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Introduction

Recently, two-dimensional materials have received widespread attention due to their special properties compared to their corresponding bulk materials.^{1–6} Due to the high carrier mobility and ultrathin nature of two-dimensional materials, it can be used to fabricate faster processing, less power-consuming, and portable devices.^{7–9} Graphene is widely used as a transparent electrode because of its unique Dirac energy band struc-

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Investigating the dynamics of excitons in monolayer WSe₂ before and after organic super acid treatment[†]

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Due to the large photoluminescence quantum yield, high mobility and good stability, organic super acid treated two-dimensional WSe₂ has drawn much attention. However, reports about the influence of organic super acid treatment on the dynamic processes of excitons of monolayer WSe₂ are still rare. In this work, through the broadband transient absorption spectra obtained using a femtosecond pump-probe system, we determine the dynamics of A' and C excitons in monolayer and bulk WSe₂ at room temperature. Besides this, we also observe the relaxation process of the holes between the two spin split states in the valence band maximum in organic super acid treated monolayer WSe₂. We find that the organic super acid treatment on monolayer WSe₂ does not change the peak positions of the exciton states, while those bleaching peaks' intensities increase significantly due to the enhancement of oscillator strength for exciton states, corresponding to stronger steady-state photoluminescence. This could be attributed to the strain release induced by the defect repairing effect during the organic super acid treatment process.

ture. However, because of its zero bandgap, graphene cannot achieve the off state.^{10,11} Since two-dimensional semiconducting transition metal dichalcogenides (TMDCs) can achieve the off state, they can be potentially used for the production of switching devices.¹² In particular, TMDCs also possess a wide variety of unique optical, physical, and electrical properties. Thus, they have broad application prospects for the production of many new devices.^{13–15}

As a member of TMDC materials, monolayer WSe₂ has a relatively high photoluminescence (PL) quantum yield, which is about two orders of magnitude higher than that of the monolayer MoS₂.^{16,40} Besides this, monolayer WSe₂ is very stable at room temperature¹⁷ and can be used to produce p-type field-effect transistors which have a high hole mobility and a high on-off ratio.¹⁸ As a result, monolayer WSe₂ can be used to design various stable optoelectronic devices and fabricate several van der Waals heterojunctions.¹⁷⁻²⁶ Hence, the study of monolayer WSe₂ is particularly significant for the manufacture of optoelectronic devices. Numerous studies on the band structure, tightly bound excitons and their dynamics of monolayer WSe₂ by PL spectroscopy, absorption spectroscopy, and ultrafast pump-probe spectroscopy at a single probe wavelength or a narrowband probe range have been reported.^{16,27,28} Even so, there is still a lack of systematic research on the energy band structure and the dynamic processes of the exciton states

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of bulk, monolayer and organic super acid treated monolayer WSe_2 (osa-monolayer WSe_2) by broadband transient absorption (TA) spectroscopy. The broadband TA experiments for osa-monolayer WSe_2 could provide deep insight into the relation-ship between the surface chemical modification and the underlying exciton dynamics. Furthermore, a comparative study of bulk and monolayer WSe_2 could help us to understand the properties of each exciton state better for WSe_2 layers.

In this work, a femtosecond pump-probe system equipped with an adjustable pump pulse fluence was used to excite bulk, monolayer and osa-monolayer WSe2, respectively. Based on the TA spectrum with a broadband probe pulse range from 400 nm to 800 nm which can be applied to record the ground state bleaching (GSB) signals and carrier dynamics processes, we observe the relaxation pathway of holes between two spinsplit energy levels as well as determine the dynamic features of A' and C excitons in osa-monolayer WSe₂. Moreover, the GSB peak intensities of osa-monolayer WSe2 enhance markedly along with the peak width narrowing compared with untreated monolayer WSe2. However, the peak positions remain unchanged, which is consistent with steady-state fluorescence enhancement. Furthermore, bulk WSe2 is found to have a blue shift of its peak positions, and a slower decay with the increase of pump pulse fluence.

