Mono-Elemental Properties of 2D Black Phosphorus Ensure Extended Charge Carrier Lifetimes under Oxidation: Time-Domain Ab Initio Analysis

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Supporting Information

ABSTRACT: An attractive two-dimensional semiconductor with tunable direct bandgap and high carrier mobility, black phosphorus (BP), is used in batteries, solar cells, photocatalysis, plasmonics, and optoelectronics. BP is sensitive to ambient conditions, with oxygen playing a critical role in structure degradation. Our simulations show that BP oxidation slows down charge recombination. This is unexpected, since typically charges are trapped and lost on defects. First, BP has no ionic character. It interacts with oxygen and water weakly, experiencing little perturbation to electronic structure. Second, phosphorus supports different oxidation states and binds extraneous atoms avoiding deep defect levels. Third, soft BP structure can accommodate foreign species without disrupting periodic geometry. Finally, BP phonon scattering on defects shortens quantum coherence and suppresses recombination. Thus, oxidation can be regarded as production of a self-protective layer that improves BP properties. These BP features should be common to other monoelemental 2D materials, stimulating energy and electronics applications.

Black phosphorus (BP) is a new functional two-dimensional (2D) material that has attracted intense attention1−10 owing to its tunable thickness-dependent direct band gap, which varies from 0.3 eV for the bulk to 1.5−2.0 eV for the monolayer10,11 high carrier mobility up to 1000 cm2/(V s) and an on/off ratio up to 104−108.12 Similar to graphite, BP is a layered material, in which interlayers are stacked together with van der Waals (vdW) interactions and intralayer phosphorus atoms covalently bond with three nearest neighbors through sp3 hybridization to form a puckered honeycomb structure.12 Furthermore, BP is a p-type semiconductor whose band gap is sensitive to external electric field and strain.13−15 BP shows peculiar in-plane anisotropic properties that can distinguish itself from other 2D materials.9,11,16 These outstanding properties make BP a promising 2D material candidate for wide applications in batteries,17,18 optoelectronics,19−21 photocatalysis,22,23 photovoltaics,24 and plasmonics.25

However, BP is reported unstable and easy to degrade in ambient conditions,7,8 which motivates a number of studies aimed at elucidating the underlying chemical mechanisms of the degradation process.30−37 Oxygen, water, and light are important factors for the photodegradation in air.30−32 Early studies observed degradation of BP surface after exposure to air even without photo assistance, supporting the combined roles of oxygen and water in the chemical breakdown of BP.34 Recently, many more experiments and calculations verified that oxygen plays a crucial role in BP’s degradation in ambient conditions.35−41 For example, Huang et al. reported joint experimental and theoretical results that the reaction with oxygen is primarily responsible for chemical modifications and changes in the electronic properties of BP.36 In contrast, BP is stable in contact with deoxygenated water, and the carrier mobility of field-effect transistors made with BP increases significantly due to efficient dielectric screening of water.36 The results suggest that the oxidation happens first during the chemical degradation of BP and then it is followed by exothermic reaction with water, because BP surface becomes more hydrophilic after oxidation.36,37

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oxygen and H2O, for both fundamental science and charge carrier dynamics in BP depend on interactions with water. Therefore, it is important and urgent to understand how the excited electron−hole (e−h) recombination of BP under low coverage of oxygen and H2O. Our results show that the oxidation slows down the e−h recombination. Rather than creating e−h recombination centers, the oxidation modifies the phonon modes that couple to the electronic subsystem, slowing down the inelastic scattering and shortening quantum coherence time. In this sense, the oxidation can be understood as generation of a self-protective layer that enhances BP optoelectronic properties. The original phonon modes around 400 cm−1, governing the e−h recombination process in pristine BP, are scattered by O atoms, generating softer phonons with frequencies below 200 cm−1. As a result, the nonadiabatic coupling (NAC) between the valence band maximum (VBM), the conduction band minimum (CBM) and the defect states decreases, and the e−h recombination rate drops. In addition, the phonon scattering accelerates decoherence between these states, which further suppresses the e−h recombination. Moreover, when the oxidized BP interacts with H2O, the deceleration of the e−h recombination is retained. Our study reveals the positive roles of oxygen and H2O in passivating BP and provides theoretical guidance for its multiple functional applications.

