Colossal switchable photocurrents in topological Janus transition metal dichalcogenides

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INTRODUCTION

With the development of strong light sources, nonlinear optical (NLO) materials have the potential to engender new physical effects. Recently, the generation of nonlinear direct photocurrent upon light illumination has evoked great interest. This is known as bulk photovoltaic effect (BPVE)\(^1\). The photocurrent under linearly polarized light, or the shift current (SC), has been theoretically predicted and experimentally observed in materials such as multiferroic perovskites\(^2\) and monolayer monochalcogenides\(^8\)\(^-\)\(^10\). The BPVE is a promising alternative source of photocurrent for energy harvesting and sensing. Compared with the conventional solar cells based on p-n junctions, BPVE is not constrained by the Shockley–Queisser limit\(^1\) and can produce open-circuit voltage above the bandgap\(^8\). Besides SC, the circular photogalvanic effect\(^12\)\(^-\)\(^16\) that generates circular current (CC) (aka injection current) under circularly polarized light is another nonlinear photocurrent effect. In time-reversal invariant systems, SC is the response under linearly polarized light, while CC is the response under circularly polarized light. The direction of CC can be effectively controlled by the handedness of the circularly polarized light.

The nonlinear photocurrent effects can be utilized for photodetection, especially in the mid-infrared (MIR) to terahertz (THz) regions, where efficient photodetectors are highly desirable. Compared with traditional infrared detectors such as MCT (Hg\(_x\)Cd\(_{1-x}\)Te) detector, photodetectors based on nonlinear photocurrent do not require biasing, hence the dark current can be minimized, which is advantageous especially at elevated temperatures. Particularly, topological materials are promising candidates for NLO photodetection. For example, Weyl semimetals (WSMs) have singular Berry curvature around the Weyl nodes, leading to strong linear and nonlinear optical responses\(^17\)\(^-\)\(^22\). Recently, the unoptimized third-order photo-responsivity of WSM TaitTe\(_x\) is reported to be 130.2 mA W\(^{-1}\) under 4 \(\mu\)m wavelength illumination at room temperature\(^23\), comparable with that of the state-of-the-art MCT detectors (600 mA W\(^{-1}\)) operating at low temperature\(^23\)\(^,\)\(^24\). Meanwhile, many other WSMs are predicted to have even larger second-order photo-responsivity\(^22\). Compared with WSMs in three dimensions (3D), which have vanishing bandgap and may lead to overheating problem under strong light, two-dimensional (2D) topological insulators (TIs) with finite bandgap on the order of 0.01–0.1 eV (within the MIR/THz range) may be a better choice, thanks to their good optical accessibility and easy band dispersion manipulation. (As a matter of nomenclature, despite small bandgap values \(\sim k_B T_{\text{room}}\), we still call these materials “insulators” due to the literature convention of TIs.) Due to the band inversion, TIs also have augmented Berry connections near the bandgap, which could enhance their optical responses\(^25\)\(^,\)\(^26\). In this article, we first use a low-energy \(k\cdot p\) model to illustrate the guiding principles for designing materials with high nonlinear photoresponse, namely, band inversion, strong spatial inversion asymmetry, and small electronic bandgap. Then, with ab initio calculations, we predict that Janus transition metal dichalcogenides (JTMDs) in the 1T\(^\prime\) phase possess giant nonlinear photoconductivity in the THz range. Being TIs\(^27\), 1T\(^\prime\) JTMDs enjoy enhanced optical responses due to the band inversion, and the maximum SC conductivity is found to be around 2300 nm \(\mu\)A V\(^{-2}\) in the THz range. Such colossal SC conductivity is also about tenfolds larger than that of many WSMs\(^22\) and other non-centrosymmetric 2D materials, such as 2H TMDS\(^29\) and monochalcogenides\(^8\)\(^-\)\(^10\). The CC conductivity of 1T\(^\prime\) JTMDs is also extremely large. The peak value of the CC conductivity is around 8.5 \(\times 10^6\) nm \(\mu\)A V\(^{-2}\), assuming a carrier lifetime of 0.2 ps. Owing to the small bandgap (\(\sim 10\) meV), the SC conductivity peaks lie within the THz region and quickly decay with increasing light frequency. The inert responsivity to light with higher frequencies renders 1T\(^\prime\)
JTMDs selective photodetectors in the THz range. Furthermore, we find that the band topology and Rashba splitting of valence and conduction bands (VB and CB, respectively) of 1T’ JTMDs can be effectively switched/tuned by small external stimuli such as in-plane strain or out-of-plane electric field. We show that such topological phase transition could lead to a sign change of the SC conductivity (and the SC direction) while maintaining its large magnitude. Such a colossal and switchable photocurrent may find applications in 2D optomechanics, nonlinear optoelectronics, etc. In addition, by tuning the Fermi level, the photocconductivity can be further enhanced. Besides nonlinear photocconductivity, other NLO effects, such as second-order harmonic generation, are enhanced in JTMDs as well.

RESULTS
A minimal k-p model: guiding principles

In order better illustrate the guiding principles for designing materials with strong nonlinear photoresponses, we first adopt a generic and minimal two-band model that can describe the band-inversion process: $H_\text{gg}(k) = d(k) \cdot \sigma$, where $\sigma = \sigma_x \sigma_y \sigma_z$ are Pauli matrices, and $d(k) = [A_k, A_k, M - B(k_x^2 + k_y^2)]$, where $A, B$ and $M$ as model parameters. Without loss of generality, we assume $A, B > 0$ here. When $M > 0$, the mass term $M - B(k_x^2 + k_y^2)$ is positive when $k_x^2 + k_y^2$ is small and becomes negative when $k_x^2 + k_y^2$ is large. Hence, there can be a band inversion. On the other hand, when $M < 0$, the mass term $M - B(k_x^2 + k_y^2)$ is always negative, and there is no band inversion. In order to obtain finite NLO current responses, the inversion symmetry needs to be broken. Hence, we add an inversion symmetry breaking term $H_\text{gb} = \mu \sigma_x$ in the model Hamiltonian, where $\mu$ is a tunable parameter that controls the strength of the inversion asymmetry and can be likened to, e.g., a static electric field. Finally, $p_x = A \sigma_x$ and $p_y = A \sigma_y$ are the momentum operators.

In ref. 26, it was demonstrated that band inversion ($M > 0$) would boost the linear optical response, because band inversion enhances the interband transition matrix $\langle c | r \rangle \langle v \rangle$ (Fig. 1 therein), where $|c\rangle$ and $|v\rangle$ are the wavefunctions of the CB and VB, respectively, and $r$ is the position operator. This is due to the orbital character mixture when band inversion occurs (e.g., both $p$ and $d$ orbital components are mixed in the VB and CB of 1T’ TMD monolayers due to band inversion). Note that $|\langle c | r \rangle \langle v \rangle\rangle$ determines the response strength of the SC and CC, thus it should be expected that the band inversion would boost the nonlinear photocurrent responses as well.

