Large Bulk Piezophotovoltaic Effect of Monolayer Transition Metal Dichalcogenides

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Abstract

The bulk photovoltaic effect in noncentrosymmetric materials is an intriguing physical phenomenon that holds potential for high-efficiency energy harvesting. Here, we study the shift current bulk photovoltaic effect in the transition metal dichalcogenide MoS$_2$. We present a simple automated method to guide materials design and use it to uncover a distortion to monolayer 2H-MoS$_2$ that dramatically enhances the integrated shift current. Using this distortion, we show that overlap in the Brillouin zone of the distributions of the shift vector (a quantity measuring the net displacement in real space of coherent wave packets during excitation) and the transition intensity is crucial for increasing the shift current. The distortion pattern is related to the material polarization and can be realized through an applied electric field via the converse piezoelectric effect. This finding suggests an additional method to engineer the shift current response of materials to augment previously reported methods using mechanical strain.

Keywords BPVE, shift current, piezoelectric, first principles, monolayer, dichalcogenide

In conventional photovoltaic devices, current is generated when the electric field created in a p-n junction separates electrons and holes. Before being collected at the electrodes, these carriers relax to the band edges through scattering events as they diffuse through the material. Energy loss during this relaxation sets fundamental limits on the efficiency of junction-based photovoltaics. In contrast with junction-based photovoltaics, materials that lack inversion symmetry can generate photocurrent in the bulk. This bulk photovoltaic effect (BPVE) was first observed in ferroelectric and piezoelectric materials, and because this process can generate above-band-gap photovoltages, devices using the BPVE are not bound by the same thermodynamic limits as junction-based devices. Leveraging the BPVE is therefore a promising avenue for controlling photocurrents and increasing the efficiency of photovoltaic devices.

Analytical treatments split the linear BPVE into two components: the ballistic current, which is a transport property resulting from an asymmetric distribution of nonthermalized carrier momenta, and the shift current, which is a quantum mechanical effect arising from off-diagonal elements of the density matrix. Recent experimental and theoretical studies have indicated that shift current is a significant component of the BPVE, so designing materials with enhanced shift current response will help improve the efficiency of photovoltaics.

Several approaches have been studied experimentally to tune the shift current response of a material. The geometry of the sample and electrodes—for example using thin films or single-tip electrodes—has been shown to play a large role in the magnitude of the BPVE.
Temperature, strain, and strain gradients can also significantly modulate the shift current of a material. Engineering the photovoltaic response through applied strain (termed the piezophotovoltaic effect) can significantly improve device performance. In one study, the photocurrent response of an iron-doped LiNbO$_3$ crystal was increased by 75% under uniaxial compressive strain. In another, the multiferroic material BiFeO$_3$ was grown on a piezoelectric material. An applied $E$-field was used to strain the BiFeO$_3$ film; this resulted in an increase in both the open-circuit voltage and the short-circuit current, enabling an increase of 218% in the power conversion efficiency. Controlling photovoltaic response through applied strain gradients (analogously named the flexophotovoltaic effect) may produce a less dramatic response, but because the nonuniform strain breaks inversion symmetry, strain gradients can be used to coerce the BPVE from otherwise inactive materials. Though the shift current has a well understood functional form, this understanding does not reveal theoretically how to increase the performance of a material. Recent analytical work has drawn a connection between the total shift current response summed over frequencies and the sum of polarization differences between filled and unfilled bands. Numerical and analytical study of monolayer transition-metal monochalcogenides also found that the integrated shift current is linearly related to the total polarization at small displacements, but that it stops increasing farther from the nonpolar structure. This relationship becomes more complicated in other materials that have both positive and negative current responses at different frequencies, such as PbTiO$_3$, and it also is not a sufficient criterion for material selection; although PbTiO$_3$ has a much higher spontaneous polarization than BaTiO$_3$, the two materials have similar shift current responses. Theoretical upper bounds have also shown that shift current can be increased in materials with a reduced band gap and more delocalized wave functions. A survey of many materials revealed that none approached this theoretical bound, indicating that there is much potential for materials with improved performance and opportunity for materials design.

