogenides

Hualing Zeng¹, Gui-Bin Liu¹,⁴,⁵, Junfeng Dai²,¹, Yajun Yan³, Bairen Zhu¹, Ruicong He¹, Lu Xie¹, Shijie Xu¹, Xianhui Chen³, Wang Yao¹,⁴ & Xiaodong Cui¹

¹Department of Physics, The University of Hong Kong, Pokfulam road, Hong Kong, China, ²Department of Physics, South University of Science and Technology of China, Shenzhen, Guangdong, China, ³Hefei National Laboratory for physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China, ⁴Center for Theoretical and Computational Physics, The University of Hong Kong, Hong Kong, China, ⁵School of Physics, Beijing Institute of Technology, Beijing 100081, China.

We report systematic optical studies of WS2 and WSe2 monolayers and multilayers. The efficiency of second harmonic generation shows a dramatic even-odd oscillation with the number of layers, consistent with the presence (absence) of inversion symmetry in even-layer (odd-layer). Photoluminescence (PL) measurements show the crossover from an indirect band gap semiconductor at multilayers to a direct-gap one at monolayers. A hot luminescence peak (B) is observed at 0.4 eV above the prominent band edge peak (A) in all samples. The magnitude of A-B splitting is independent of the number of layers and coincides with the spin-valley coupling strength in monolayers. Ab initio calculations show that this thickness independent splitting pattern is a direct consequence of the giant spin-valley coupling which fully suppresses interlayer hopping at valence band edge near K points because of the sign change of the spin-valley coupling from layer to layer in the 2H stacking order.

Motivated by the triumph and limitation of graphene for electronic applications¹, atomically thin layers of group VI transition metal dichalcogenides are attracting extensive interest as a class of graphene-like semiconductors with a desirable band-gap in the visible frequency range²–⁷. This family of dichalcogenides MX2 (M = Mo,W; X = S,Se) has a structure of X-M-X covalently bonded hexagonal quasi-2D network stacked by weak Van der Waals forces. MX2 thin films exhibit 2H stacking order: the neighboring layers are 180 degree in plane rotation of each other with the metal atom of a given layer sitting exactly on top of the chalcogenide atom of the adjacent layer. There is an even-odd variation in the structural symmetry of ultrathin films: inversion symmetry is absent (present) in films with odd (even) number of layers with space group of D1₃h (D4₆h). Ab initio calculations predict that MX2 exhibits a transition from an indirect-gapped semiconductor in multilayer form to a direct band-gap one at visible range in monolayer, which has been experimentally verified in MoS2⁷,⁸.

MX2 monolayer, the elementary unit to form ultrathin films by weak stacking, features a novel spin-valley coupled band structure⁹. At the corners of the 1st Brillouin zone, the valence (conduction) band has two inequivalent valleys described by massive Dirac fermions. Owing to the broken inversion symmetry in monolayers, the strong spin-orbit coupling from the d-orbitals of metal atom results in a valence band spin splitting at K points, with a magnitude as large as ~0.4 eV in tungsten dichalcogenides⁹–¹⁰. The spin-splitting has opposite signs at the K and K’ valleys as they are time reversal of each other. This spin-valley coupling forms the basis for manipulation of spin and valley degrees of freedom in these novel 2D semiconductors when combined with valley contrasted electric, magnetic and optical properties arising from inversion symmetry breaking⁹–¹⁶.

Here we report our experimental study on optical properties of ultrathin WS2 and WSe2 mono-, bi-, tri- and quad-layer samples by means of Raman scattering, second harmonic generation (SHG) and photoluminescence (PL). The efficiency of SHG at normal incidence on WS2 and WSe2 ultrathin films shows a dramatic even-odd oscillation with the number of layers: negligible at even-layer and nonzero at odd-layer, with maximum strength at monolayers. PL measurements demonstrate that WS2 and WSe2 exhibit a transition from an indirect-gap semiconductor at multi-layers to a direct-gap one at monolayers with an enhancement of the PL quantum efficiency (QE) at a factor of more than 10³ compared to bulk samples. Remarkably, a weak emission peak (B) is observed at an energy ~0.4 eV higher than the prominent direct bandgap transition peak (A) in all monolayer

and multilayer samples. Unlike the case in MoS2 (B exciton absent in MoS2 monolayer PL though), the magnitude of A-B splitting in both WS2 and WSe2 is independent of the number of layers and coincides with the spin-valley coupling strength in monolayers. Ab initio calculations show that this thickness independent splitting pattern is a direct consequence of the giant spin-valley coupling which fully suppresses interlayer hopping at valence band edge at K points because of the sign change of the spin-valley coupling from layer to layer in the 2H stacking order.