Then we can calculate the SC response function $\sigma_{\text{g}g}^\text{xx}$ (we will elaborate on the formula for calculating the SC conductivity later, as in Eq. (2)) for the model Hamiltonian above. We first set $A = 2$, $B = 1$, $\mu = 0.1$, and vary $M$. The results are shown in Fig. 1a. One can see that when $M$ is positive (with band inversion, blue curve, $|\sigma_{\text{g}g}^\text{xx}|$ is ~3 times larger than that when $M$ is negative (no band inversion, red curves)) with the same absolute value $|M|$. This clearly shows that band inversion can boost the nonlinear photocurrent responses for low frequencies near the bandgap. Besides, one can see that, for positive and negative $M$, $\sigma_{\text{g}g}^\text{xx}$ has different signs, indicating that the photocurrents flows in opposite directions. Another remarkable feature is that, when $|M|$ becomes smaller, the magnitude of the photocconductivity would increase, and there is a rough scaling relation $|\sigma_{\text{g}g}^\text{xx}| \sim 1/|M|$. Note that, in the current model, $|M|$ measures the bandgap ($E_g \sim 2 |M|$). Hence, we suggest that small bandgaps would also boost the nonlinear photocconductivity. We would like to note again that it is the band inversion, rather than the topological nature, that enhances the nonlinear photocurrent. Materials with band inversion can be topologically trivial. Furthermore, the magnitude of the photocurrent response is also dependent on the strength of inversion asymmetry. To elucidate this effect, we fix $A = 2$, $B = 1$, $M = 1$ and vary $\mu$. The results are shown in Fig. 1b. One can see that $\sigma_{\text{g}g}^\text{xx}$ scales approximately linearly with $\mu$.

The model above suggests that materials with (1) band inversion, (2) strong spatial inversion asymmetry, and (3) small electronic bandgaps may well have large nonlinear photocconductivity. Guided by these principles, we predict that monolayers of JTMDs (denoted as MXY, $M = Mo,W$ and $XY = S,Se,Te$) in their 1T’ phase possess colossal nonlinear photocurrent conductivity, as we will show in the following. In addition, we would like to remark that the guiding principles stated above are generic regarding all linear and nonlinear optical effects that depend on electron interband transitions, such as second-harmonic generation, etc.

Monolayer JTMDs: atomic and electronic structures

The monolayer JTMDs are composed of three atomic layers: the middle layer of transition metals is sandwiched by two side layers with different chalcogen atoms (Fig. 2). Inherited from pristine TMDs (PTMDs), JTMDs also have different crystalline phase structures. Among them, the 2H and 1T’ are two (meta-)stable structures. The 2H phase JTMDs (space group P31m, Fig. 2a) have a quasi-Bernal (ABA’) stacking pattern with three-fold

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Fig. 1 Shift current conductivity of a minimal k-p model. The shift current conductivity $\sigma_{\text{g}g}^\text{xx}$ for the model Hamiltonian $H(k) = d(k) \cdot \sigma + \mu \sigma_x$, where $d(k) = [A_k, A_k, M - B(k_x^2 + k_y^2)]$ and $\sigma = [\sigma_x, \sigma_y, \sigma_z]$ are Pauli matrices. $M$ is varied. For positive and negative $M$ with the same absolute value, $|\sigma_{\text{g}g}^\text{xx}|$ is larger when $M$ is positive due to band inversion. $A = 2$, $B = 1$, $\mu = 0.1$ is used. Blue and red solid curves are $\sigma_{\text{g}g}^\text{xx}$ for $M > 0$ and $M < 0$, respectively. For better visibility, the red dashed curve is flipped (red dashed curve, with an extra minus sign) to be compared with the blue curve. $\mu$ is varied. $\sigma_{\text{g}g}^\text{xx}$ scales approximately linearly with $\mu$, which determines the strength of inversion symmetry breaking. $A = 2$, $B = 1$, $M = 1$ is used.
orbitals are inverted around the Pm, Fig. 2b) has an ABC stacking pattern, and the in-plane energy in 2H phase than in 1T x rotational symmetry is broken by a Peierls distortion along the a-axis. With fully relaxed lattice constants, all six MXY have lower energy in 2H phase32, with a small energy difference (<0.1 eV per formula unit), thus 1T-jmtds. On the contrary, 1T and giant second-order NLO effects can be unleashed. Published in partnership with the Shanghai Institute of Ceramics of the Chinese Academy of Sciences

2H and 1T' phases of JTMDs. a, b Atomic structure of 2H and 1T' phase of JTMD. The black box in b shows the unit cell of 1T' phase. The top and bottom chalcogens are shifted a bit for better visibility. c The 2H-1T' phase diagram of WSeTe. α and β0 are the fully relaxed lattice constants of the 1T' phase. The color map indicates the energy difference between 1T' and 2H phases. 1T' and 2H phases are energetically favored in red and blue regions, respectively.

in-plane rotational symmetry and have been successfully fabricated recently29–31. On the other hand, the 1T' phase (space group Pm, Fig. 2b) has an ABC stacking pattern, and the in-plane rotational symmetry is broken by a Peierls distortion along the a-axis. With fully relaxed lattice constants, all six MXY have lower energy in 2H phase than in 1T' phase32, with a small energy difference (<0.1 eV per formula unit). Similar to the PTMDs, the relative stability of these two phases can be effectively tuned by strain (see Supplementary Fig. 4). For example, we plot the phase diagram of WSeTe in Fig. 2c, which clearly suggests a tensile strain of <1% along the a-axis can render the 1T' phase more stable. Also, the energy barriers between 2H and 1T' phases are high (>1 eV per formula unit), thus 1T' JTMDs are fairly stable even in the strain-free state.

The JTMDs inherit many salient properties of PTMDs. As the top–bottom chalcogen layers break the inversion (mirror) symmetry of the 1T' (2H) phase, JTMDs possess extra properties apart from those of PTMDs, such as larger Rashba spin splitting33,34, more efficient charge separation35, etc. The 1T' PTMDs are Z2 TIs36 with small bandgaps on the order of 10 meV, indicating a strong optoelectronic coupling in the THz range, because both inverted band structure and small bandgaps would enhance the interband transitions. However, due to the centro-symmetry, the second-order NLO effects are forbidden for 1T' PTMDs. On the contrary, 1T' JTMDs are inherently non-centrosymmetric owing to the two different chalcogen layers, and giant second-order NLO effects can be unleashed.

