Beating the exclusion rule against the coexistence of robust luminescence and ferromagnetism in chalcogenide monolayers

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Introduction

Monolayer transition-metal dichalcogenides (TMDCs) with sub-nanometer thickness have emerged as a frontier for the exploration of new physics and novel next-generation valleytronic devices. In the monolayer TMDCs, the inversion symmetry is broken, giving rise to a new valley degree of freedom (DOF) that is strongly coupled with spin in the momentum space. Effective manipulation and detection of the valley DOF are key issues for practical applications of monolayer TMDCs in valleytronics. Unfortunately, the optical detection is limited by the low PL quantum yield of TMDCs obtained so far. In order to realize simultaneous polarization and detection of the valley DOF, monolayer TMDCs with both robust room-temperature ferromagnetism and PL are highly desired. High PL intensity could only be obtained in TMDCs deficient in magnetic ions and sulphur vacancy. However, the presence of abundant magnetic ions and sulphur vacancies are essential prerequisites for achieving ferromagnetism of MoS_2. A dilemma then presents itself immediately. On the one hand, magnetic TM dopants or sulphur vacancy is indispensable to ferromagnetism. But on the other hand, magnetic ions and sulphur vacancy tend to form defect-mediated nonradiative recombination and charged exciton (trion) that are detrimental to the luminescence. In other words, in analogy to the nonexistence of ferromagnetism in a superconductor, the presence of ferromagnetism and PL in the monolayer MoS_2 is mutually exclusive: ferromagnetic ordering rely on the magnetic dopants and/or sulphur vacancy, which however quench the PL. This dilemma might be solved through the synergetic doping of two types of TMs with distinct natures. The first magnetic dopant is employed to induce the spin-polarized band-gap impurity. Provided that a second dopant is introduced that could reduce the state-density of this impurity band, then the nonradiative channel of the

photo-excited electrons could be cut off and hence the radiative recombination probability could be enhanced. In this work, we propose a practical approach to bring strong PL and ferromagnetism to TMDCs, by using two types of transition-metal dopants which play distinct roles in introducing magnetic moments and suppressing the nonradiative recombination of excitons. Experimentally, taking MoS_2 monolayers as a prototype material and using the CVD method, we successfully observed both luminescent and room-temperature ferromagnetism in (Co, Cr)-codoped MoS_2 monolayers with a lateral size of ~20 μm and a thickness of 0.78 nm. Detailed characterizations of the structure-property correlations unravel that the substitutional Co atoms induce a bandgap impurity band that gives rise to the ferromagnetic ordering but reduces the PL intensity because of the nonradiative recombination of excitons. After incorporating Cr atoms standing on atop sites of the monolayer, the nonradiative recombination is suppressed by the electronic interactions between the Cr- and Co-induced impurity levels. Consequently, the (Co, Cr)-codoped MoS_2 monolayers exhibit a 90-fold enhancement in saturation magnetization and a 35-fold increase in PL intensity relative to the pristine monolayer MoS_2.

Experimental section

The transmission electron microscopy (TEM) measurement was carried out on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. The high-resolution TEM (HRTEM) and corresponding energy-dispersive spectroscopy (EDS) mapping analyses were performed on a JEOL JEMARF200F TEM/STEM with a spherical aberration corrector. High-resolution high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) was performed in a JEOL ARM200F with STEM aberration (Cs) corrector operated at 80 kV. Mo, Co and Cr concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Jarrel Ash model 955). The atomic force microscope (AFM) image was taken with *Veeco NanoScope* MultiMode V scanning probe microscope in tapping mode. Magnetization studies were carried out using a superconducting quantum interference device (SQUID) magnetometer. In the

testing process of Raman/PL spectra and mapping (Horiba HR Evolution), 50× objective was used to focus incident 532 nm laser with the spot size about 1 μm, and the step size was 600 nm for the mapping. The backscattered light was dispersed by 1200 grating/mm. In order to uniformly contrast the change of PL peak intensity, the laser power was fixed at 2.5 mW and the integral time was 10 s. The Cr *K*-edge and Co *K*-edge X-ray absorption fine structure (XAFS) spectra were measured at the 4W7B beamline of the Beijing Synchrotron Radiation Facility (BSRF), China. And the Mo K-edge XAFS spectra were measured at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), China.

Results and discussion

The (Co, Cr)-codoped monolayer MoS_2 were grown on 300-nm thick SiO_2/Si substrates prepared by chemical vapor deposition (CVD). The morphology and crystal structure of these as-obtained monolayers are shown by the optical microscope, atomic force microscope (AFM), transmission electron microscopy (TEM) images. The domains with an average size of ~20 μm are clearly seen with a homogeneous color together with flakes having an equilateral triangular shape and the AFM indicates the ~0.78 nm thickness of the as-grown flake. Meanwhile, the energy-dispersive X-ray (EDX) mapping images in Figure 2(d) qualitatively reveal that the chemical composition of the samples include not only the Mo and S elements, but also the Cr and Co elements. From the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements results, we can see randomly distributed darker spots marked by red circles and brighter spots marked by yellow circles in the medium white (Mo atoms) atomic lattice. The corresponding cross-sectional intensity of the atom contrast in Figure 2(f) reveals that the Cr or Co atoms possibly anchor on Mo atop sites or substitute for Mo atoms.

To further detect the real occupation positions of the Co and Cr dopants at the atomic level, detailed analysis of element specific XAFS spectra was carried out. Like the Mo *K*-edge FT curve of bulk MoS_2, the FT at Co *K*-edge exhibits two prominent coordination peaks at 1.9 Å (Co-S coordinations) and 2.8 Å (Co-Mo coordinations),

suggesting the substitutional doping of Co in the MoS_2 host. However, only the 1.9 Å peak is prominent in the FT curve at Cr *K*-edge. In combination with the HADDF result, it can be inferred that the Cr dopants are anchored on the Mo atop sites of the monolayer MoS_2. Based on the structural model of Co substituting for the interior Mo sites and Cr anchored on the atop Mo sites, we calculated the x-ray absorption near-edge structure (XANES) spectra. The calculations could well reproduce the spectral features of the experimental data, affording further support to the validity of the structure. After Co-doping, the saturation magnetization is greatly enhanced to ~0.09 emu/g (~0.3μ_B/Co), 90 times higher than that of the pristine monolayer MoS_2. However, the PL intensity of the Co-doped MoS_2 becomes weaker. Surprisingly, after codoping Cr into the monolayer MoS_2, the PL intensity map shows a bright red color, and the PL intensity shows a 35-fold enhancement. The electrical transport in monolayer MoS_2 before and after Co-doping and (Co, Cr)-codoping indicate the Co and Cr in monolayer MoS_2 act as *p*-type dopants and reduce the electron density.

Conclusion

In conclusion, using the monolayer MoS_2 as an example, we have experimentally demonstrated that the codoping strategy to engineer the electronic band structure is an effective way to realize the coexistent optical and ferromagnetic properties in two-dimensional chalcogenide semiconductors. As shown by a detailed study of structural, optical and magnetic properties, this idea is successfully applied to (Co, Cr)-codoped monolayer MoS_2. As compared with the pristine monolayer MoS_2, the saturation magnetisation and PL intensity of the (Co, Cr)-codoped monolayer MoS_2 is enhanced by 90 and 35 times, respectively. To the best of our knowledge, this is the first report on the coexistence of robust ferromagnetism and strong PL in monolayer MoS_2. We expect that this idea can be generalized to tune the optical and magnetic properties of other two-dimensional semiconducting materials, and it opens up new possibilities for simultaneous polarization and detection of the valley degree of freedom for future valleytronics applications.