Our calculations employ the quantum-classical decoherence induced surface hopping (DISH) technique implemented within the time-dependent Kohn−Sham theory under the classical path approximation. The geometry optimization, electronic structure calculations, and adiabatic molecular dynamic are performed using the Vienna Ab initio Simulation Package (VASP), the projector augmented wave (PAW) method to describe electron−ion interaction, and the Perdew−Burke−Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) to treat electron exchange−correction interactions. The van der Waals corrected functional with Becke86 optimization (optB86-vdW) is used for treating dispersive interaction to get accurate lattice geometry. The NAMD simulation for e−h recombination is carried out by the PYXAID code. This method has been proven reliable in a variety of materials such as BP, MoS2, graphene/TiO2 interface, and many other systems.

The current method focuses on electron−phonon interactions, treating phonons at the fully atomistic ab initio level, e.g., without the harmonic approximation. The NAMD calculations require thousands of electronic structure calculations along the MD trajectories, and due to computational difficulties, excitonic effects cannot be included. Note that...
excitonic interactions between electrons and holes bring them closer together in space and lower the excited state energy. In general, one expects these factors to favor faster recombination. However, defects already create localized states, and excitonic effects on defect wave functions and energy levels should be less significant than on free charges. Therefore, if charge recombination proceeds faster in defect-free than defected systems without excitonic effects, this conclusion should be even stronger if excitonic effects were included.

We use a $5 \times 4 \times 1$ supercell to model the BP monolayer. A 22 Å vacuum layer in the $z$-direction is used to eliminate spurious interactions between the periodic images. The relaxed lattice constants along the zigzag and armchair directions are $a = 3.31$ Å and $b = 4.56$ Å for the unit cell of the BP monolayer, respectively. We choose the energy cutoff of 450 eV and the first Brillouin zone is sampled at the $\Gamma$ point only, which contains the fundamental band gap. All the structures are fully relaxed until the total energy and atomic forces are smaller than $10^{-5}$ eV and 0.01 eV/Å, respectively. After geometry optimization, the systems are heated to room temperature for 5 ps by velocity rescaling. Then, 6 ps adiabatic MD trajectories are obtained in the microcanonical ensemble with a 1 fs atomic time step. To simulate the charge carrier recombination dynamics over a nanosecond time scale, the 6 ps nonadiabatic

![Figure 2. Total and partial DOSs of (a) pristine BP monolayer, (b) BP-O, (c) BP-2O, (d) BP-O$_{sub}$, (e) BP-O-H$_2$O, and (f) BP-2O-H$_2$O. The black, red, and blue lines represent contributions from P atoms, the O atom, and the water molecule, respectively. The partial DOSs of O and H$_2$O are multiplied by a factor of 30 to make it visible.](image)

![Figure 3. Side and top views of the charge densities of the VBM, CBM, and defect state in (a) pristine BP monolayer, (b) BP-O, (c) BP-2O, (d) BP-O$_{sub}$, (e) BP-O-H$_2$O, and (f) BP-2O-H$_2$O. The isosurface value is set to 0.0004 e/bohr$^3$.](image)
Hamiltonians are iterated 200 times. The simulation results are based on averaging 50 random initial configurations and 2000 surface hopping trajectories for each initial structure.