Considering MoSSe as an example, we show the electronic properties of 1T' JTMDs. The band structure of MoSSe is shown in Fig. 3a. Like PTMDs37, the metal d-orbitals and chalcogen p-orbitals are inverted around the Γ point, and the inverted bandgap is around 0.8 eV. The fundamental bandgaps are along the Γ-Y line (±Λ point, inset of Fig. 3b) with a magnitude of E0 ≈ 4 eV. We find that the fundamental bandgaps of all six 1T' JTMDs lie in the range of 1–50 meV, corresponding to the THz range (Fig. 3b). Interestingly, despite the band inversion around the Γ point, not all 1T' JTMDs are topologically nontrivial. With fully relaxed atomic structures, MSSe and MSeTe have Z2 = 0 while MTe have Z2 = 1 (M=W,Mo. Z2 = 0 and 1 indicate trivial and nontrivial band topology, respectively). This is because the large Rashba splitting from the inversion symmetry-breaking could change the band topology by remixing the wavefunctions around the ±Λ point. As we will show later, both in-plane strain and out-of-plane electric field can induce a topological phase transition by closing and reopening the fundamental bandgap38–39. Regardless of the band topology (Z2 number), the band inversion around Γ point gives rise to a strong wavefunction mixing between VBs and CBs40, which could significantly boost the linear and nonlinear responses.

SC and CC

In materials without inversion symmetry P, NLO direct currents (dcs) can be generated upon photoillumination. This current can be divided into two parts, the SC fSC and the CC fCC

\[
\mathbf{J}_\text{SC} = 2 \alpha \mathbf{E} \mathbf{E}^\dagger - \mathbf{E} \mathbf{E}^\dagger \mathbf{E} \mathbf{E}^\dagger
\]

\[
\mathbf{J}_\text{CC} = 2 n \mathbf{E} \mathbf{E}^\dagger - \mathbf{E} \mathbf{E}^\dagger \mathbf{E} \mathbf{E}^\dagger
\]

where a, b, c are Cartesian indices and E(ω) is the Fourier component of the optical electric field at angular frequency ω. Equation (1) indicates that, when the optical electric field has both a and b components (a and b can be the same), there will be a dc along the cth direction when fab/nc is non-zero. In materials with time-reversal symmetry T, the response functions within the independent particle approximation in clean, cold semiconductors are

\[
f_{ab}(0; \omega, -\omega) = -\frac{e^2}{2\hbar} \left( \frac{\partial}{\partial \omega} \right) \int \frac{dk}{(2\pi)^d} \int \sum_{m,n} \frac{r_{mn}^a r_{mn}^b}{\omega_{mn} - \omega - i\eta} r_{mn}^c r_{mn}^c
\]

Here all dependencies on k are omitted. τ is the carrier lifetime. m, n are band indices, while \( f_{mn} = f_{rn} - f_{rm} \) and \( \Delta_{mn} = \omega_{mn} - \omega - i\eta \) are the differences in occupation number, energy, and band velocity between bands m and n, respectively. \( r_{mn} = i \langle m | \tilde{V}_x | n \rangle \) is the interband Berry connection, \( \langle f_{mn} f_{rn} \rangle = \langle f_{rn} f_{mn} \rangle \) is the interband Berry curvature, while \( n_{mn} = \frac{f_{mn}}{\omega_{mn} - \omega - i\eta} \) is the generalized gauge covariant derivative of \( f_{mn} \) defined as

\[
\xi_{mn} = \frac{\partial}{\partial \omega} - i (\tilde{V}_x - \tilde{V}_y) f_{mn}
\]

where \( \tilde{V}_\alpha = i \langle m | \tilde{V}_x | n \rangle \) is the interband Berry connection and \( \langle n_{mn} \rangle \) is the periodic part of the wavefunction. Equation (2) is slightly different from those in ref.40 by explicitly including the τ-dependence. Here, for simplicity, we assume the carrier lifetime τ is mode independent and takes a uniform value of τ = 0.2 ps.

When the carrier lifetime satisfies τ ≫ h/\( E_g \), the i/τ term in the denominator of Eq. (2) can be neglected. In this case, \( f_{ab}(0; \omega, -\omega) \) is purely real, while \( n_{ab}(0; \omega, -\omega) \) is purely imaginary. Considering that the dc should be a real quantity, \( E' \) and \( E'' \) should have 0 @ phase difference to yield non-vanishing SC (CC), which indicates that SC and CC are responses under linearly and circularly polarized light, respectively. Another noteworthy feature is that, upon light illumination, \( J_{\text{CC}} \) grows with time at the initial stage, and the saturated static CC should be \( J_{\text{CC}} \propto n_{ab}(0; \omega, -\omega) \), with τ as the carrier lifetime. Therefore \( n_{ab} \) can be regarded as the effective CC photocconductivity.

Another formula describing the nonlinear photocurrents can be obtained from quadratic Kubo response theory41,42 and reads

\[
J' = \frac{e^2}{2\hbar} \left( \frac{\partial}{\partial \omega} \right) \int \frac{dk}{(2\pi)^d} \int \sum_{m,n} \frac{r_{mn}^a r_{mn}^b}{\omega_{mn} - \omega - i\eta} \tilde{V}_x \tilde{V}_y
\]

This formula can be used to compute the nonlinear photocurrents in realistic materials.
Here $\nu_{\text{eff}} \equiv \langle n|\hat{\nu}|l\rangle$ is the velocity matrix element. Equation (2) uses the length gauge, while Eq. (3) uses the velocity gauge. It can be shown (Supplementary Note 2) that, in the presence of time-reversal symmetry $T$, Eq. (3) is generally equivalent to Eqs. (1) and (2), and the real and imaginary parts of Eq. (3) correspond to the SC and CC, respectively. Compared with Eqs. (1) and (2), Eq. (3) is more general. However, numerically Eq. (3) can experience convergence problems at small $\omega$. Therefore, Eqs. (1) and (2) are adopted for computations in this work, which do not involve magnetism. More detailed discussions on the relationship between Eqs. (1) and (2) and Eq. (3) can be found in Supplementary Notes 1 and 2. The consistency between these two methods is well tested. In practice, the Brillouin zone (BZ) integration is carried out by k-mesh sampling with $\sigma_{3D} = \int \frac{dk}{(2\pi)^2} \langle k|\hat{\nu}|l\rangle = \frac{1}{V} \sum_k w_k^c(k)$, where $V$ is the volume of the unit cell, $w_k^c$ is weight factor, and $f(k)$ is the integrand. However, for 2D materials, the definition of volume $V$ is ambiguous, because the thickness of 2D materials is ill-defined. Thus we replace volume $V$ with the area $S$ and define $\sigma_{2D} = \frac{1}{S} \sum_k w_k^c(k)$. Note that all ingredients, $S$, $w_k^c$, and $f(k)$, are well defined and can be directly obtained from numerical computations, hence $\sigma_{2D}$ is unambiguous for 2D materials. As a result, in this work we mainly show $\sigma_{2D}$. The 2D and 3D conductivities satisfy $\sigma_{2D} = \sigma_{\text{eff}} \sigma_{3D}$, where $\sigma_{\text{eff}}$ should be the effective thickness of the material (not the thickness of the computational cell, which includes the thickness of the vacuum layer). $\sigma_{\text{eff}}$ has no standard definition and is usually set as the interlayer distance when the monolayers are van der Waals stacked along z direction. We use an effective thickness of $\sigma_{\text{eff}} = 6 \AA$ for JTMDs when $\sigma_{3D}$ is required for, e.g., the comparison with other materials. Unless explicitly stated, the carrier lifetime is set as $\tau = 0.2$ ps, which should be a conservative value considering that the carrier lifetimes of 2H TMDS are $\sim 1$ ps at room temperature.

