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The investigation and control of quantum degrees of freedom (DoF) of carriers lie at the heart of condensed-matter physics and next-generation electronics/optoelectronics. Van der Waals heterostructures stacked from distinct two-dimensional (2D) crystals offer an unprecedented platform for combining the superior properties of individual 2D materials and manipulating spin, layer and valley DoFs. MoS_2/graphene heterostructures, harboring prominent spin transport properties of graphene, giant spin-orbit coupling and spin-valley polarization of MoS_2, are predicted as a perfect venue for optospintronics. Here, we report the epitaxial growth of commensurate MoS_2 on graphene with high-quality by chemical vapor deposition, and demonstrate robust temperature-independent spin-valley polarization at off-resonant excitation for the first time. We further show that the helicity of B exciton is larger than that of A exciton, allowing the manipulation of spin bits in the commensurate

heterostructures by both optical helicity and wavelength. Our results open a window for controlling spin DoF by light and pave a way for taking spin qubits as information carriers in the next-generation valley-controlled optospintronics.

Graphene is an exotic spintronics candidate featured by Dirac fermions, two inequivalent valleys [1], ultrahigh electron mobility, room temperature ballistic transport [2], long spin-relaxation lengths and times [3-6]. However, electric field modulation of spin DoFs in graphene is almost impossible due to a tiny intrinsic spin-orbit coupling (SOC) (~ 10 μeV) [7]. In contrast, monolayer transition metal dichalcogenides (MX_2), in which the chalcogen atoms in two hexagonal planes are separated by a single layer of metal atoms in a trigonal prismatic structure, have a strong SOC resulting from d orbitals of heavy metal atoms and inversion symmetry breaking [8]. In combination with time-reversal symmetry, the spin and valley DoFs are inherently entangled [9] and carriers in different valleys are associated with contrasted Berry curvature and magnetic moment, allowing the excitation of spin and valley polarized carriers by circularly polarized light [10-12]. Therefore, monolayer MX_2 is an ideal material integrating both valleytronics and spintronics. On the other hand, unavoidable defects and low mobility of carriers ($\mu < 100$ $cm^2V^{-1}s^{-1}$) in monolayer MX_2 are critical barriers to the application and development of spintronics and valleytronics [13].

MX_2/graphene heterostructures with weak van der Waals coupling offer a playground to combine these excellent performances of both graphene and MX_2, including ultrahigh mobility, micrometer-scale spin transport lengths [14] and nanosecond-scale spin relaxation times [15] in graphene and strong SOC [8], coupled spin and valley [9], and valley-selective circular dichroism [10] in monolayer MX_2. Recent experiments have demonstrated strong proximity SOC acquired by graphene [16-18] and ultrafast charge transfer [19] in MX_2/graphene heterostructures. And the MX_2/graphene heterostructures have been theoretically proven to be promising for novel optospintronics, because spin polarized carriers can be nicely provided by MX_2 and optically injected into graphene with spin S_z as a good quantum number [20]. Moreover, Luo *et al.* recently demonstrate the spin injection and opto-valleytronic spin valves of MoS_2/graphene heterostructures produced by transfer approach [21]. However, there are some disadvantages for those MoS_2/graphene heterostructures obtained by transfer approach. For example, interlayer

twisting angles are arbitrary and bubbles, wrinkles and residuals at interface are always problematic. To the best of our knowledge, commensurate MoS_2/graphene heterostructures with cleaner interface and stronger interlayer coupling can be obtained via chemical vapor deposition (CVD) [22-24] and solve these problems perfectly. Thus, the commensurate MoS_2/graphene heterostructures are expected to be more suitable for optospintronics application.

In this article, we performed polarization-resolved photoluminescence (PL) on commensurate MoS_2/graphene heterostructures obtained by van der Waals epitaxial growth. It is experimentally demonstrated that contrasting spin polarization could be generated in the commensurate MoS_2/graphene heterostructures by not only distinct optical polarization but also the same helicity at different excitation energy. In addition, temperature-dependent measurements show that the valley-controlled spin polarization is almost independent temperature and can be persisted up to room temperature. In combination with our theoretical calculation that the SOC in graphene is strongly enhanced, our commensurate MoS_2/graphene heterostructures are unprecedented candidates for realizing optospintronics.