Following a different approach, Wang et al. studied the photocurrent enhancement in Ni-doped PbTiO$_3$ resolved in the Brillouin zone. They showed that the shift current is mostly generated around a few high-symmetry points in $k$-space, and that cancellation of the shift vector (a quantity related to the distance a carrier travels during excitation) between these points suppresses the total current when the dopants are uniformly distributed. This cancellation could be removed by constructing a layered heterostructure, and similar effects could be achieved using artificial atom displacements to change the wave function character at these special points.

Layered two-dimensional materials, and transition-metal dichalcogenides in particular, hold great promise in optoelectronic applications. The transition-metal dichalcogenide MoS$_2$ is a prototypical example of this class of materials that exists in several phases, each of which exhibits different optical and electronic properties. The metastable 1$T$ phase of MoS$_2$ initially preserves inversion symmetry, but by changing the strain or temperature, this symmetry can be spontaneously broken to induce various ferroelectric phases, which makes MoS$_2$ a candidate for nonlinear optical processes. The shift current has been predicted for the distorted 1$T'''$ phase of MoS$_2$, where it was found to be tunable using biaxial strain. The 2$H$ phase of monolayer MoS$_2$ shown in Figure 1a is noncentrosymmetric yet nonpolar, and so it also can exhibit nonlinear optical phenomena, even though the polarization vanishes in this structure. Other important properties of monolayer 2$H$-MoS$_2$ include a direct band gap, bright photoluminescence, and electroluminescence. The electronic properties are also highly tunable: strong coupling with strain is demonstrated by an anisotropic piezoelectric response and a strain-controlled band gap. Strain has also been used to control the photoresponse of MoS$_2$-containing heterostructures. In addition, optical properties like the refractive index and phonon modes can be controlled with an applied electric field. These intriguing properties make 2$H$-MoS$_2$ a good candidate for
materials design.

In this Letter, we outline an optimization method which can uncover atomic displacements that significantly enhance the single-frequency and integrated shift current responses. Through analysis of the momentum-resolved shift current, we show that overlap of the transition intensity and the shift vector in the Brillouin zone is crucial for large shift current. Finally, we connect a displacement identified through optimization with changes in the material polarization and note that the required distortion is realizable experimentally via the converse piezoelectric effect; thus, we name this phenomenon as “the bulk piezophotovoltaic effect”.

The shift current is a second-order optical effect and arises through a net displacement of excited electrons as the excited states evolve in an asymmetric crystal potential. There have been a variety of analytical descriptions of the shift current, including several that are amenable to numerical evaluation. The frequency-dependent response tensor $\sigma$ may be split into two physically meaningful quantities:

$$J_q = \sigma_{qrs}^{rs} E_i E_s$$

$$\sigma_q^{rs}(\omega) = e \sum_{m,n} \int dk I^{rs}(m, n, k; \omega) R_q(m, n, k)$$

The quantity $I$ is the intensity of a transition and $R$ is the shift vector, which has units of length and describes the instantaneous travelling distance by carriers during excitation. These quantities are defined in (2) and (3), where $A$ is the Berry connection, $\phi$ gives the phase of the transition dipole, and $\omega_{nm}$ and $f_{mn}$ denote differences in band energies and fillings:

$$I^{rs}(m, n, k; \omega) = \pi \left( \frac{e}{m \hbar \omega} \right) ^2 f_{nm}(k) P^r_{nm} P^s_{nm} \times \delta[\omega_{nm}(k) \pm \omega],$$

$$R_q(m, n, k) = \partial_{k_q} \phi_{nm}(k) - [A_{nq}(k) - A_{mq}(k)].$$

In this form, the shift current can be readily calculated from Bloch wave functions generated by standard density functional theory (DFT) calculation. Calculation details are given in the Supporting Information.