Note that 1T' JTMDs have mirror symmetry $\mathcal{M}_x$. The yth components of $j$ and $E$ should be flipped under $\mathcal{M}_x$, while other components do not change. Consequently, $\mathcal{M}_x$ enforces $\sigma_{2D}^y = \sigma_{2D}^r$ to be zero when there is an odd number of $y$ in $\{a, b, c\}$, such as $\sigma_{2D}^x$. The different nonzero SC conductivities of 1T MoTe$_2$ are plotted in Fig. 4a. We observe that both in-plane polarizations $\sigma_{xy}^x$ and $\sigma_{xy}^y$ have striking magnitudes of $\gtrsim 10^{3} \text{nm} \mu\text{A} \text{V}^{-2}$ in the THz range ($\omega < 10 \text{THz} = 41 \text{meV}$). The peak values of $\sigma_{xy}^x$ and $\sigma_{xy}^y$ are around 2300 and 850 $\text{nm} \mu\text{A} \text{V}^{-2}$, respectively, more than tenfold larger than those of other non-centrosymmetric 2D materials, such as hexagonal BN (hBN), 2H MoS$_2$, GeS, and SnSe, which are on the order of $10–100 \text{nm} \mu\text{A} \text{V}^{-2}$ (inset of Fig. 4e). When light with intensity 10 mW cm$^{-2}$ is shining on single layer MoTe$_2$ with 1 cm x 1 cm dimension, the photocurrent generated is on the order of 1 nA. Note that the nonlinear photocurrent can be boosted by (1) focusing the light beam and (2) stacking single-layer detectors to increase the cross-section. For example, when the light with the same total power as above is focused onto a 0.01 cm$^2$ spot size, the electric field is enhanced $10^3 \times$, the photocurrent density would be $10^2 \times$, and the total photocurrent would be 100 nA. Notably, the SC conductivities quickly decay for $\omega \gtrsim 0.1 \text{eV}$, indicating that 1T' MoTe$_2$ is relatively insensitive to light beyond the THz range, which can be advantageous when selective photodetectors in the THz range are desired. In addition, an interesting observation is that the SC conductivities remain almost constant in the THz range, which could make the calibration of the THz detectors easier. Besides, an in-plane electric field can induce a large photocurrent in the out-of-plane direction: $\sigma_{xy}^x$ and $\sigma_{xy}^y$ have peak values of 180 and 25 nm $\mu\text{A} \text{V}^{-2}$, respectively. Such an out-of-plane current can be measured if transparent electrodes like graphene are attached directly above and below the MoSeTe monolayer.

To understand the origin of such giant photoconductivity, the k-specific contribution to the total SC conductivity, $SC(k) \equiv \text{Re} \left\{ \sum_{\kappa, \kappa'} \frac{\Gamma_{\kappa, \kappa'}^{\text{mn}}, \Gamma_{\kappa, \kappa'}^{\text{mn}}}{} \right\}$ at $\omega = 10 \text{meV}$ is shown in Fig. 4c. We can see that, around the fundamental bandgap $\Delta$, $SC(k)$ has a peak amplitude of about $\pm 10^3 \text{A}^2 \text{eV}^{-1}$. Away from $\Delta$, $SC(k)$ rapidly decays. This phenomenon is consistent with the argument that the inverted band structure would lead to enhanced Berry connection magnitudes. We also calculate the SC conductivity for the other five 1T' JTMDs, and their peak values are shown in Fig. 4e. All of six 1T' JTMDs possess colossal photovoltaic effect and the peak values of $\sigma_{xy}^x$ and $\sigma_{xy}^y$ are on the order of $10^3 \text{nm} \mu\text{A} \text{V}^{-2}$. Generally, MSeTe exhibits stronger BPV than MoSe$_2$ and MoSeTe. This is due to the larger out-of-plane asymmetry in the MTe$_2$ system. The electron affinity of S, Se, and Te atoms are 2.08, 2.02, and 1.97 eV, respectively. Consequently, the out-of-plane asymmetry should be more significant in MTe$_2$, leading to stronger BPV. This point is also verified by the out-of-plane electric dipole $P_x$. We find that $P_x$ of MTe$_2$ is around $0.15 \text{eA} \text{ps}^{-1}$ per unit cell, while for MoSe$_2$ and MoSeTe, $P_x$ is only around 0.07–0.08 eA/ps per unit cell.

The CC conductivities are plotted in the lower panels of Fig. 4 (Fig. 4b, d, f). With in-plane polarization, the only non-vanishing element of the CC tensor is $\eta_{\mu\nu}^{xy}$, based on the symmetry analysis above. $\eta_{\mu\nu}^{xy}$ of MoSeTe has a peak value of $8.5 \times 10^3 \text{nm} \mu\text{A} \text{V}^{-2}$ around $\omega = 50 \text{meV}$ (Fig. 4b). Since $\eta_{\mu\nu}^{xy}$ is sensitive dependent on the carrier lifetime, we vary $\tau$ and obtain the peak values of $\eta_{\mu\nu}^{xy}$ (inset of Fig. 4b). Even with $\tau = 0.04 \text{ps}$, $\eta_{\mu\nu}^{xy}$ still has a peak value of around 400 nm $\mu\text{A} \text{V}^{-2}$. The k-specific contribution to the total CC conductivity, $CC(k) \equiv \text{Re} \left\{ \sum_{\kappa, \kappa'} \frac{\Gamma_{\kappa, \kappa'}^{\text{mn}}, \Gamma_{\kappa, \kappa'}^{\text{mn}}}{} \right\}$ at $\omega = 50 \text{meV},
JTMDs are shown in Fig. 4f. Similar as in SC, the CC conductivity is comparable with room temperature (part should be zero. But since 1T transitions. For insulating materials at zero temperatures, the intraband nonlinear photocurrent, there could also be intraband contributions. The arguments above are verified by the \( k \)-specific contribution to \( \sigma_{xx}^{\text{pri}} \) and \( \eta_{\text{app}} \). c shows SC(k) at \( \omega = 10 \) meV while d shows CC(k) at \( \omega = 50 \) meV. The color maps are in logarithmic scale. \( k_{x} \) and \( k_{y} \) are in the unit of reciprocal lattices. e, f The peak values of the SC (e) and CC (f) conductivities of six MXY. Inset of e: The peak values of SC conductivities of several other 2D materials, including hBN, 2H MoS\(_2\), Ge\(_2\)S\(_4\), and SnSe.

is plotted in Fig. 4d. Similar to SC, the major contributions also lie in the vicinity of \( \Lambda \). Finally, the peak values of \( \tau \) for all six 1T JTMDs are shown in Fig. 4f. Similar as in SC, the CC conductivity in MSe, which has stronger spatial inversion asymmetry, is stronger than those in MS\(_2\) and MS\(_{2}\). Here we would like to mention that besides SC and CC, which are interband contributions to the nonlinear photocurrent, there could also be inband contributions. For insulating materials at zero temperatures, the inband part should be zero. But since 1T JTMDs have small bandgaps comparable with room temperature \( (k_{B}T_{\text{room}} \approx 26 \) meV), we have also calculated the inband contribution due to anomalous velocity at finite temperatures. The results are shown in Supplementary Discussion 1, and one can find that the inband contributions can be on the same order as the interband contributions.