MoS_2/graphene heterostructures, a prototypical MX_2/graphene heterostructures, were fabricated via epitaxial growth of MoS_2 on graphene through an oxygen-assisted CVD process [24] (more details in Supplementary Section S1 [25]). A schematic of the epitaxial growth process is demonstrated in Fig. 1(a), illustrating the formation of MoS_2 on graphene by MoO_3 reacting with S. As-grown MoS_2/graphene heterostructures were characterized by Raman spectroscopy (Fig. 1(b)). We can see some prominent features in the spectrum, such as the first-order E′ (~ 382 cm^{-1}) and A'_1 (~ 404 cm^{-1}) modes of MoS_2, G band (~ 1600 cm^{-1}) and 2D band (~ 2710 cm^{-1}) of graphene, and a broad background at high wavenumber associated with the PL of MoS_2. As compared with mechanically exfoliated MoS_2 and graphene, the frequency difference between E′ and A'_1 modes increases, and both G and 2D peaks blue shift in MoS_2/graphene heterostructures, indicating a strong interlayer coupling (Supplementary Section S1 [25]) [26,27]. The asymmetric and broad E′ mode in the MoS_2/graphene heterostructures evidences the lattice strain in MoS_2. This is in harmony with our recent work [24], demonstrating that commensurate MoS_2/graphene heterostructures posssess the largest strain for all the twisting angles and strain for commensurate MoS_2/graphene heterostructures is about 0.3% larger than that for MoS_2/graphene heterostructures

at twisting angle =30°. Atomic force microscopy (AFM) image (Fig. 1(c)) reveals the thickness of 7.1 Å for MoS_2, in agreement with monolayer level. Atomic-resolution AFM lateral image (Supplementary Section S1 [25]) clearly shows the hexagonal lattice of the higher-lying S atoms, and the periods of atomic corrugation of 3.18 Å, corresponding to the in-plane S−S distance.

MoS_2/graphene heterostructures, akin to graphene/boron nitride (hBN) heterostructures or twisted graphene layers [28,29], exhibit a rotation-dependent topographic moiré pattern, determined by the lattice mismatch and relative rotation angle between MoS_2 and graphene (Supplementary Section S2 [25]). Scanning tunneling microscopy (STM) topographic image (Fig. 1(d)) shows the distinct moiré pattern of MoS_2/graphene heterostructures with moiré wavelength of 1.4 nm, indicating the van der Waals commensurate epitaxial growth and zero twisting angle between MoS_2 and graphene (Supplementary Section Fig. S3 [25]).

With the aberration-corrected annular dark-field scanning transmission electron microscopy (ADF-STEM), the honeycomb lattice structures of MoS_2 with two sublattice sites occupied by one molybdenum (brighter spots) and two stacked sulfur atoms (dimmer sports) are clearly visible, as illustrated by the top-view schematics (Fig. 1(e)). The MoS_2 layer displays a perfect hexagonal atomic structure with low number of vacancies and topological defects, being consistent with the high quality for van der Waals epitaxial growth [30] and confirmed by our optical results (see below). Selected-area electron diffraction (SAED) pattern (Fig. 1(f)) reveals that two sets of six-fold symmetry diffraction spots, originated from MoS_2 and graphene respectively, are of the same orientation, in line with the moiré pattern of STM topographic image.

We measured the PL spectrum at 10 K (Fig. 2(a)) and the magneto-optical Raman effect at room temperature (Fig. 2(b)) of the commensurate MoS_2/graphene heterostructures to further examine their quality. The emission spectrum for mechanically exfoliated MoS_2 was found to contain four features: (1) the strong emission around 1.92 eV contributed by neutral exciton A and negatively charge exciton (trion) A^-, with trion binding energy of 38 meV [10,31], (2) the weak feature from B exciton (~ 2.1 eV), arising from SOC (158 meV) in valence band, and (3) a broad feature near 1.8 eV, originated from emission of defect-trapped exciton [10]. On the other hand, there are some distinct features in the PL spectrum of the commensurate MoS_2/graphene heterostructures: (1) A and B excitons from MoS_2, associated with direct optical transitions from the lowest conduction band to the highest spin-split valence band, and (2) G and 2D bands, arising

from lattice vibrations of graphene. The full width at half maximum (FWHM) of the A exciton at 10 K is 42 meV and 48 meV for the commensurate MoS_2/graphene heterostructures and exfoliated MoS_2, respectively. The absence of both defect-trapped exciton and trion in the commensurate MoS_2/graphene heterostructures are strong evidences for a more homogeneous charge distribution with no unintentional doping and higher quality of the commensurate heterostructures.