Results and discussion

Experiments are performed on bulk WSe_2 , monolayer WSe_2 and osa-monolayer WSe_2 . By first-principles calculations, we obtain the atomic and band structure of monolayer WSe_2 . Monolayer WSe_2 possesses a honeycomb lattice,²⁹ as shown in Fig. 1(a). The energy band structure of bulk WSe_2 exhibits an



Fig. 1 (a), (c), (d): Structures of monolayer and bulk WSe₂. (b), (e), (f): Raman, absorbance and emission spectra of monolayer WSe₂ before and after organic super acid treatment. (a) Schematic of monolayer WSe₂. Atoms color coding: purple for W and green for Se. (b) Raman analysis of monolayer and bulk WSe₂, which are normalized to the A1_g peak and vertically offset for clarity. (c) Band structure of bulk WSe₂. (d) Band structure of monolayer WSe₂. (e) Absorbance spectra of monolayer WSe₂ before and after organic super acid treatment. The spectra are normalized to the intensity at 400 nm. (f) PL spectra of monolayer WSe₂ before and after organic super acid treatment under 532 nm excitation.

indirect bandgap; however, its monolaver WSe₂ presents a direct bandgap, displayed in Fig. 1(c) and (d) respectively. The main difference is the position of the conduction band minimum (CBM). In bulk WSe₂, the CBM locates between Γ and K points in the momentum space. In contrast, the CBM of monolayer WSe₂ moves to the K point. Both their valence band maxima (VBM) display split at the K point. To distinguish between bulk and monolayer WSe2, Raman spectroscopy has been performed by exciting these samples with a 532 nm laser line, as demonstrated in Fig. 1(b). The A1g peak located at 252 cm^{-1} of monolayer WSe₂ which is assigned the in-plane vibrational mode almost exhibits no difference with bulk WSe₂. The E_{2g}^{1} peak located at 252 cm⁻¹ of monolayer WSe₂ which is assigned the out-of-plane vibrational mode $(E_{2g}^{1})^{1}$ and A1g are virtually degenerate in monolayer WSe2 as demonstrated in ref. 30) shifts to 250 cm^{-1} in bulk WSe₂. Due to the large atomic mass of WSe₂, A_{1g} and E_{2g}^{1} peaks have a small dependence on thickness. The most prominent characteristic peak appearing near the E_{2g}^{1} peak is labeled as 2LA (M). This peak is the second-order Raman mode of the LA phonon at point M in the Brillouin zone. This peak shifts from 262 cm^{-1} to 259 cm⁻¹ when WSe₂ changes from monolayer to bulk. Steady-state absorption spectra of monolayer WSe₂ before and after organic super acid treatment are recorded on a Shimadzu UV-2550 UV-VIS scanning spectrophotometer and are shown in Fig. 1(e). The steady-state absorption peak appears at 422 nm, 503 nm, 593 nm, and 743 nm, respectively. PL spectra of monolayer WSe₂ before and after organic super acid treatment are shown in Fig. 1(f). Both monolayer WSe₂ before and after organic super acid treatment show a PL peak at 746 nm. However, the PL intensity of osa-monolayer WSe₂ has a sharp increase of about 3.3 times compared with monolayer WSe₂.

We obtained the TA spectra of osa-monolayer WSe₂ by exciting it under a 400 nm pump pulse as shown in Fig. 2(a), where the GSB peak appeared at ~422 nm, ~505 nm, ~595 nm, and ~743 nm, respectively. The TA spectra of osa-monolayer WSe₂ by exciting it with different fluences are shown in Fig. S1 in the ESI.[†] Among the four GSB peaks, GSB peaks at ~595 nm and 743 nm correspond to B- and A-excitons, respectively. There have been several reports about the inter-valley exciton scattering for the band-edge A- and B-excitons through different optical methods.³¹⁻³³ Here we explore the relaxation process of holes from the B-exciton state to the A-exciton state in osa-monolayer WSe2 by selective excitation at first. 610 nm and 730 nm pump pulses with similar pump fluences are used to excite the sample as presented in Fig. 2(b) and (c), respectively, and then we could observe the difference between the normalized dynamics of the A exciton at 743 nm shown in Fig. 2(d).

