Sulfur Adatom and Vacancy Accelerate Charge Recombination in MoS$_2$ but by Different Mechanisms: Time-Domain Ab Initio Analysis

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Supporting Information

ABSTRACT: Two-dimensional transition metal dichalcogenides (TMDs) have appeared on the horizon of materials science and solid-state physics due to their unique properties and diverse applications. TMD performance depends strongly on material quality and defect morphology. Calculations predict that sulfur adatom and vacancy are among the most energetically favorable defects in MoS$_2$ with vacancies frequently observed during chemical vapor deposition. By performing ab initio quantum dynamics calculations we demonstrate that both adatom and vacancy accelerate nonradiative charge carrier recombination but this happens through different mechanisms. Surprisingly, holes never significantly populate the shallow trap state created by the sulfur adatom because the trap is strongly localized and decoupled from free charges. Charge recombination bypasses the hole trap. Instead, it occurs directly between free electron and hole. The recombination is faster than in pristine MoS$_2$ because the adatom strongly perturbs the MoS$_2$ layer, breaks its symmetry, and allows more phonon modes to couple to the electronic subsystem. In contrast, the sulfur vacancy accelerates charge recombination by the traditional mechanism involving charge trapping, followed by recombination. This is because the hole and electron traps created by the vacancy are much less localized than the hole trap created by the adatom. Because the sulfur adatom accelerates charge recombination by a factor of 7.9, compared to 1.7 due to vacancy, sulfur adatoms should be strongly avoided.

KEYWORDS: Transition metal dichalcogenides, electron–hole recombination, sulfur vacancy and adatom defects, time-dependent density functional theory, nonadiabatic molecular dynamics

S
ingle-layer graphene has opened up the exploration and research into the physics of atomically thin two-dimensional materials.

However, its applications in electronic and optoelectronic devices are strongly hindered by lack of an intrinsic band gap. As a result, the lifetimes of excited charge carriers are too short to make practical devices. More recently, two-dimensional transition metal dichalcogenides (TMDs) of the general formula MX$_2$, M = Mo, W; X = S, Se, Te, have drawn strong attention in the areas of materials science and solid-state physics due to their unique properties and diverse applications. TMD performance depends strongly on material quality and defect morphology. Calculations predict that sulfur adatom and vacancy are among the most energetically favorable defects in MoS$_2$ with vacancies frequently observed during chemical vapor deposition. By performing ab initio quantum dynamics calculations we demonstrate that both adatom and vacancy accelerate nonradiative charge carrier recombination but this happens through different mechanisms. Surprisingly, holes never significantly populate the shallow trap state created by the sulfur adatom because the trap is strongly localized and decoupled from free charges. Charge recombination bypasses the hole trap. Instead, it occurs directly between free electron and hole. The recombination is faster than in pristine MoS$_2$ because the adatom strongly perturbs the MoS$_2$ layer, breaks its symmetry, and allows more phonon modes to couple to the electronic subsystem. In contrast, the sulfur vacancy accelerates charge recombination by the traditional mechanism involving charge trapping, followed by recombination. This is because the hole and electron traps created by the vacancy are much less localized than the hole trap created by the adatom. Because the sulfur adatom accelerates charge recombination by a factor of 7.9, compared to 1.7 due to vacancy, sulfur adatoms should be strongly avoided.

The generated insights highlight the diverse behavior of different types of defects, reveal unexpected features, and provide the mechanistic understanding of charge dynamics needed for tailoring TMD properties and building high-performance devices.

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and found that a sulfur adatom (Ad_S) and a sulfur vacancy (V_S) are among the most energetically favorable point defects. Wu et al. detected several intrinsic point defects in monolayer MoS_2 synthesized via chemical vapor deposition (CVD). S vacancy was frequently observed in all their samples. Since charge transport and optical properties of semiconductors are closely related to dynamics of excited charge carriers, numerous experiments have been carried out to study such dynamics in MoS_2. It is generally accepted that defects introduce charge traps and accelerate electron–hole recombination; however, the atomistic mechanisms of these processes are not well understood. For example, it is not known whether all defects are equally detrimental to material’s electronic and optical properties or whether certain defect types are particularly important and why. Such understanding is essential to guide synthetic efforts in producing higher quality materials.