We investigate six systems including the pristine BP monolayer and five oxidized layers, Figure 1. Because oxidation tends to happen in the outermost layer of a multilayer BP, the current systems can be viewed also as models for oxidized multilayer BP. We consider three different oxidation structures: (i) a single O atom adsorbed on BP (BP-O) forming a dangling O; (ii) two O atoms adsorbed separately on top and bottom P atoms (BP-2O), forming one dangling O and one bridging O; (iii) a P atom substituted by an O atom (BP-Osub). These structures are in agreement with the previous investigations.36,70,71 According to ref 36, the structures shown in Figure 1b,c are the most stable structures of oxidized BP. Oxygen substitution is also observed to exist in experiment.71 These oxidation structures are consistent with two kinds of bonds, O≡P—O and P—O≡P, formed during degradation of the BP structure.70,72 DFT calculations predict the adsorption energies per O atom for the BP-O and BP-2O structures to be 2.85 and 2.86 eV respectively, indicating that their stabilities are very similar. The most stable O substitution structure contains an O atom substituting a P atom and bonded with two other P atoms to form a P—O≡P bond, as shown in Figure 1d. The formation energy of BP-Osub is 1.34 eV. The relatively small value suggests that the O substitution can happen quite easily in the experiments. Two more systems are investigated, involving the BP-O and BP-2O structures interacting with an H2O molecule. These structures (labeled as BP-O-H2O and BP-2O-H2O) are shown in Figure 1e,f. H2O adsorbs on the oxidized BP layer by forming a hydrogen bond (Hb) with the dangling O atoms in BP-O and BP-2O. The H2O adsorption energies are 0.38 and 0.47 eV for BP-O and BP-2O, respectively. The energy is larger for BP-2O since the interaction of H2O with two oxygens is stronger than with one oxygen. The adsorbed O atom and H2O molecule have little influence on the original BP structure, except that the bridge O atom upshifts the bonded P atom by 0.62 Å.

It is important to investigate the BP electronic structure prior to considering the charge—phonon dynamics. Figure 2 shows the densities of states (DOSs) of the six different systems. The calculated band gap of the pristine BP monolayer is 0.85 eV, which is underestimated due to the well-known self-interaction error of DFT. The band gap increases to 0.90 eV upon adsorption of O and H2O. The band gap increases to 1.0 eV in the BP-Osub structure, and a deep isolated defect level appears 0.3 eV above the VBM because of the additional electron introduced by O relative to P. The charge densities of the VBM and CBM of all systems and the defect state in BP-Osub are shown in Figure 3. VBM of the pristine BP monolayer is derived from the bonding orbitals between P atoms in different sublayers and the antibonding orbitals between P atoms in the same sublayer. The adsorption of single or double O eliminates electron density of both VBM and CBM around the adsorption sites because of the O–P bond formation, as shown in Figure 3b,c. For BP-Osub, the substitution of an O atom introduces one excess electron, which localizes on the P atoms around the O atom as shown in Figure 3d. Adsorption of H2O on BP-O and BP-2O does not change the DOSs and orbital distributions of VBM and CBM significantly.

The time-dependent e–h recombination dynamics in the different BP systems are shown in Figure 4. For the pristine BP, the e–h recombination time scale is 285 ps, which is consistent with the previous theoretical report, and the experimental time scales range from 100 ps to 1 ns. After the single and double oxygen adsorption, the e–h recombination is significantly decelerated. As shown in Figure 4b,c, the e–h recombination time scales are increased to 468 and 1080 ps in BP-O and BP-2O, respectively. They are longer than in the pristine BP by factors of 1.6 and 3.8. The charge relaxation dynamics in the BP-Osub system (Figure 4d) start by hole trapping on a 115 ps time scale. After that, the hole recombines with the CBM electron on a 575 ps time scale. The ground
state recovery takes 724 ps, which is about 2.5 times longer than in the pristine BP. The singly occupied trap level of the BP-Osub system can act as an electron trap as well. The electron trapping takes longer than hole trapping, because the trap state is farther in energy from CBM than VBM, Figure 2d. The electron trapping processes is considered in Supporting Information. With H2O adsorption, the e–h recombination time scales for BP-O-H2O and BP-2O-H2O are 540 and 644 ps, respectively, which are still significantly slower than in the pristine BP. In order to establish that the carrier recombination is limited by nonradiative rather than radiative decay, we calculated the radiative lifetimes for the pristine and oxidized BP monolayers, as described in Supporting Information. The radiative decay times are significantly longer than the nonradiative electron–hole recombination times, indicating that nonradiative relaxation is the main process responsible for the carrier decay.