Figure 2(b) presents the magnetic field dependent polarized Raman spectra of the commensurate MoS_2/graphene heterostructures with two scattering configurations: co-polarized (e_i □ e_s) and cross-polarized (e_i □ e_s). The E′ mode of MoS_2 and 521 cm^{-1} mode of Si substrate are almost magnetic field-independent (Supplementary Section S3 [25]). In contrast, the A'_1 mode of MoS_2 displays a gigantic anticorrelated Raman intensity modulation with magnetic field in the two orthogonally polarization configurations (Fig. 2(b) inset), revealing that the commensurate MoS_2/graphene heterostructures favor fascinating magnetically tunable Raman effect and novel magneto-optical applications. This magneto-optical Raman effect stems from magnetic field induced horizontal two fold symmetry breaking and has been carefully studied in mechanically exfoliated MoS_2 [32]. The resonance magnetic field strength at which the phonon intensity achieves its extremum (maximum or minimum) is inversely proportional to optical mobility and hence a good index of intrinsic electronic scattering. The resonance magnetic field obtained by fitting the field dependence of Raman intensities to the functions given in ref. 32 is at 4.66 T (Fig. 2(b) inset) in the commensurate MoS_2/graphene heterostructures, less than the value (~ 6 T) in mechanically exfoliated MoS_2 [32], reflecting that the commensurate MoS_2/graphene heterostructures enjoys higher intrinsic optical mobility and carriers suffer less scattering. This result is in good harmony with the PL spectrum, STEM and STM topographic images of the heterostructures.

Chiral interband transitions are exactly at two valleys (left circularly polarized σ_- and right circularly polarized σ_+ at K and K′ valleys, respectively) and can evolve to excitons as a result of lattice structures and time-reversal symmetry (Fig. 3(c)). The helicity polarized PL spectra at 10 K, excited by σ_- radiation on resonance with the A exciton at 1.96 eV, are presented in Fig. 3(d) (mechanically exfoliated MoS_2) and 3(e) (commensurate MoS_2/graphene heterostructures). Following the convention used in Ref. 10, the degree of valley-spin polarization is defined as the

helicity: $\rho = \frac{I(\sigma_-) - I(\sigma_+)}{I(\sigma_-) + I(\sigma_+)}$, where $I(\sigma_-)/I(\sigma_+)$ is the intensity of the left/right-handed circular component. The valley-spin polarization of mechanically exfoliated MoS_2 drops dramatically with increasing temperatures and almost disappears above 240 K (Fig. 3(f)), in line with refs 10, 11. In sharp contrast, the helicity of commensurate MoS_2/graphene heterostructures exhibits a rather slow decay tendency and holds valley-spin polarization (~ 0.26) at room temperature (Fig. 3(f)). The helicity of commensurate MoS_2/graphene heterostructures at low temperatures is found to be lower than that of the exfoliated MoS_2. It may be ascribed to the strain induced by the immense lattice mismatch and van der Waals interaction between MoS_2 and graphene [33,34]. The polarization-resolved PL spectrum under σ_- excitation off resonance (2.33 eV) with excitons are also measured for mechanically exfoliated MoS_2 (Fig. 3(g)) and MoS_2/graphene heterostructures (Fig. 3(h)). No polarization is observed for mechanically exfoliated MoS_2, while commensurate MoS_2/graphene heterostructures harbors valley-spin polarization that is almost temperature-independent for both A and B excitons (Fig. 3(i)). More surprisingly, the helicity at 10 K for B exciton (~ 0.61) is much larger than that for A exciton (~ 0.22), being similar to anomalous spin-valley polarization in $MoSe_2$ [35]. The higher spin-valley polarization for B exciton may be stemmed from that the B exciton is closer to 2.33 eV. The finding indicates that we could generate opposite spin polarization by tuning not only circular polarization of incident light but also the excitation energies, because of opposite spins for A and B excitons [21,36]. This result is of particular significance for practical optospintronics applications, as will be seen in below.