Obviously, the rising dynamic process of the A exciton excited by the 610 nm pump pulse is slower than that excited by the 730 nm pump pulse. This shows the hole transfer process (since the hole transfer time is close to the instrument response function, it is difficult to fit the rising process of the signal by an exponential function). This is because that, in principle, when osa-monolayer WSe₂ is excited by the 610 nm



Fig. 2 Measurements of osa-monolayer WSe₂ using a femtosecond pump-probe system. (a) Transient absorption (TA) spectra of osa-monolayer WSe₂ excited by a 400 nm pump pulse with a pump fluence of 16 μ J cm⁻². (b) TA spectra of osa-monolayer WSe₂ excited by a 610 nm pump pulse with a pump fluence of 0.33 μ J cm⁻². (c) TA spectra of osa-monolayer WSe₂ excited by a 730 nm pump pulse with a pump fluence of 0.27 μ J cm⁻². (d) The normalized dynamic process of the GSB peak at 743 nm of (b) and (c). (Inset) Schematic of the band-edge structure of monolayer WSe₂.

pump pulse, it corresponds to the transition between the energy level 1 to the bottom of the conduction band (see the inset of Fig. 2(d)). Thus, the holes will first relax from energy level 1 to energy level 2, both of which arise from the spinorbit split at the top of the valence band, assigned process (1) in the Fig. 2(d) inset. Then, they will recombine with the electrons in the conduction band minimum (process (2) in the Fig. 2(d) inset). While, for the 730 nm pump case, corresponding to the transition between the energy level 2 to the bottom of the conduction band, the holes in the valence band maximum will directly recombine with the electrons in the conduction band minimum (process (2)).

The remaining two high-energy GSB peaks are previously labeled as A' and B', respectively.³⁴ Here, we assign it to the A' exciton (~505 nm) and the C exciton (~422 nm), respectively, according to our latest research presented below, though there is still a matter of dispute about where the A' exciton originates from in osa-monolayer WSe₂. For a direct comparison, the normalized dynamics of the four bleaching peaks under 610 nm excitation with different pump fluences is shown in Fig. 3. It is obvious that the decay trend of the GSB peak at 422 nm is much slower than the other three decay traces, and barely dependent on pump fluences. In particular, within the first 3 ps, there is almost no decay for the GSB signal at 422 nm. This is similar to the case of monolayer MoS₂ (ref. 35 and 36). Thus, we assign the GSB peak at 422 nm to the C exciton of osa-monolayer WSe2, which could arise from a parallel band between the valence band and the conduction band. On the other hand, the decay of all other three excitons occurs from the beginning. It seems that the relaxation properties of the so-called A' exciton (GSB peak at 505 nm) are intermediary



Fig. 3 The normalized dynamics of the four GSB peaks of osa-monolayer WSe₂ excited by the 610 nm pump pulse with different pump fluences. (a) The normalized dynamics of the four ground state bleaching (GSB) peaks of osa-monolayer WSe₂ excited by the 610 nm pump pulse with a pump fluence of 0.33 μ J cm⁻². (b) The normalized dynamics of the four GSB peaks of osa-monolayer WSe₂ excited by the 610 nm pump pulse with a pump fluence of 0.52 μ J cm⁻². (c) The normalized dynamics of the four GSB peaks of osa-monolayer WSe₂ excited by the 610 nm pump pulse with a pump fluence of 1.1 μ J cm⁻². (d) The normalized dynamics of the four GSB peaks of osa-monolayer WSe₂ excited by the 610 nm pump pulse with a pump fluence of 2 μ J cm⁻².

between the tightly bound A-/B-exciton and the C exciton purely arising from the nesting effect.