The PBE functional used in the calculations is computationally efficient, however, it is known to underestimate energy gaps. As an additional test, we used the hybrid HSE06 functional74,75 to compute the DOSs and charge densities for the optimized geometries of the six systems. Further, we scaled the PBE energy gaps to the corresponding HSE06 values and repeated the NAMD calculations. The data shown in Supporting Information confirm the original conclusions. The DOSs and charge densities of the key levels are very similar in the PBE and HSE06 calculations, apart from the larger HSE06 energy gaps, Figures S1 and S2. The charge recombination is still slowest in the pristine system, Figure S3.

There are two main factors that affect the e–h recombination time scale in the present calculation. These are the NAC, which governs inelastic charge–phonon scattering, and the pure-dephasing time, which controls loss of coherence between the electronic states. Larger NAC and longer coherence typically lead to faster dynamics. In Table 1 we list the NAC and the pure-dephasing times between the VBM, CBM, and defect states. All the five systems with defects have smaller NAC and shorter pure-dephasing time compared with the pristine BP. The underlying physics can be revealed by the following analysis of the NAC and pure-dephasing time.

First, consider the NAC that can be written as

\[
\mathcal{d}_{jk} = \langle \phi_k | \frac{\partial}{\partial t} | \phi_j \rangle = \frac{\langle \phi | \nabla_k H | \phi_j \rangle}{\epsilon_k - \epsilon_j} \mathcal{R}
\]

(1)

where \( H \) is the Kohn–Sham Hamiltonian, \( \phi_k, \phi_j, \epsilon_k \), and \( \epsilon_j \) are the wave functions and eigenvalues for electronic states \( k \) and \( j \), and \( \mathcal{R} \) is velocity of the nuclei.76 Thus, the NAC depends on the energy difference \( \epsilon_k - \epsilon_j \), the electron–phonon coupling matrix element \( \langle \phi | \nabla_k H | \phi_j \rangle \), and the nuclear velocity \( \mathcal{R} \). The dominant phonon modes contributing to the charge–phonon coupling can be characterized by Fourier transforms (FT) of the evolution of the energies of the VBM, CBM, and defect states in different systems (Figure 5). The intensity of the FT peaks is determined by the amplitude of phonon-induced fluctuations in the corresponding energies and characterizes the electron–phonon coupling strength. Since NAC is also a measure of electron–phonon coupling, the NAC values and FT intensities are related. As shown in Figure 5a for the pristine BP layer, the CBM and VBM couple with the out-of-plane \( \Lambda_1 \) mode and in-plane \( \Lambda_2 \) and \( \Lambda_3 \) modes along the zigzag and armchair directions at around 400 cm\(^{-1}\).77,78 VBM also couples with the interlayer \( \Lambda \) mode around 80 cm\(^{-1}\).79 After oxygen adsorption or substitution, especially for the BP-2O and BP-Osub systems (Figure 5c,d), the three dominant peaks around 400 cm\(^{-1}\) are replaced by many small peaks over a wide range, indicating that the BP modes are scattered strongly by the interaction between the P and O atoms. Significant contributions to the charge–phonon coupling arise from phonon modes below 200 cm\(^{-1}\). The low phonon frequencies lead to small nuclear velocities, and hence, small NAC, eq 1 and Table 1. The interaction with H2O reduces slightly the phonon scattering, especially for BP-2O-H2O, as shown in Figure 5f. As a result, the e–h recombination accelerates from 1080 to 644 ps. But due to the significant contribution of low frequency phonons in the range of 100–200 cm\(^{-1}\), the e–h recombination time scale of BP-2O-H2O is still 2.3 times longer than that in the pristine BP.

In addition to the phonon frequencies, orbital distributions also affect the NAC through the charge–phonon coupling matrix element \( \langle \phi | \nabla_k H | \phi_j \rangle \), eq 1. The oxygen adsorption eliminates charge densities around the adsorption sites (Figure 3b,c and Figure 3e,f). The oxygen substitution induces a localized defect state (Figure 3d). The CBM and VBM orbital redistribution in BP-O/BP-O-H2O and BP-2O/BP-2O-H2O, and the localization of the defect state in BP-Osub reduce overlap between the electron and hole orbitals states and decrease the \( \langle \phi | \nabla_k H | \phi_j \rangle \) term, and hence, the NAC.