**Results**

For MX2 layered compounds, there are generally four Raman-active modes, namely A1g, E1g, E2g and E2g modes. E1g mode and low energy E2g mode are absent in our measurements due to the forbidden selection rule in the back-scattering geometry and the limited rejection against Rayleigh scattering respectively. The presented study focuses on the in-plane vibrational E2g mode and the out-of-plane vibrational A1g mode. As these two modes are both polarization sensitive, the exciting laser was tuned to an unpolarized state. Figure 2.a–d present the representative Raman spectra of WS2 and WSe2 slabs with layer number N = 1 to 4 and bulk. In the case of WS2, we observe the E2g mode at ~350 cm⁻¹ and the A1g mode at ~420 cm⁻¹ (Fig. 2.a). The E2g mode shows little dependence on the film thickness, while the A1g mode undergoes a blue shift with increasing layer number, showing a lattice stiffening effect as expected when additional layers are added. By examining the frequency differences (Δω) between the E2g mode and A1g mode, the sample thickness could be identified accordingly. As indicated in Fig. 2.b showing the frequency difference as a function of layer number N, we label Δω = 65.5 cm⁻¹, 68.3 cm⁻¹ and 69.2 cm⁻¹ to monolayer, bilayer and trilayer respectively. For slabs composed of four and more layers, Δω converges to the bulk value at around 70 cm⁻¹. Notably, from monolayer to trilayer the A1g peak is roughly 0.5, 1 and 1.8 times the height of the E2g peak (Fig. 2.b), demonstrating that the ratio of the intensity of A1g mode to that of E2g mode could also be used as an indicator of sample thickness. For WSe2, two dominant peaks are observed around 250 cm⁻¹ in various samples from monolayer to bulk (Fig. 2.c). However, little systematic trend could be observed on both the two modes as shown in Fig. 2.d.

An experimental method to examine the inversion symmetry in ultrathin film is to study the nonlinear optical effect such as SHG determined by the second order susceptibility χ(2). In the presence of inversion symmetry, χ(2) is zero. A dramatic even-odd oscillation pattern is indeed observed on the SHG intensity consistent with the presence (absence) of inversion symmetry in even-layer (odd-layer) as shown in Fig. 1.c and 1.g. WS2 and WSe2 ultrathin slabs are scanned by a 150 fs pulsed laser beam with a wavelength of 800 nm at normal incidence and the signal at the double frequency (400 nm) is collected. As expected, in both WS2 and WSe2 slabs with even layer number or bulk samples, negligible SHG are observed as same in the case of the bare substrate (SiO2 on Si), and strong second harmonic emission arises from multilayer slabs with odd layer number. Notably, the brightest second harmonic emission is observed in monolayers of both WS2 and WSe2. The intensity of the second harmonic emission decays gradually with the increasing layer number, as indicated in Fig. 1.d and 1.h.

The Photoluminescence study shows that WS2 and WSe2 exhibit a transition from indirect band-gap semiconductor in the form of bulk and multilayers to direct band-gap one in monolayers, similar to MoS2. Figure 3 illustrates the PL spectra of WS2 and WSe2 samples with various thicknesses measured under the same condition with an excitation at 2.41 eV. Fig. 3.a and 3.d show the PL peak intensity as a function of thickness. The PL intensity is found to be extremely weak on bulk samples, consistent with an indirect band-gap semiconductor in bulk form. As WS2 and WSe2 thin to a few atomic layers, the intensity of PL from direct interband transition dramatically increases and reaches maximum at monolayers, more than 3 orders of magnitude stronger than that from bulk. Both WS2 and WSe2 monolayers show much brighter PL with intensity at one order of magnitude higher than bilayers. The peak originating from the indirect band-gap transition (labeled as **“I”** in Fig. 3.b and 3.e) gradually shifts toward higher energy and fades to null at monolayers. These behaviors are fully consistent with the calculated band structures (see Fig. 4 and supplementary information).

Besides the peaks from indirect transition and the prominent direct transition peak (A), weak PL peak (B) is observed at higher energy in WS2 and WSe2 at all thickness. Note that the similar peak B appearing in MoS2 multilayers is absent in monolayers. The line-width of peak A and B implies their excitonic origin as the case in
MoS$_2$ \cite{2,3}. Strikingly, the splitting between A and B peaks are almost identical, around 0.4 eV for mono-, bi-, tri- and quad-layer samples (see Fig 3.c and 3.f). In monolayers, it is now well understood that the valence band edges at K points have a spin splitting purely arising from the strong spin-orbit coupling in the d-orbitals of the W atom, and we can attribute A and B to the direct-gap transitions between the spin split valence bands and the conduction band at the K points\cite{7}. However, in multilayers, both the spin-orbit coupling and the inter-layer hopping contribute to the valence band splitting at K points. Besides, even layer samples are inversion symmetric while odd layer samples are asymmetric. These in general would result in complex and layer-number dependent splitting patterns in multilayers, which

Figure 2 | (a) and (c): Raman spectra of WS$_2$ (a) and WSe$_2$ (c) ultrathin layers; (b) and (d): The frequency difference (red) and the peak intensity ratio (blue) between E'$_{2g}$ and A$_{1g}$ modes as a function of film thickness in WS$_2$ (b) and WSe$_2$ (d) respectively.