In this paper, we use ab initio quantum dynamics calculations to show that sulfur defects accelerate nonradiative electron–hole recombination in MoS_2; however, the acceleration mechanisms are different for adatom and vacancy. The hole trap state created by the adatom is very localized, and therefore it couples weakly to charge carriers and is barely populated. Still, the adatom accelerates charge recombination because it distorts the symmetry of the MoS_2 layer, introduces new phonon modes that couple to the electronic subsystem, and increases the nonadiabatic charge-phonon coupling. The sulfur vacancy creates a deep, fairly localized electron trap and a shallow, less localized hole trap that can couple well to the free hole. As a result, charge recombination through the hole trap dominates in MoS_2 with sulfur vacancies. Our calculations show that the sulfur adatom is more fatal in reducing the lifetime of charge carriers in MoS_2 than sulfur vacancy, even though the adatom trap state is not populated. Hence, sulfur adatoms should be avoided to produce high quality TMD materials and devices.

The geometry optimization, electronic structure, and adiabatic molecular dynamic trajectories were computed with the Quantum Espresso program. Nonadiabatic molecular dynamics were simulated using decoherence-induced surface hopping implemented in the Pyxaid software under the classical path approximation. This method has been proven reliable in closely related MoS_2/MoSe_2 and MoS_2/WS_2 heterojunction systems and other related materials such as graphene, black phosphorus, and so forth. The methodology, its justification, and simulations details are presented in the Supporting Information.

Figure 1 shows a diagram of the electronic energy levels involved in the charge carrier trapping and relaxation dynamics. After photoexcitation, electrons in the conduction band (CB) can directly recombine with holes in the valence band (VB) ①. A fraction of photoexcited electrons can get trapped by the unoccupied defect levels (electron trap states) ②. Following the trapping, electrons can undergo recombination with the VB holes ③. Similarly, holes can get trapped by the occupied defect levels (hole trap states) ④ and then recombine with the CB electrons ⑤ or the trapped electrons ⑥. Electron is orange. Hole is emerald.

Figure 2 depicts the side and top views of the perfect, Ad_S, and V_S MoS_2 monolayers. Defects are denoted with red arrows and red circles. The single point defects are introduced in our calculations within the 5 × 5 supercell of the MoS_2 monolayer, corresponding to the defect concentration of 4.6 × 10^13 defects/cm^2. The defect concentration is high, due to the computational limitations associated with modeling of large simulation cells. Such defect concentration can have a strong influence on device performance.

Figure 3 shows the densities of states (DOS) of the perfect, Ad_S, and V_S MoS_2 monolayers. The charge densities of the VB and CB edge states in each system are shown to the right of the DOS plots. The inserts within the DOS plots present observed in MoS_2 monolayer samples. The extra S atom in the Ad_S system is rather mobile. Its potential of binding to the MoS_2 surface is shallow, and the adatom can undergo large scale anharmonic motions. A sulfur vacancy creates unsaturated chemical bonds at the Mo atoms, which attempt to interact with adjacent S atoms, amplifying their motions. Both adatom and vacancy perturb the symmetry of the MoS_2 layer and give rise to phonon modes that are not available in the pristine system.

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The changes in the trap, which shrinks the band gap by 0.030 eV, and a deep localized electron trap 0.069 eV. The S vacancy creates two trap states: a shallow hole trap close to the VB edge and a deep localized electron trap 0.6 eV below the CB edge. The charge densities of the VB edge states are strongly perturbed by defects, while CB edge states remain unchanged.

The VB and CB edge states are delocalized within the monolayer, and the CB edge states are barely perturbed by the defects. The VB edges are perturbed more strongly, because both Ad_S and V_S create defect energy levels close to the VB edge. These shallow hole trap states hybridize with the VB edge states. The shallow hole trap state created in the Ad_S system is strongly localized. In comparison, the shallow hole trap observed in the V_S system is much more delocalized. Even the deep electron trap created by the sulfur vacancy is quite delocalized, compared to the hole trap in the Ad_S system. The latter fact is unexpected, because deep traps cannot hybridize with CB and VB states, while shallow traps can and, hence, should delocalize by borrowing density of the delocalized CB and VB orbitals. The fact that the shallow trap in the Ad_S system is strongly localized is unusual for shallow traps, already suggesting that the traditional trap-mediated charge recombination mechanism may not work for Ad_S.

Figure 4 presents evolution of populations of the key states involved in the electron–hole recombination dynamics in the three systems, including populations of the electron and hole trap states and the ground state. The shown time scales are obtained by exponential fitting of the data. The ground state populations are fitted by a single exponent. The trap states are populated transiently, involving both rise and decay of the population. In these cases, the rise and decay are fitted by separate exponents, and the reported times are the sums of the times of the two exponential fits. These times provide a measure of how long the trap states are populated.