**Topological phase transitions**

As discussed above, around the \( \pm \Lambda \) points, the Rashba splitting breaks the degeneracy and could close and reopen the bandgap, leading to topological phase transitions. The magnitude of the Rashba splitting could be engineered with external stimuli, such as in-plane strain, external electric field, etc. For example, with a tensile strain, the vertical distance between two chalcogen layers of 1T JTMD shrinks (inset of Fig. 5a). The bandgap of MoSSe as a function of biaxial in-plane strain \( \epsilon \) is plotted in Fig. 5a, where a band closing occurs around \( \epsilon = 0.3\% \). This band closing/reopening indicates a topological transition. For \( \epsilon < 0.3\% \), 1T MoSSe has trivial band topology with \( Z_{2} = 0 \), while with \( \epsilon > 0.3\% \), 1T MoSSe becomes a \( Z_{2} = 1 \) TI. Such sensitive dependence on in-plane strain provides a convenient pathway to trigger topological phase transitions in 1T JTMD. An even more intriguing phenomenon arises in the SC responses. In Fig. 5b, we show the SC conductivity of 1T MoSSe as the function of \( \epsilon \). All four components of \( \sigma_{ab}^{\text{pri}} \) undergo an abrupt jump upon the topological transition. Particularly, \( \sigma_{xx}^{\text{pri}} \) and \( \sigma_{yy}^{\text{pri}} \) flip their directions. Such an abrupt jump originates in the change in the band characteristics around \( \Lambda \) upon the topological transition\(^{32}\). As discussed above, the major contributions to the total SC conductivity come from \( k \)-points around \( \Lambda \) point (Fig. 3b). When the bandgap is closed and reopened, the wavefunctions of the lowest CB and highest VB around \( \Lambda \) point undergo a substantial remixing. In ideal cases such as the aforementioned two-band model, \( I_{ab}^{\text{pri}} = I_{mn}^{\text{ab}} + I_{mn}^{\text{ab}} \) would flip sign since \( m \) and \( n \) is interchanged and \( \eta_{\text{app}} \) is purely imaginary. When more band contributions are incorporated, \( I_{ab}^{\text{pri}} \) does not always flip its sign but would still experience a drastic change. The arguments above are verified by the \( k \)-specific contribution to \( \sigma_{xx}^{\text{pri}} \) and \( \eta_{\text{app}} \) as shown in Fig. 5c–f, where we can see that SC(k) are significantly different on two sides of the topological transition. In addition to in-plane strain, an out-of-plane electric field, which also modifies the magnitude of the Rashba splitting, can trigger the topological transition and alter the SC conductivities as well (see Supplementary Fig. 6 and 7).

Thus we propose that the abrupt jump of nonlinear photocurrent can be a universal signature of the topological phase transition in non-centrosymmetric materials and can be used as an online diagnostic tool. The mechanical, electrical, and even optomechanical\(^{48,49}\) approaches to switching the NLO responses would pave the way for efficient and ultrafast nonlinear optoelectronics.

**Fermi-level tuning**

It is also interesting how the nonlinear photocurrents vary when the Fermi level is buried in the CB or VB by carrier doping. The SC and CC conductivities of MoSTe as the function of the Fermi level \( E_{F} \) are shown in Fig. 6a. We can see that for \( E_{F} \) within \( \pm 50 \) meV (\( E_{F} \) is set as 0 when the Fermi level is on the top of the VB), the SC and CC conductivities remain extremely large in their magnitudes, while for \( E_{F} \) far away from the fundamental bandgap (heavily carrier doped), both SC and CC conductivities gradually decay to zero. Here the pure intraband nonlinear anomalous Hall current discussed above\(^{50}\) is not considered. A noteworthy feature is that, when \( E_{F} \) is slightly above (below) the bandgap, \( \sigma_{xx}^{\text{pri}} \) would jump to an enormously positive (negative) value, about ten times larger in amplitude than that when \( E_{F} \) is inside the bandgap. This effect can...
be understood by looking at the band structure (Fig. 3a) and the \( k \)-specific contribution \( \Sigma(k) \) (Fig. 4c). As discussed above, the major contribution to the total \( \Sigma \) conductivity comes from \( k \)-points close to the fundamental bandgap \( \Lambda \). When the VB and CB are occupied and empty, respectively, \( \Sigma(\Lambda + \delta k_y) \) and \( \Sigma(\Lambda - \delta k_y) \) (\( \delta \) is a small positive parameter) have opposite values and tend to cancel each other. On the other hand, with a positive \( E_F \), those CB below the Fermi level would be occupied as well, and the CB-VB transition cannot contribute to \( \Sigma(k) \) anymore (Fig. 6b). However, a larger region on the \( \Lambda - \delta k_y \) side would have occupied CB than on the \( \Lambda + \delta k_y \) side. This is because the CB cone is tilted and the band velocity is smaller on the \( \Lambda - \delta k_y \) side, leading to a larger partial density of states in this region. As a result, the positive \( \Sigma(k) \) on the \( \Lambda + \delta k_y \) side would be canceled less by the negative \( \Sigma(k) \) on the \( \Lambda - \delta k_y \) side, leading to a larger total \( \Sigma \) conductivity (Supplementary Fig. 8 and 9). A similar analysis could show that, when \( E_F \) is within the VB, the total \( \Sigma \) would have a significant negative value. These observations indicate that the photocurrent conductivity could be further enhanced by Fermi-level tuning in materials with tilted CB and/or VB, such as type-II WSM. From Fig. 6a, one can see that an \(-1\) meV shift in \( E_F \) can dramatically enhance \( \sigma_{xy} \). In practice, \( E_F \) can be tuned by, e.g., gate voltage. Assuming a gate coupling efficiency of 0.1, then an \(-10\) mV gate voltage would be able to achieve the enhancement.