To examine the influence of organic super acid treatment on the exciton dynamics, the TA spectra of untreated monolayer WSe₂ obtained by exciting it under 590 nm excitation (pump density of 4.0 μ J cm⁻²) and 730 nm excitation (pump density of 0.76 μ J cm⁻²) are also presented in Fig. 4(a) and (b) respectively. Apparently, there are four GSB peaks, too, whose positions are similar to the monolayer WSe₂ with organic super acid treatment. But comparing the TA spectra of osamonolayer WSe₂ with that of untreated monolayer WSe₂ both under 730 nm excitation, shown in Fig. 2(c) and 4(b), respectively, it is quite clear that the GSB peak intensity of the organic super acid treated sample is much larger than the untreated sample, though for the latter it is excited by a higher pump density (~3.0 times larger than the case of osa-monolayer WSe₂). In addition, the full width at half maximum (FWHM) of the A exciton bleaching signal for the former is narrower than that of the latter. For instance, both under 610 nm excitation, it decreases from 29 nm in the untreated sample to 20 nm in osa-monolayer WSe_2 as shown in Fig. 4(c). Note that in Fig. 4(c), the GSB intensity of the A exciton for osa-monolayer WSe₂ shown in Fig. S1(d)^{\dagger} is ~5.0 times larger than the untreated monolayer WSe₂ shown in Fig. S2,† while the pump fluence for the latter is ~8.5 times larger than that for the former. A detailed list of enlargement factors of GSB signals of monolayer WSe₂ after organic super acid treatment under different pump fluences is presented in Table S1.† Since it is hard to obtain good enough TA data for untreated monolayer



Fig. 4 TA spectra of monolayer WSe₂ and normalized TA and PL spectra of monolayer WSe₂ before and after organic super acid treatment. (a) TA spectra of monolayer WSe₂ excited by a 590 nm pump pulse with a pump fluence of 4 μ J cm⁻². (b) TA spectra of monolayer WSe₂ excited by a 730 nm pump pulse with a pump fluence of 0.76 μ J cm⁻². (c) The normalized TA spectra (probed at 500 fs) of monolayer WSe₂ before and after organic super acid treatment excited by a 610 nm pump pulse, in which the original TA spectrum for untreated monolayer WSe₂ and osa-monolayer WSe₂ is shown in Fig. S2 and S1(d),† respectively. (d) The normalized PL spectra peaked at 746 nm of monolayer WSe₂ before and after organic super acid treatment (the original PL spectra are shown in Fig. 1(f)).

WSe₂ in a lower pump fluence, we could estimate according to Table S1[†] that if the pump fluence is the same (i.e., ~4.0 μ J cm⁻²) for both organic super acid treated and untreated samples, the GBS intensity of the A exciton in the former could be \sim 4.0 times larger than that in the latter. On the other hand, the FWHM for the steady-state PL also decreases from 30 nm in the untreated sample to 23 nm in osa-monolayer WSe_2 as shown in Fig. 4(d), accompanied by enhanced oscillator strength for steady-state absorption and enhanced intensity for steady-state PL presented in Fig. 1(e) and (f). Those transient and steady-state phenomena reflect a fact that there are numerous lattice defects in untreated monolayer WSe₂, and when an organic super acid is used to deal with monolayer WSe2, those lattice defects will be reconstructed to some extent, and the intrinsic lattice strain would also be relaxed. Passivation of dangling bonds at the Se vacancy site could also enhance the oscillator strength for exciton states. However, this passivation reaction could be energetically unfavorable, as pointed out for the similar case in organic super acid treated monolayer MoS₂.^{2,37}

For comparison, the TA spectra of bulk WSe₂ were acquired by exciting it with different pump fluences, as shown in Fig. S3.† The TA spectrum (probed at 400 fs) gained with three pump fluences under 400 nm excitation is demonstrated in Fig. 5(a), exhibiting power dependence. As the pump density increases from 29 μ J cm⁻² to 141 μ J cm⁻², the initial TA signal amplitudes of the A-/B-/A'-/C-exciton states probed at 400 fs will not only enhance obviously, but also show a red shift of