Second, the nonradiative charge carrier relaxation dynamics depends on the coherence (pure-dephasing) time between the electronic states. Loss of coherence within the electronic subsystem is induced by elastic electron–phonon scattering. The pure-dephasing time between a pair of states is calculated using the optical response theory from the autocorrelation function of evolution of their energy difference.53 Listed in Table 1, the time of coherence between the VBM and the CBM in the pristine system is 82.4 fs. This value corresponds to the period of the dominant optical phonon modes around 400 cm\(^{-1}\), which couple with both the VBM and the CBM. After O adsorption, the VBM–CBM pure-dephasing time is decreased to 35.2 and 22.9 fs in BP-O and BP-2O, respectively. The pure-dephasing times between the VBM, CBM, and defect states in BP-Osub are also shorter than the VBM–CBM time in the pristine system. They are 55.4, 18.3, and 22.1 fs, Table 1. After oxygen adsorption or substitution, the dominant phonon peaks around 400 cm\(^{-1}\) are changed into multiple peaks over a wide frequency range due to scattering of the original BP phonons by the oxygen atoms. Such scattering enhances decoherence between the electronic states. The VBM–CBM pure-dephasing time in BP-O-H2O is similar to that in BP-O. For BP-2O-H2O, the interaction with H2O decreases the
phonon scattering slightly and the pure-dephasing time is increased to 66.2 fs. The accelerated loss of coherence within the electronic subsystem due to scattering of the BP phonons by the O atoms provides another mechanism of suppression of the e−h recombination dynamics in BP interacting with oxygen and H2O.

To summarize, we have investigated how BP oxidation and interaction with water influence the nonradiative charge carrier recombination. We have found that both the oxidation and the interaction with water suppress the e−h recombination, in contrast to the a priori expectation that defects and fast polar molecules should trap charges, enhance charge–phonon coupling, and accelerate charge losses. Adsorption of the double oxygen in particular can decelerate the e−h recombination by a factor of 4. The e−h recombination is slowed down mainly because of scattering of the higher frequency phonons of the pristine BP induced by oxygen adsorption or substitution. On the other hand, the phonon scattering by the oxygen atoms accelerates decoherence between the electronic states. Both the decreased NAC and the accelerated decoherence suppress the e−h recombination. The effect is maintained when the oxidized species interact with H2O.

The arguments presented in the current work apply to monoelemental 2D materials that contain no ionic or polar bonds and are flexible. The arguments can be extended to similar materials, such as graphene, graphene quantum dots and ribbons, graphyne, borophene, germanene, silicone, stanene, bithmuthene, etc. Previous calculations demonstrate that in stiff materials, such as carbon nanotubes, large amounts of water can accelerate charge recombination by decreasing the energy gap. Exposure to large amounts of water accelerate charge recombination in halide perovskites by coupling the charges to high frequency water motions, while small amounts of water slow down the recombination by facilitating charge separation. In the absence of ionic character, monoelemental materials interact with impurities weakly, experiencing little perturbation to its geometric and electronic structure. Elements such as phosphorus can support a variety of oxidation states and accommodate extraneous atoms, avoiding deep trap states. 2D materials are soft and flexible and can incorporate foreign species, avoiding significant disruption to their periodic structure. The enhancement of the charge carrier lifetimes in the presence of oxygen and water can be interpreted as arising from a self-protection oxide layer created during material fabrication. The reported results provide valuable insights into the roles of oxygen and water in BP passivation and generate important theoretical guidance for future energy and electronics applications of BP and other 2D materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcl.lett.9b00042.

Figure 5. FT of the phonon-induced fluctuations of the VBM, CBM, and defect state energies in (a) the pristine BP monolayer, (b) BP-O, (c) BP-2O, (d) BP-Osub, (e) BP-O-H2O, and (f) BP-2O-H2O.
Densities of states, charge densities, and recombination dynamics obtained with the help of the HSE06 functional, analysis of the electron trapping pathway in the BP-O\textsubscript{sub} system, and radiative decay times (PDF)

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**Notes**

The authors declare no competing financial interest.

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