**DISCUSSION**

Before concluding, we would like to note that, in addition to nonlinear photocurrents, other NLO effects such as the second-harmonic generation are also colossal in 1T’ JTMDs (Supplementary Fig. 10). Besides, the inversion symmetry of 1T’ PTMDs can be broken externally by, e.g., an out-of-plane electric field, resulting in nonlinear photocurrents, which can be regarded as a third-order nonlinear effect. The \( \Sigma \) conductivity can be giant as well and can flip direction under a vertical electric field (Fig. 7). Also, the \( \Sigma \) conductivity depends approximately linearly on the electric field, which characterizes the strength of inversion asymmetry. This is consistent with results with the model Hamiltonian before, when...
\[ \partial \text{i} \]


effect in 1T' MoS₂ and a current in the energy of 520 eV, respectively. For the DFT calculations, the interactions. Core and valence electrons are treated by projector lead to sensitive manipulation of NLO effects. The colossal and which can be used as a signal of the topological transition and can

\[ H^{W}_{\text{in}} = (n\hat{H}|n\tilde{R}) \]

Wannier Hamiltonian in the k space can be obtained with a Fourier transformation

\[ H^{W}_{\text{in}} = \sum_{\mathbf{R}} e^{i \mathbf{R} \cdot (\mathbf{r}_a - \mathbf{r}_i)} j^{W}_{\text{in}}(\mathbf{R}) \tilde{R} \]

where we have included the Wannier centers rₐ in the phase factor. By diagonalizing \( H^{W}_{\text{in}} \) at each k-point, one obtains the energy and wavefunctions \( E^{W}_{n}(\mathbf{k}) \) and \( |n\tilde{R}\rangle \).

\[ \text{Band velocity, Berry connection, and sum rule} \]

The Wannier Hamiltonian and wavefunctions are directly applied to calculate the band velocity \( v^{W}_{n} \) with

\[ v^{W}_{n} = \left\{ \left| \frac{\Delta H}{\partial \mathbf{k}} \right| n \right\}^{W} \]

Then the interband Berry connections \( r^{W}_{nm} \) can be obtained with the relation

\[ r^{W}_{nm} = \frac{v^{W}_{n} - v^{W}_{m}}{v^{W}_{n}} (n|m) \]

And the generalized gauge covariant derivative of \( r^{W}_{nm} \) is calculated with the sum rule

\[ \dot{r}^{W}_{nm} = \frac{1}{\omega_{nm}} \left[ \left( \frac{\partial v^{W}_{n}}{\partial \mathbf{k}} \right) \left( \frac{\partial v^{W}_{m}}{\partial \mathbf{k}} \right) - w^{W}_{nm} \right] \sum_{\mathbf{p}} \left( \frac{\partial v^{W}_{n}}{\partial \mathbf{k}} \right) \left( \frac{\partial v^{W}_{m}}{\partial \mathbf{k}} \right) \]

where \( \Delta_{nm} = v^{W}_{n} - v^{W}_{m} \) and \( w^{W}_{nm} = \left\{ \left| \frac{\partial H^{W}_{nm}}{\partial \mathbf{k}} \right| n \right\}^{W} \).

\[ \text{Nonlinear photoconductivity} \]

After all the ingredients, \( v^{W}_{n} \), \( r^{W}_{nm} \), and \( \dot{r}^{W}_{nm} \) are obtained from the Wannier interpolations, the nonlinear photoconductivity is calculated based on Eq. (3) in the main text. The BZ integration is sampled with a \( 1601 \times 3201 \) k-mesh in the first BZ. The k-mesh convergence is tested with a denser \( 2251 \times 4501 \) k-mesh, and the difference is found to be negligible (Supplementary Fig. 5).

\[ \text{CODE AVAILABILITY} \]

The data that support the findings within this paper and the MATLAB code for calculating the shift and circular current conductivity are available from the corresponding authors upon reasonable request.

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ADDITIONAL INFORMATION

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Supplementary Information

of

Colossal Switchable Photocurrents in Topological Janus Transition-Metal Dichalcogenides

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Supplementary Note 1. Two sets of equations: velocity gauge and length gauge

There are two sets of equations that could describe the second-order nonlinear photocurrent. The first equation uses the velocity gauge and three summations over bands, and reads

$$
\chi_{abc}^{(0; \omega, -\omega)} = \frac{e^3}{2 \omega^2 \hbar^2} \sum_{l,n,m} \int_{BZ} \frac{d^3 k}{(2\pi)^3} \frac{f_{nl} v_{nl}^b}{\Omega - \omega_{ln} - i/\tau} \left[ \frac{v_{lm}^a v_{mn}^a}{(\omega_{mn} - i/\tau)} - \frac{v_{lm}^a v_{mn}^b}{(\omega_{ml} - i/\tau)} \right]
$$

(1)

where $v_{mn}^a = \langle m | v^a | n(k) \rangle$, $\omega_{mn} = \omega_m(k) - \omega_n(k)$, and $f_{mn} = f_m(k) - f_n(k)$ are the velocity matrix, difference in band energy, difference in occupation number between band $m$ and $n$, respectively. $\tau$ is the carrier lifetime. In the following we will drop the clear dependence on $k$. This equation is derived
in Ref. [1] based on quadratic response theory, and is used in, e.g., Refs. [2, 3]. The photocurrent can be obtain as

\[ j^a = \text{Re}\{\chi^a_{bc}(0; \omega, -\omega)E^b(\omega)E^c(-\omega)\} \]

The second set of equations are more popular, and look fancier. They adopt the *length gauge* and have only two band summations. In a time-reversal symmetric system, the nonlinear photocurrent is divided into two parts: the *shift current* and the *circular (or injection)* current

\[
\begin{align*}
  j^a_{\text{shift}} &= 2\sigma^a_{bc}(0; \omega, -\omega)E^b(\omega)E^c(-\omega) \\
  \frac{dj^a_{\text{circular}}}{dt} &= 2\eta^a_{bc}(0; \omega, -\omega)E^b(\omega)E^c(-\omega)
\end{align*}
\]

with

\[
\sigma^a_{bc}(0; \omega, -\omega) = -\frac{\pi e^3}{2\hbar^2} \int_{BZ} \frac{d^3k}{(2\pi)^3} \sum_{n,m} f_{nm}(r^b_{mm}r^c_{nm} + r^c_{mn}r^b_{mn}) \delta(\omega_{mn} - \omega)
\]

and

\[
\eta^a_{bc}(0; \omega, -\omega) = -\frac{i\pi e^3}{2\hbar^2} \int_{BZ} \frac{d^3k}{(2\pi)^3} \sum_{n,m} f_{nm} \Delta^a_{nm} [r^c_{mn}, r^b_{nm}] \delta(\omega_{mn} - \omega)
\]

where

\[
r^a_{nm,b} = \frac{\partial r^a_{nm}}{\partial k^b} - i[\xi^a_{nm} - \xi^b_{nm}] r^a_{nm}
\]

and \(\xi^a_{mn} = i\langle u_m|\partial_{k^a}|u_n\rangle\) is the Berry connection, \(|u_n\rangle\) is the periodic part of the wave function. Note that for Bloch waves, it is not straightforward to define the position operator \(r_{mn} = \langle m|r|n\rangle\). Usually \(r_{mn}\) is defined with

\[
r_{mn} = \begin{cases} 
  \xi_{mn} = \frac{v_{mn}}{i\omega_{mn}}, & m \neq n \\
  0, & m = n
\end{cases}
\]

But the definition of \(\xi\) is valid for \(m = n\) as well.