Fig. 5 Measurements of bulk WSe₂ using a femtosecond pump-probe system in reflection mode. (a) TA spectra (probed at 400 fs) with three pump fluences under 400 nm excitation. Green line: Pump fluence of 29 μ J cm⁻², purple line: pump fluence of 71 μ J cm⁻², red line: pump fluence of 141 μ J cm⁻². (b) The normalized dynamics of the A exciton under three pump fluences of (a). (c) The normalized dynamics of four excitons under 400 nm excitation with a pump fluence of 71 μ J cm⁻². (d): The normalized dynamics of four excitons under 400 nm excitation with a pump fluence of 141 μ J cm⁻².

 \sim 4 nm. In comparison with the osa-monolayer WSe₂, the red shift of the GBS peaks for bulk WSe2 is ~21 nm, ~2.0 nm, ~68 nm, and ~60 nm for A-, B-, A'-, C-excitons, respectively. The normalized dynamics of the A exciton under three different pump fluences is demonstrated in Fig. 5(b). Its decay presents a slowdown as the pump fluence increases. When the pump fluence is relatively low, for example, at 29 μ J cm⁻², the normalized Δ O.D. intensity of this A exciton state decays to zero with a delay time longer than 100 ps. When bulk WSe₂ is excited with a pump fluence of 71 μ J cm⁻², the normalized Δ O.D. intensities of the GSB signals still tend to zero with a delay time longer than 1 ns, as shown in Fig. 5(c). However, as the pump fluence further increases, for example, to 141 µJ cm^{-2} , the normalized $\Delta O.D.$ intensities of the GSB signals do not return to zero within our whole probe window, presented in Fig. 5(d). In this high pump fluence case, the normalized Δ O.D. intensities of the A'- and B-excitons are almost the same, and both become 0.14 when the delay time is 1382 ps; meanwhile, that of the A exciton becomes 0.1. For the C exciton of bulk WSe₂, its normalized Δ O.D. intensity tends to zero when the delay time is 1382 ps. A similar phenomenon can be observed when the bulk WSe2 is excited by an 800 nm pump pulse (Fig. S4[†]). It is attributed to the indirect bandgap feature of bulk WSe2, which affects all the exciton relaxation processes, compared to the monolayer WSe₂ with a direct bandgap structure. For indirect bandgap semiconductors, when the fluence of the pump pulse is relatively low, a few carriers are excited and soon relax to the lowest energy state, so that there is no bleaching signal finally. On the other hand, when a lot of excited carriers generate in the case of a relatively

high pump fluence, the lowest energy state is filled first, which leads to a red shift of the GSB signals, accompanied by the following slower decay to relax to the lowest energy state.

Conclusions

Bulk, monolayer and osa-monolayer WSe₂ were excited using a femtosecond pump-probe system equipped with an adjustable pump pulse fluence. We observe the relaxation processes of the holes between the two lowest energy spin split states, the A- and B-exciton states. Compared with monolayer WSe₂, the peak positions of the exciton states in the TA spectra of osa-monolayer did not change, but its A-exciton bleaching peak width is narrower and the bleaching peak intensity is enhanced greatly, which matches with the observations in steady-state absorption and luminescence. In addition, the PL peak of bulk WSe₂ is observed to display a red shift and a slower decay with the increase of pump fluence due to its indirect bandgap feature. Our work offers a useful approach to study the dynamics of excitons in two-dimensional layered semiconductors and their bulk materials.