Figure 3 | (a) and (d): The relative PL intensity of WS$_2$ (a) and WSe$_2$ (d) multilayers respectively as a function of film thickness under the same conditions (normalized by the PL intensity of monolayer at 1). Insets present PL spectra from WS$_2$ (a) and WSe$_2$ (d) monolayers and bilayers respectively. The spectra were taken at the same conditions (excitation power, exposure time, etc.); (b) and (e): The normalized PL spectra (with respect to the peak A) of WS$_2$ (b) and WSe$_2$ (e) ultrathin films. I labels the luminescence from indirect gap interband transition, A and B label the direct-gap transitions from the split valence band edge to the conduction band edge at K points (see text). Spectra (dash line) in the zoom windows have been multiplied by a factor as indicated for clarity; (c) and (f): The peak positions of I, A and B transitions as a function of the film thickness in WS$_2$ (c) and WSe$_2$ (f). Both cases show a nearly constant energy difference of ~0.4 eV which corresponds to the splitting of the valence band edge. The universal A-B splitting implies a suppression of interlayer hopping in tungsten dichalcogenides ultrathin thin films.
is obviously different from the universal A-B splitting in the PL spectra observed. It implies a novel cause in tungsten dichalcogenides ultrathin films.

Discussion

To understand the A-B splitting pattern in WS$_2$ and WSe$_2$ films, we perform ab initio calculations of the band structures using the projector augmented wave method$^{24}$ and generalized gradient approximation$^{25}$ implemented in the ABINIT code$^{26,27}$. The structure parameters are taken from Ref. 10. Figure 4.a–d show the band structures of mono-, bi-, tri-, and quad-layer WS$_2$ in the absence of SOC. As expected, the valence band edge at K point splits into two, three, and four bands respectively for bi-, tri-, and quad-layer WS$_2$ due to the interlayer hopping. A hopping matrix element $t \sim 0.1$ eV can be extracted from the splitting pattern. However, when spin-orbit coupling (SOC) is included, the splitting pattern is completely changed as shown in Fig. 4.e–h. The valence band edges split into two degenerate manifolds with a splitting magnitude independent of the film thickness for both WS$_2$ and WSe$_2$. The band structures of WSe$_2$ ultrathin films could be found in supplementary information. This is in perfect agreement with the A-B splitting patterns observed in the photoluminescence of mono-, bi-, tri-, and quad-layer WS$_2$ and WSe$_2$. The calculated valence band edge splittings of 0.43 eV in WS$_2$ and 0.47 eV in WSe$_2$ also agree with the measured A-B splitting of 0.4 eV as shown in Fig. 3 and the supplementary information.

In fact, the unexpected splitting patterns in multilayer WS$_2$ and WSe$_2$ are manifestations of the giant spin-valley coupling in valence band$^9$. In monolayers, the Kramer’s doublet $|K\uparrow\rangle$ and $|K\downarrow\rangle$ are separated by the higher energy band edge, giving rise to hot luminescence, i.e. the direct bandgap transition peak B$^8$. In multilayers, we have the same picture for hot carrier relaxation and hot luminescence at the valence band edges near K points where interlayer hopping is fully suppressed by the spin-valley coupling. The giant spin-valley coupling offers a new strategy to manipulate electron spin and makes tungsten dichalcogenides ultrathin films promising materials for semiconductor based spintronics and conceptual valley-based electronics.

Methods

WS$_2$ and WSe$_2$ flakes were mechanically exfoliated from synthesized single crystal bulk samples onto silicon wafers capped with a 300 nm thick SiO$_2$ by a method analogous to the way of producing graphene$^1$. WS$_2$ and WSe$_2$ slabs were first visually confirmed by atomic force microscope. PL spectra are also used as an indicator of exfoliation of Layered Materials. (2005).


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Author contributions

X.C. and H.Z. designed the experiments. X.Chen. and Y.Y. fabricated the single crystal WS2 and WSe2 monolayers by optical pumping. Nat Nano 7, 490–493 (2012).

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

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