In a time-reversal symmetric system, the shift current is induced by a linearly polarized light \((b = c)\), and is a static current. On the other hand, the circular current is generated by a circularly polarized light, and should grow with time. If the carrier lifetime is \(\tau\), then there should be a dissipation term \(-j_{\text{circular}}/\tau\). And in the static limit \((t \to \infty)\), one has

\[
j_{\text{circular}} = 2\tau\eta^a_{bc}(0; \omega, -\omega)E^b(\omega)E^c(-\omega)
\]

so the *effective* conductivity should be defined as \(\tau\eta^a_{bc}(0; \omega, -\omega)\). These equations in length gauge are derived in Ref. [4] and is widely used in many papers.

The shift current conductivity \(\sigma^a_{bc}(0; \omega, -\omega)\) is sometimes written in an even fancier format when \(b = c\)

\[
\sigma^a_{bb}(0; \omega, -\omega) = -\frac{\pi e^3}{2\hbar^2} \int_{BZ} \frac{d^3k}{(2\pi)^3} \sum_{n,m} f_{nm} R^a_{nm} |r^b_{nm}|^2 \delta(\omega_{mn} - \omega)
\]
Supplementary Figure 1: CC($\mathbf{k}$) = Re \left\{ \sum_{nm} f_{nm} \frac{\Delta_a^{mn} [r_{nm}^b, r_{nm}^c]}{\omega_{mn} - \omega - i/\tau} \right\} for MoSTe. For time-reversal pairs $\pm \mathbf{k}$, CC($\mathbf{k}$) is equal.

where

$$ r_{nm}^b = |r_{nm}^b| e^{-i\phi_{nm}} $$

and

$$ R_{nm}^a = \frac{\partial \phi_{nm}}{\partial k_a} + \xi_{nn}^a - \xi_{mm}^a $$

is called the shift vector. Here $|r_{nm}^b|^2$ is actually the transition rate between band $n$ and $m$ under light, while $R_{nm}^a$ is a shift in the geometric center of the wavefunction when the electron transits between band $m$ and $n$. The equivalence between Eqs. (3, 8) can be easily obtain with Eq. (5) [5].

Note that the symmetry requirement for non-vanishing $\sigma_{bc}^a$ and $\eta_{bc}^a$ is the breaking of inversion symmetry, while time reversal symmetry $\mathcal{T}$ does not have any constraints on $\sigma_{bc}^a$ and $\eta_{bc}^a$. Here we take $\eta_{bc}^a$ as an example, and the analysis on $\sigma_{bc}^a$ is similar. Under $\mathcal{T}$, one has $\mathcal{T} v_{mn}(\mathbf{k}) = - v_{nm}^*(\mathbf{-k})$, and $\mathcal{T} r_{mn}(\mathbf{k}) = r_{mn}^*(-\mathbf{k})$. Thus the Berry curvature $\Omega_{mn}^{bc}(\mathbf{k}) = [r_{mn}^b, r_{mn}^c]$ satisfies $\mathcal{T} \Omega_{mn}^{bc}(\mathbf{k}) = - \Omega_{mn}^{bc}(\mathbf{-k})$. The velocity difference $\Delta_{mn}^a(\mathbf{k})$ satisfies $\mathcal{T} \Delta_{mn}^a(\mathbf{k}) = - \Delta_{mn}^a(-\mathbf{k})$. Thus CC($\mathbf{k}$) = Re \left\{ \sum_{nm} f_{nm} \frac{\Delta_a^{mn} [r_{nm}^b, r_{nm}^c]}{\omega_{mn} - \omega - i/\tau} \right\} satisfies $\mathcal{T}$CC($\mathbf{k}$) = CC($\mathbf{-k}$). As a result, $\mathcal{T}$ does not impose a zero $\eta_{bc}^a$ after the Brillouin zone integration. The analysis above is verified by the numerical results on MoSTe (Figure 1).

Supplementary Note 2. The velocity gauge and the length gauge are equivalent

In the cases where both Eq. (1) and Eqs. (3, 4) are applicable, they should be equivalent. The reason is because they both originate from second-order perturbation of the light field and are dealing
with the same physical effect [6]. Note that Eqs. (3, 4) are applicable only when the time reversal symmetry is present.

In order to illustrate the equivalence, here we assume a sufficiently long carrier relaxation time \( h/\tau \ll E_g \), where \( E_g \) is the bandgap, so that the algebras are greatly simplified. Under this assumption, in a time-reversal symmetric system the real part and imaginary part of Eq. (1) correspond to the shift current Eqs.(3) and circular current Eqs.(4), respectively.

**Shift current** To see the real part of Eq. (1) is equivalent to Eq. (3), we need to take two steps. The first step is to factorize the denominator of Eq. (1) with

\[
D_1 = \frac{1}{\omega_{nm} - i/\tau} = \frac{P}{\omega_{nm}} + i\pi\delta(\omega_{nm})
\]

\[
D_2 = \frac{1}{\omega_{nl} - \Omega - i/\tau} = \frac{P}{\omega_{nl} - \Omega} + i\pi\delta(\omega_{nl} - \Omega)
\]

The factorizations are valid when \( h/\tau \ll E_g \) and we used one of many definitions of delta function

\[
\delta(x) = \lim_{\epsilon \to 0} \frac{1}{\pi} \frac{\epsilon}{\epsilon^2 + x^2}.
\]

\( P \) stands for the Cauchy principle value in \( k \) integration.

Next, due to time reversal symmetry, we have \( v_{mn}(k) = -v^*_{nm}(-k) \), and the integration in Eq. (1) depends only on imaginary part of the numerator \( v^a_{nl}v^b_{lm}v^c_{mn} \). This is because the real part of \( v^a_{nl}v^b_{lm}v^c_{mn} \) gets a minus sign after \( k \to -k \), thus has to be zero after BZ integration. Since we are taking the real part of Eq. (1), only the imaginary part of \( D_1D_2 \) contributes to the final result. And we have

\[
\text{Im}(D_1D_2) = \pi \frac{P}{\omega_{nm}}\delta(\omega_{nl} - \Omega) + \pi \frac{P}{\omega_{nl} - \Omega}\delta(\omega_{nm})
\]

The second term in symmetric with respect to the permutation of \( m, n \) (after summation over \( m, n \)), while the imaginary part of \( v^a_{nl}v^b_{lm}v^c_{mn} \) is asymmetric with respect to \( m, n \). Therefore only the first term in Eq. (10) would not vanish in the final result. Now it’s straightforward to check that that the integrand in Eq. (1) is of the format

\[
\text{Re} \{ \chi^{a}_{bc}(\omega) \} \sim \sum_{l,n,m}^{\Omega=\pm\omega} \int_{BZ} \frac{d^3k}{(2\pi)^3} f_{ln} v^a_{nl}v^b_{lm}v^c_{mn} \omega_{nm} \delta(\omega_{nl} - \Omega)
\]

The second step is to rewrite Eq. (3) with

\[
r^a_{nm} = \frac{v^a_{nm}}{i\omega_{nm}} \quad (m \neq n)
\]

and use the sum rule [5]

\[
r^b_{nm,a} = \frac{r^a_{nm}\Delta^b_{mn} + r^b_{nm}\Delta^a_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}} \sum_{l} (\omega_{lm}r^a_{ln}r^b_{lm} - \omega_{ln}r^b_{lm}r^a_{ln})
\]

Eq. (13) can cast the two band summations in Eq. (3) into a three band summation.
Now, the equivalence between the real part of Eq. (1) and shift current Eq. (3) can be obtained with some algebras.