How to understand the robust spin-valley polarization of the commensurate MoS_2/graphene heterostructures? The helicity is determined by the steady-state spin-valley population (Supplementary Section S8 [25]), $\rho = \frac{N_K - N_{K'}}{N_K + N_{K'}} = \frac{1}{1 + 2\tau/\tau_S}$, where $\frac{1}{\tau}$ and $\frac{1}{\tau_S}$ denote the nonradiative decay rate (exciton lifetime) and the intervalley relaxation rate (valley lifetime), respectively. The radiative decay rate is not taken into account since it is assumed to be much lower than the nonradiative rate [10,12]. The exciton lifetime and valley lifetime for both the commensurate MoS_2/graphene heterostructures and mechanically exfoliated MoS_2 are almost identical since the degree of the spin-valley polarization of the commensurate MoS_2/graphene heterostructures at 10 K, excited by σ_- radiation at 1.96 eV, is akin to that of the mechanically exfoliated MoS_2 (Fig. 3(f)). Thus, it should not be the major cause of robust spin-valley

polarization in the commensurate MoS_2/graphene heterostructures.

Due to the spin-valley coupling in monolayer MoS_2, intervalley scattering is accompanied by spin-flipping, putting constraints on possible spin scattering mechanisms related to the relaxation of spin-valley polarization. There are three main principal spin relaxation channels in semiconductors: Elliot-Yafet (EY) mechanism [37,38], D'yakonov-Perel (DP) mechanism [39], and Bir-Aronov-Pikus (BAP) mechanism [40]. In the DP mechanism, carriers with oriented spins experience a momentum-dependent internal magnetic field, leading to the spin Lamor process. Spin scattering through DP mechanism is completely suppressed in monolayer MoS_2, because the exact 2D nature and mirror symmetry give zero value for in-plane component of internal magnetic field. The negligible effect of magnetic field on polarization also rules out the DP mechanism (Supplementary Section S7 [25]). Electron spin-flipping can occur via electron-hole exchange and annihilation interactions (BAP mechanism) as the electron-hole interaction is strongly enhanced by dielectric screening reduction in 2D limit. However, the electron-hole exchange in the commensurate MoS_2/graphene heterostructures and mechanically exfoliated MoS_2 has a similar scale and BAP mechanism is unlikely to be the major factor for the robust spin-valley polarization in MoS_2/graphene heterostructures. EY mechanism is attributed to the fact that Bloch electrons are not spin eigenstates in real crystals and spin-independent interaction with vacancies, gain boundaries, and phonons can lead to spin relaxation. A high density of sulfur vacancies in mechanically exfoliated MoS_2 cause the low mobility and PL quantum yield [13,41,42] and act as sharp magnetic scattering centers through exchange interactions between extra electrons and Mo^{4+} ions [43] to cause the effective relaxation. Spatial charge inhomogeneous distribution (coexistence of A and A^- excitons) in mechanically exfoliated MoS_2 can give rise to electron-hole puddles [44-46] and spin scattering. For the high-quality commensurate MoS_2/graphene heterostructures with homogenous charge distributions and a low density of sulfur vacancies, the scattering is strongly suppressed. However, contribution of the exotic massless Dirac fermions in graphene to robust spin-valley polarization is not confirmed here. Further quantitative studies are needed to elaborate the mechanism.

Density functional theory (DFT) calculations (Fig. 3(a)) reveal that Dirac point of graphene is within the MoS_2 band gap and the lowest conduction band of MoS_2 is practically unchanged by the presence of graphene. Dirac fermions of graphene in the commensurate MoS_2/graphene