We induce atomic displacements to probe how structural change influences the magnitude of shift current responses of monolayer $2H$-MoS$_2$. In one unit cell, there are nine degrees of freedom for ionic displacement. Previous study has revealed that the shift current is correlated with the wave function delocalization and the covalent bonding between neighboring atoms. To capture this effect, we use a local Cartesian coordinate system aligned along the Mo–S bond for atomic displacements. In this system, shown in Figure 1(b) for Mo displacement, the first orthogonal axis is aligned along the Mo–S bond, while the other two are perpendicular to the bond with one axis contained in the $xy$-plane and the other with an out-of-plane component.

We use a gradient descent optimization scheme to reach the structure with the maximum shift current (SC) response. We focus on tensor elements with light polarized in the plane of the material, and focus specifically on the largest component, which is the $\sigma_{xxy}$ element. To optimize the structure, the shift current response is first calculated with small atomic displacements from a reference structure along the local Cartesian coordinates. Because SC is dependent on the electronic wave functions, which change continuously with ionic configuration, the SC response also varies smoothly with atomic displacement (for example see Figure 2c). This property allows the real space derivative of the frequency-dependent response tensor to be calculated using the finite-difference method in order to construct a linear approximation of the SC response as a function of atomic position. Using this approximation, the displacement of atoms with the steepest increase in the SC performance is identified. The SC performance is quantified using two different figures of merit: the maximum value of the response function over a specific frequency range and the integrated response over a frequency range. For photovoltaic applications, as the solar spectrum is continuous, the integrated response $\int \sigma_q^{rs}(\omega)d\omega$ is more
relevant than a single-frequency response. The structure is optimized starting from the equilibrium structure by calculating the shift current gradient about a reference structure and then choosing a new reference based on this gradient. This procedure is applied iteratively to find high performing structures.

We present the optimal displacement pattern of $2H$-MoS$_2$ in Figure 2b. The distortion is very simple; displacement is primarily confined to the $y$ direction, and when the Mo atoms move forward towards one side of the triangle or backward towards a column of sulfur atoms on the vertex of the triangle, the maximal SC response can be realized. The photovoltaic tensor element $\sigma_{xxY}$ for the structure with Mo displacements of 0.2 Å in the $\pm y$ direction are shown in Figure 2a. Compared to the reference structure, the maximum SC peak at 2.8 eV is increased five-fold and can reach 40 µA/V$^2$. The integrated SC response in the frequency range of 0–4 eV is increased even more (more than ten-fold), because unlike in the equilibrium geometry, where the SC response has both positive and negative parts that will be largely cancelled after integration, responses in the optimal structure are mostly all the same sign, resulting in a larger integrated value. In contrast, biaxial strain of 5% triples the integrated response. Comparing the responses shown in Figure 2a, we note that the SC responses in the optimal structure are controllable. By reversing the displacement direction, the SC can also be reversed, with a similar peak magnitude.

To understand the large enhancement of SC response due to this simple displacement, we refer to Eq. 1, which shows that the shift current is an integrated result over every $k$-point in the Brillouin zone (BZ). At each $k$-point, the contribution is a summation over band pairs of the product of the transition intensity and the shift vector (SV) of the corresponding band pair. For a 2D material, the contribution from the full BZ can be visualized. Following this idea, we plot the $k$-resolved transition intensity, shift vector, and SC separately, for transitions close to the $\omega = 2.8$ eV peak (Figure 3a). After displacing the Mo atom, the range of the transition intensity increases only slightly, but its distribution in the BZ is altered considerably (Figure S1). In addition, more $k$-points with large shift vectors emerge after Mo displacement (Figure S2). With both increased intensity and shift vector, the range of SC variation is also increased. Inspecting Figure 3a, the SC shares a similar distribution pattern with the shift vector. Peaks of $k$-resolved SC coincide with peaks in the $k$-resolved shift vector, but only in regions with appreciable transition intensity. This underscores a design principle of shift current that the enhancement requires a large overlap between the shift vector and transition intensity in the BZ. We also note that at these places, the shift vectors all have the same sign, so their co-
Figure 2: (a) $\sigma_{xxY}$ component of the MoS$_2$ shift current tensor with Mo displaced at $dy = 0.2$ Å and $dy = -0.2$ Å; (b) optimal displacement pattern; (c) smooth change in shift current response ($z$-axis) with continuous Mo displacement in the $y$ direction.