Nonradiative electron–hole recombination constitutes a major pathway for charge losses and energy dissipation in optoelectronic applications. The direct recombination of a CB electron and a VB hole, corresponding to process ① in Figure 1, needs 388 ps in the perfect MoS2 monolayer. This time scale is consistent with the experimentally reported recombination times of several hundreds of picoseconds. Both defects accelerate the recombination, Figure 4, however the mechanisms of the acceleration are substantially different for the adatom and the vacancy. Traditionally, defect-induced acceleration of charge recombination is explained by introduction of energy levels within the semiconductor band gap. It is assumed that the defect levels get populated, and that the relaxation is faster because it involves transitions across smaller energy gaps. This mechanism operates with the S vacancy, Figure 4c. However, the S adatom creates no states deep inside the band gap, Figure 3b. Moreover, the shallow hole trap is never significantly populated, Figure 4b. Nevertheless, the electron–hole recombination becomes faster by a factor of 8 in the presence of the S adatom.

The enhancement of the electron–hole recombination rate by the S adatom defect is rationalized by the stronger nonadiabatic coupling (NAC) between the CB and VB edges (8.44 meV). This is because the localized orbital of the trap state has negligible overlap with the VB edge orbital, which exhibits a depletion near the defect, Figure 3b. In comparison, the NAC between the hole trap and the free electron occupying the CB edge is as large (8.41 meV) as the NAC between the CB and VB edges (8.44 meV). This is because the density of the CB edge orbital has no depletion near the defect and exhibits significant overlap with the hole trap density. The difference in the NAC values for the hole trapping and trap-assisted electron–hole recombination explains why the population of the hole trap state never builds up above a few percent, Figure 4b.
The acceleration of the electron–hole recombination by a factor of 1.7 due to the S vacancy follows the traditional mechanism. First, the shallow hole trap is populated, red line in Figure 4c. Second, the deep electron trap is populated, purple line in Figure 4c. Finally, electrons and hole recombine, black line in Figure 4c. The electron trapping and electron–hole recombination exhibit similar time scales and, therefore, about half of electron–hole recombination events bypass the electron trap state. In contrast, hole trapping is involved in most recombination events in the V_S system. The NAC values are 2.5–4 meV for all processes observed in the V_S system with the exception of the electron trapping, which involves a 0.9 meV NAC, Table 1. The pure-dephasing times, representing elastic electron–phonon scattering, are on the order of 10 fs in all cases. Such values are typical of many nanoscale materials.43–47 Both S adatom and vacancy defects accelerate the electron–hole recombination within the MoS2 monolayer.

In order to provide further insights into the nonradiative relaxation and recombination of the charge carriers in the pristine and defected MoS2, we computed Fourier transforms of the fluctuations of the energy gaps between the relevant energy levels, Figure 5. Electron–hole recombination in the pristine MoS2 monolayer is promoted by the 400 cm−1 phonon, which corresponds to the out-of-plane A1g mode of MoS2 with the 404.1 cm−1 frequency.51 Similar findings have been reported in other TMD systems.28,29 The S adatom perturbs the symmetry of the MoS2 layer and introduces new phonons that couple to the electron and hole. The adatom is loosely bonded to the monolayer and vibrates at low frequencies that contribute strongly to the overall electron–phonon coupling. The effect is seen with all transitions in the Ad_S system, including recombination directly between CB and VB edges and via

### Table 1. Root-Mean-Square of Nonadiabatic Coupling (NAC) and Pure-Dephasing Time for Charge Carriers Trapping and Recombination Dynamics