heterostructures acquires meV-scale SOC (Fig. 3(b)) through interfacial induced global spin-orbit proximity effect which is three orders of magnitude higher than the intrinsic value, making it possible to manipulate spin DoFs by electric field [16,20]. The manipulation of spin DoFs is the key for spintronics. In combination with robust spin-valley polarization, the high-quality commensurate MoS_2/graphene heterostructures become an exciting platform for optospintronics. Under 1.96 eV excitation on resonance with the A exciton, spin-up polarized (spin-down polarized) carriers can be manipulated by left (right) circularly polarized light. Since electron-hole pairs do not recombine immediately, the spin polarized electron will inject into graphene from MoS_2 [19] and graphene harbours spin-up polarized (spin-down polarized) carriers, excited by left (right) polarized light. Using left circularly polarized light at 2.33 eV excitation, both A and B excitons of K valley are excited. Since the spin states of A and B excitions are opposite and spin-valley polarization of B exciton is much larger than that for A exciton (Fig. 3(i)), we can obtain the opposite spin polarized carriers in graphene, as compared with the same helicity at 633 nm excitation. This is in consistent with recent results bases on MoS_2/graphene heterostructures produced by transfer approach [21]. We can define spin bits as following: spin-up state as "1" and spin-down state as "0". Thus, spin-up polarized (state "1") carriers can be manipulated by left circularly polarized light at 633 nm excitation (Fig. 4(b)), while we can obtain spin-down (state "0") polarized carriers by either right circularly polarized light at 633 nm excitation (Fig. 4(a)) or left circularly polarized light at 532 nm excitation (Fig. 4(c)). The manipulation of spin bits in the commensurate MoS_2/graphene heterostructures through optical helicity and excitation energies enables intrinsic spin DoF for information processing and modern electronics.

In summary, high quality commensurate MoS_2/graphene heterostructures has been obtained by van der Waals epitaxial growth and anomalously robust spin-valley polarization is found in the commensurate heterostructures. The successful control of the spin DoF by both optical heilicity and wavelength, and the gigantic spin-orbit coupling for Dirac fermions in the commensurate MoS_2/graphene heterostructures pave the way towards future opto-spintronic applications.

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FIG. 1. (a) Schematic illustration of the growth process. Yellow, blue, red, and black balls represent sulfur, molybdenum, oxygen, carbon atoms, respectively. (b) Raman spectra for MoS_2/graphene heterostructures (blue line), mechanically exfoliated MoS_2 (magenta line) and mechanically exfoliated graphene (red line) at 2.33 eV excitation. (c) AFM image of MoS_2/graphene heterostructures. A height profile was extracted along the white line. (d) STM topographic image showing 1.4 nm moiré patterns. (e) Atomic-resolution ADF-STEM image of suspended MoS_2/graphene heterostructures on a TEM grid. The brighter (dimmer) spots are molybdenum (sulfur) atoms. The hexagonal lattice shows alternate molybdenum and sulfur sites with the top-view schematics overlaid. (f) SAED pattern of MoS_2/graphene heterostructures.

FIG. 2. (a) Photoluminescence spectrum for MoS_2/graphene heterostructures (black) and mechanically exfoliated MoS_2 (red) at 2.33 eV excitation and 10 K. (b) Polarized Raman spectra for MoS_2/graphene heterostructures at room temperature with applied magnetic field and in the cross-polarized (upper) configuration (incident light polarization e_i and scattered light polarization e_s are perpendicular to each), and co-polarized (lower) configuration (e_i and e_s are parallel to each). Inset: magnetic field dependence of the A'_1 mode intensity for MoS_2/graphene heterostructures.

FiG. 3. All optical excitation is left circularly polarized (σ-). (a) Electronic band structure of MoS_2/graphene heterostructures from DFT with SOC. (b) Zoom-in near the *K* valley (highlighted by the dashed box in (a)) shows graphene bands appearing gapped and spin polarized due to proximity to MoS_2. The red (blue) bands are for spin-up (spin-down) states. (c) Schematics of valley-dependent optical selection rules and spin-valley locking at K/K′ valleys in the momentum space of MoS_2. (d,e) Polarization-resolved PL spectra of mechanically exfoliated MoS_2 (d) and MoS_2/graphene (e) versus photon energy for 1.96 eV excitation. (f) Degree of PL polarization as a function of temperature at 1.96 eV excitation. (g,h) Polarization-resolved PL spectra of mechanically exfoliated MoS_2 (g) and MoS_2/graphene (h) versus photon energy for 2.33 eV excitation. (i) Degree of PL polarization versus temperature at 2.33 eV excitation.

FIG. 4. (a, c) Spin-down polarization and state “0” by right circularly polarized light at 633 nm excaitation (a) and left circularly polarized light at 532 nm excitation (c). (b) Spin-up polarization and state “1” by left circularly polarized light at 633 nm excitation.