distributions are not cancelled. As a contrast, the $k$-resolved signatures at $\omega = 3.75$ eV are shown in Figure 3b. Despite the large negative peaks in the shift vector, there are no corresponding peaks in the shift current because those peaks are not in regions of high transition intensity. Cancellation between positive and negative shift vectors at different locations in the BZ further reduces the net current after BZ integration. These two effects reduces the SC performance at this light frequency.

The sum of the transition intensity over occupied states is proportional to the imaginary part of the dielectric function $\epsilon_{bb}(\omega)$, and the BZ integral of the shift vector is related to the interband polarization difference $P_n - P_m$ with an additional gauge-dependent quantity related to $\phi_{mn}(k)$. Previous studies show that while geometric phase quantities like the shift current are only reproduced accurately with a full wave function description, the frequency-dependent dielectric function and the joint density of states are well approximated by a simple $k \cdot p$ model; therefore in Ref. 21, the dipole matrix elements were approximated as a constant in the BZ. This enabled the integrated SC response to be approximately written in the simplified form $\sum_{mn} \epsilon_{bb}(P_n - P_m)$, which is much simpler than equation 1. It directly relates the integrated SC response as a simple product of the frequency-dependent dielectric constant and the polarization difference of band pairs. However, as shown in Figure 3, the approximation of a constant dipole matrix is not always well founded. Instead, the analysis in Figure 3 shows that the transition intensity can be highly nonuniform over the BZ.

Although the dependence of the shift vector and the transition intensity on $k$ are crucial for fully explaining the shift current response, we can gain qualitative insight by examining these quantities averaged over the BZ at a single frequency. The aggregated shift vector $\bar{R}$, defined in Eq. 4, is related to the polarization difference between conduction and valence bands, and the aggregated transition intensity is proportional to the imaginary dielectric function.

$$\bar{R}_q(\omega) = \sum_{m,n} \int d\vec{k} R_q(m, n, \vec{k}) \delta(\omega_{mn} \pm \omega)$$

These averaged quantities are plotted in Figure 4 for both the reference structure and a distorted structure with Mo displaced by $dy = -0.2$ Å. The averaged transition intensity does not increase significantly in magnitude under distortion, while the averaged SV varies over a much wider range—at particular frequencies such as $\omega = 2.8$ eV and 3.75 eV, the averaged SV increases nearly 100-fold under atomic displacement. However, the increase in averaged shift vector does not guarantee the same increase in
Figure 3: $k$-resolved shift current, shift vector and intensity for transitions close in energy to (a) $\omega = 2.8$ eV and (b) $\omega = 3.75$ eV. The shading indicates the $k$-resolved shift current, the dashed contours show the $k$-resolved intensity, and the solid contours show the $k$-resolved shift vector.

Figure 4: MoS$_2$ (a) photovoltaic tensor, (b) Brillouin-zone-averaged transition intensity, and (c) Brillouin-zone-averaged shift vector for both equilibrium and distorted structures.