<table>
<thead>
<tr>
<th></th>
<th>perfect</th>
<th>Ad_S</th>
<th>V_S</th>
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<tr>
<td></td>
<td>recomb. of CB e and VB h</td>
<td>recomb. by h-trapping</td>
<td>recomb. by e-trapping</td>
</tr>
<tr>
<td>NAC (meV)</td>
<td>2.78</td>
<td>8.44</td>
<td>3.67</td>
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<tr>
<td>Hole trapping</td>
<td>0.82</td>
<td>0.81</td>
<td>0.92</td>
</tr>
<tr>
<td>Hole trapping</td>
<td>8.41</td>
<td>8.41</td>
<td>2.53</td>
</tr>
<tr>
<td>Recomb. by e-trapping</td>
<td>6.81</td>
<td>11.46</td>
<td>6.69</td>
</tr>
<tr>
<td>Recomb. by e and h-trapping</td>
<td>7.00</td>
<td>12.84</td>
<td>7.38</td>
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Figure 5. Phonon modes involved in the charge carrier dynamics in (a) perfect MoS2 monolayer, (b) Ad_S, and (c) V_S (two bottom rows). The peak height characterizes the strength of electron–phonon coupling. The adatom allows many phonon modes to couple to the charge carriers, accelerating the recombination (Figure 4).
hole trapping. The spectrum amplitude for the hole trapping process is small, in agreement with the small value of the NAC, Table 1. The CB to VB charge recombination in MoS$_2$ with the S vacancy is also promoted by the 400 cm$^{-1}$ out-of-plane mode. The processes involving electron and hole traps are facilitated by a wider range of phonons, including both the 400 cm$^{-1}$ phonon and other vibrations that are typically at lower frequencies. The higher frequency modes are more important for hole trapping than electron trapping. Because the NAC is proportional to nuclear velocity, higher frequency modes create larger NAC at a given temperature. The differences in the spectrum intensities for the higher and lower frequency modes involved in electron and hole trapping, Figure 5c, are consistent with the corresponding NAC values, Table 1.

To summarize, we have investigated how the two most common intrinsic point defects, S adatom and S vacancy, influence charge carrier trapping and recombination in the MoS$_2$ monolayer. We have found that both defects can accelerate electron–hole recombination but the acceleration happens through different mechanisms. The adatom enhances the recombination by a factor of 8, while the vacancy does so only by a factor of 2. Surprisingly, the shallow hole trap state created by the adatom is never significantly populated during the relaxation dynamics. Nevertheless, the recombination becomes much faster. The wave function of the trap state created by the S adatom near the VB edge is very localized and, therefore, it very weakly overlaps with the delocalized VB wave functions. The trap–VB coupling is weak, and the trapping is slow. The acceleration arises because the S adatom perturbs strongly the structure and symmetry of the MoS$_2$ layer. In addition to the 400 cm$^{-1}$ out-of-plane phonon that operates in pristine MoS$_2$, the adatom introduces many other vibrational modes that couple strongly to the electronic subsystem and induce electron–hole recombination directly between the CB and VB edges. In contrast, the S vacancy creates both electron and hole traps, and these traps are populated during the nonradiative relaxation process. The electron–hole recombination proceeds by the traditional mechanism in this case. First, the hole is trapped by the shallow state, then the electron is trapped by a state deep inside the band gap, and finally the charges recombine.

The novel mechanism of the defect-induced charge carrier losses in MoS$_2$ uncovered by the reported simulations, can operate in most semiconductors. It should be particularly important for TMD and other two-dimensional materials, because they have extremely high surface-to-volume ratio and are prone to mechanical deformation. A single adatom can strongly influence the phonon spectrum of a two-dimensional material, by perturbing the system symmetry and geometry, and introducing new, highly anharmonic motions. Two key elements determine the unusual behavior of the sulfur adatom. First, it creates a very localized trap state, which is decoupled from free charges. Second, the defect creates a significant perturbation to the system. The trap is localized because the sulfur adatom is not integrated into the MoS$_2$ layer. Such situation can arise in any system and depends on defect chemistry and stability. In order for a defect to create a significant perturbation to the pristine system, the system has to be flexible and soft. Few dimensional and organic systems are more prone to such perturbation than bulk inorganic semiconductors. Therefore, in large inorganic systems one can see surface defects that are decoupled from charge dynamics; however, these defects are unlikely to modify the dynamics. Zero-, one-, and two-dimensional materials, as well as organic systems, such as conjugated polymers and molecular crystals, can exhibit the behavior very similar to that predicted for the sulfur adatom in MoS$_2$. From the practical perspective, the reported results indicate that S vacancies should be much more benign to performance of TMD devices than S adatoms. The MoS$_2$ properties can be adjusted significantly by small variations in the layer stoichiometry. Our results agree well with the available experimental data, demonstrate how point defects influence the properties of the MoS$_2$ monolayer, generate theoretical insights into defect engineering and excited state dynamics in TMDs, and suggest routes for optimizing performance of TMD based electronic and photovoltaic devices.

**ASSOCIATED CONTENT**

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b04374.

Description of the theoretical methodology and simulation details (PDF)

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**Notes**

The authors declare no competing financial interest.

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