Materials and methods

Preparation and transfer of a WSe₂ film

The monolayer WSe₂ film was grown on sapphire by the chemical vapor deposition (CVD) method.^{38,39} The WO₃ powders (0.3 g) were placed in a ceramic boat located in the center of the furnace and the Se powders were placed in a separate ceramic boat at the upper stream side maintained at 270 °C during the reaction. The sapphire substrates for growing WSe₂ were put at the downstream side. An Ar/H₂ flowing gas (Ar = 80 sccm, H₂ = 20 sccm, chamber pressure = 1 Torr) was used to bring the Se and WO₃ vapors to the targeting sapphire substrates. The center heating zone was heated to 925 °C at a ramping rate of 25 °C min⁻¹. When the center heating zone reaches 925 °C, the temperature of the sapphire substrates is ~750 to 850 °C. After reaching 925 °C, the heating zone was kept for 20 min and the furnace was then naturally cooled down to room temperature.

The wet transfer method was used to transfer the WSe₂ film from the sapphire substrates to quartz substrates.³⁸ The WSe₂ film grown on a SiO₂/Si substrate was first coated with a layer of PMMA (950 K, A5) by spin-coating (step 1: 500 rpm for 10 s; step 2: 4000 rpm for 60 s), followed by annealing at 130 °C for 2 min. The PMMA at the edges of the sapphire substrate was removed with a sharp blade to facilitate the following exfoliation of PMMA-capped sapphire from the substrate. Then, a NaOH (3 mol L⁻¹) solution at 100 °C was used to exfoliate the PMMA-capped WSe₂ from the sapphire substrate. To remove the etchant and residues, the PMMA-supported WSe₂ film was transferred to deionized (DI) water. Fresh quartz substrates were used to 'fish out' the PMMA-capped WSe₂ film, followed by drying on a hot-plate (75 °C for 5 min and then 100 °C for 10 min). Finally, the PMMA was removed by acetone and the sample was cleaned with isopropyl alcohol (IPA).

Chemical treatment

The monolayer WSe₂ was chemically treated with bis(trifluoromethane) sulfonamide (TFSI) by using the technique reported by Ali Javey *etc.*^{2,40} First, 20 mg of TFSI (Sigma-Aldrich) was dissolved in 100 ml of 1,2-dichloroethane (DCE) (Sigma-Aldrich) to make a 0.2 mg ml⁻¹ solution. Then, the sample was immersed in this solution in a tightly closed vial for 10 min on a hotplate at a temperature of 100 °C. Finally, the sample was removed, blow dried with nitrogen and subsequently annealed at 100 °C for 5 min.

First-principles calculations

The first-principles density functional theory (DFT) calculation is performed in the Vienna *Ab initio* Simulation Package (VASP) code.^{41,42} The electron–ion interaction is described using the projector augmented wave (PAW) pseudopotential.⁴³ Besides this, the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional is used for the electronic exchange–correlation interaction.^{44,45} We use a 300 eV energy cutoff for the plane wave basis set. The $5 \times 5 \times 2$ and $5 \times$ 5×1 Monkhorst–Pack *k*-points are used for structure optimization of bulk and monolayer WSe₂, respectively. The monolayer WSe₂ model contains a 21.6 Å thick vacuum. The lattice parameters of the optimized monolayer WSe₂ are a = b =3.318 Å, c = 25.012 Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$. The band structure is calculated based on the optimized model.

Femtosecond pump-probe system setup

In all TA experiments,^{46,47} a mode-locked titanium sapphire laser/amplifier system (Solstice, Spectra-Physics) was used. A beam laser with a frequency of 250 Hz and a wavelength of 800 nm is divided into two laser beams through a beam splitter. The laser beam with a larger energy is converted to a 400 nm laser beam through the BBO frequency doubling crystal or a specific wavelength through the TOPAS system. Then, the frequency of this laser beam turns into 125 Hz through a 125 Hz chopper. After the delay by a certain delay line, its polarization direction has been changed. Finally, the laser beam is focused on the sample through the lens, forming the pump light. Another laser beam passes through the lens and focuses on the non-linear medium, what we use is water, producing a super continuous white light with wavelengths ranging from 400 nm to 800 nm. Then, the laser beam passes through the lens and is focused on the same position as the pump light on the sample, forming the probe light. The signal is finally received by an Avantes spectrometer.

Conflicts of interest

There are no conflicts to declare.

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