SC because the product of the averaged quantities is not equal to the SC response. For example, the response at $\omega = 3.75$ eV is much weaker than that at $\omega = 2.8$ eV, although the averaged shift vector is larger for the former. This is consistent with the results shown in Figure 3, where we showed that the misalignment between the shift vector and the transition intensity suppresses SC response associated with transitions that have large shift vectors. As a generalization of the SC design rule, we propose that the zone-averaged shift vector and intensity are good indicators of strong SC response. Since the shift vector can change more drastically, it is a more decisive factor. However, the overlap of transitions with large shift vector and high transition intensity at the same momentum is most important for determining the overall SC response, and this can be altered significantly with changed wave functions and different structures.

2H-MoS$_2$ does not exhibit spontaneous polarization, but the optimal displacement identified above involves moving the different atomic species in opposite directions, causing polarization along the direction of displacement (Figure 5). As is observed in transition-metal monochalcogenides, the integrated shift current response is linearly related to polarization at small displacements, while at larger displacements, the relationship is sublinear and has maxima at both positive and negative displacements.
Figure 5: Change in $y$-axis polarization and integrated shift current during Mo displacement.

Due to the relationship between polarization and the optimal displacement, the desired distortion can be realized with an externally applied electric field. This is analogous to the thermo-photovoltaic effect, which works when the instantaneous atomic displacements from phonons are altered with temperature variation, except the applied electric field drives only a single distortion. We approximate the influence of an electric field on the structure using the Born effective charges of the distorted structure and find the field required to produce such a distortion by equating the \textit{ab initio} force on the structure and the force due to the electric field. Solving the force balance equation $F = Z \cdot E$ in the plane of the monolayer indicates that an in-plane electric field of $6.9 \times 10^{10} \text{ V/m}$ could be used to realize the displacement outlined above. This finding suggests that external electric field is an additional avenue for engineering the shift current response of materials, in complement to mechanical methods explored in previous work.

In conclusion, using a gradient descent materials design strategy, we show that the shift current response of monolayer $2H$-MoS$_2$ can be greatly enhanced with an atomic displacement aligned on the $y$-direction. This displacement increases the integrated $\sigma_{22y}$ response more than ten-fold and can be realized experimentally by applying an external electric field. This result not only poses applied electric field as a new method to engineer the BPVE response of materials, but it also shows the potential benefits of materials design—perhaps with the right perturbations, such large enhancements can be coerced from many materials.

Supporting Information Available

The following files are available free of charge. Details of computational methods, momentum-resolved shift vector and transition intensity maps.

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Large Bulk Piezophotovoltaic Effect of Monolayer Transition Metal Dichalcogenides: Supporting Information

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Calculation details

The Quantum Espresso package was used to perform density functional theory (DFT) calculations of the electronic structure using a generalized gradient approximation functional.\textsuperscript{1–3} Calculations used norm-conserving pseudopotentials designed using the OPUIM package.\textsuperscript{4,5} Self-consistent calculations of the electron density were performed on an $12 \times 12 \times 1$ Monkhorst-Pack grid.\textsuperscript{6} Wavefunctions were calculated non-self-consistently on a denser $96 \times 96 \times 1$ grid. A vacuum gap of 12 Å between layers was included to reduce spurious inter-layer interactions. The shift current and related quantities were calculated according to the method described by Young and Rappe.\textsuperscript{7} Born effective charge tensors were calculated using density functional perturbation theory (DFPT), and polarization was calculated using the Berry phase method.\textsuperscript{8} The convergence threshold was $10^{-11}$ Ry/cell for DFT calculations and $10^{-18}$ Ry/cell for DFPT calculations.
Momentum-resolved shift vector and transition intensity

Figure S1: Momentum-resolved transition intensity of the equilibrium and distorted structures of MoS$_2$ for transitions near $\omega = 2.8$ eV and 3.75 eV.

Figure S1: Momentum-resolved transition intensity of the equilibrium and distorted structures of MoS$_2$ for transitions near $\omega = 2.8$ eV and 3.75 eV.
Figure S2: Momentum-resolved shift vector of the equilibrium and distorted structures of MoS$_2$ for transitions near $\omega = 2.8$ eV and 3.75 eV.
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