**Circular current** The circular current Eq. (4) is equivalent to the imaginary part of Eq. (1), under the same assumption as in the previous section. To see this point, we use Eq. (9) again. This time, we need to take the real part of $D_1D_2$, because for a circularly polarized light, there is $\pi/2$ phase difference, which leads to an $i$ factor. We have

$$\text{Re}(D_1D_2) = \frac{P}{\omega_{nm}(\omega_{nl} - \Omega)} - \pi^2 \delta(\omega_{nm})\delta(\omega_{nl} - \Omega) \quad (14)$$

Eq. (14) already separates Eq. (1) into two parts. The two parts correspond to $n \neq m$ and $n = m$ contributions, respectively. We first discuss the second term, which is a direct resonant transition between two bands $n$ and $l$. Actually $i\pi\delta(\omega_{nm})$ should be $1/(\omega_{nm} - i\tau) = i\tau$ when $\tau$ is not really infinite. Then one can see that the imaginary part of Eq. (1) is

$$\text{Im}\{\chi^{a}_{bc}(\omega)\} \sim \sum_{l,n} \int_{BZ} \frac{d^3k}{(2\pi)^3} f_{ln} \frac{1}{2}[v_{ln}^a, v_{ln}^c](v_{nn}^a - v_{ll}^a)\delta(\omega_{nl} - \Omega) \quad (15)$$

After transforming $v$ to $r$, we can obtain the circular current Eq. (4).

Then, the first term in Eq. (14) corresponds to $n \neq m$. in this case $n, m, l$ are all involved and this is a three band contribution. Note that this term is independent of $\tau$. The ratio of the three band contribution to the two band contribution is (approximately) $\frac{1}{\tau\omega_{nm}}$. In the limit that $\tau \to \infty$, the three band contribution can be neglected, and the imaginary part of Eq. (1) is equivalent to Eq. (4).

**Supplementary Discussion 1. Intraband nonlinear photoconductivity**

As discussed in the main text, since the bandgaps of 1T$'$ JTMDs are small (comparable with room temperature $k_B T_{room} \sim 25$ meV), the electrons can be excited to the conduction band due to thermal activation, which leads to an intraband contribution to the total nonlinear photoconductivity.

We have calculated the intraband part of the nonlinear photoconductivity, according to [8]

$$\sigma_{ab}^c(\omega) = \epsilon_{cda} \frac{e^3\tau}{\hbar^2(1 + i\omega\tau)} \int \frac{d^3k}{(2\pi)^3} \sum_n \Omega_n^d \frac{\partial f_n}{\partial k_b} + \frac{e^3\tau^2}{\hbar^2(1 + i\omega\tau)} \int \frac{d^3k}{(2\pi)^3} \sum_n c_{nn}^a \frac{\partial^2 f}{\partial k_a \partial k_b} \quad (16)$$

Where the dependences on $k$ have been omitted. $f_n$ is the occupation of band $n$. $\tau$ is the carrier lifetime and is set as 0.2 ps as in the main text. $\Omega_n^d = i\epsilon_{dob} \sum_{m \neq n} r_{mn}^a r_{nm}^b$ is the intraband Berry curvature, while $\epsilon_{abc}$ is the Levi-Civita symbol. The first term in Eq. (16) is the nonlinear anomalous Hall effect.
Supplementary Figure 2: Intraband contribution to the nonlinear photoconductivity. (a) $\sigma_{yy}(\omega)$ at different temperatures below 600 K. (b) Zero-frequency conductivity $\sigma_{yy}(\omega = 0)$ as a function of temperature.

(NAHE) that depends on the anomalous velocity (Berry curvature), while the second term is a Drude-like intraband term. Note that in systems with time reversal symmetry, the Drude-like term must vanish. Hence, we focus on the NAHE. The NAHE part depends on $\frac{\partial f_n}{\partial k}$, which is vanishing for an insulating material at zero temperature. However, at finite temperatures, some electrons would be excited to the conduction band due to thermal activation, leading to finite $\frac{\partial f_n}{\partial k}$. Here we take the Fermi-Dirac distribution $f_n(T) = \frac{1}{\exp[\beta(E_n-\mu)]+1}$, where $E_n$ is the band energy of the band $n$, and $\beta = 1/(k_B T)$ is the inverted temperature. The chemical potential $\mu(T)$ is a function of temperature, and is determined by $\int \frac{\text{DOS}(E)}{\exp[\beta(E_n-\mu)]+1} dE = N_e$, where DOS($E$) is the density of states, while $N_e$ is the total number of electrons. We calculate $\sigma_{yy}^x(\omega)$ for MoSSe at different temperatures, and the results are shown in Figure 2. One can see that at room temperature, $\sigma_{yy}^x(\omega)$ is on the order of $10^2 \sim 10^3$ nm $\cdot$ $\mu$A/V$^2$, comparable with the interband contribution.

There is an interesting phenomenon that the maximum of $\sigma_{yy}^x(\omega)$ is located around $T \sim 30$ K, which is comparable with the bandgap of MoSSe (4 meV $\sim$ 46 K). The reason is as follows. The Berry curvature peaks around the bandedge (±$\Lambda$ points for 1T’ JTMDs), thus the NAHE conductivity should be the largest when $\frac{\partial f}{\partial k}$ also has significant value near the bandedge, which is realized when the temperature is comparable with the bandgap. This behavior is similar to that of the interband contribution when the Fermi level is tuned (Figure 6 in main text): the interband term is the strongest when the Fermi level is slightly above the conduction band minimum or slightly below the valence band maximum.
Supplementary Figure 3: The (a) absorbance and (b) reflectance of 1T’ MoSSe.

Supplementary Discussion 2. Reflectance and absorbance

We have calculated the reflectance $R(\omega)$ and absorbance $A(\omega)$ of monolayer 1T’ MoSSe (Figure 3), according to

$$R(\omega) = \left( \frac{C}{1 + C} \right)^2$$

$$A(\omega) = \frac{2C}{(1 + C)^2}$$

(17)

Here $C = \frac{2\pi nkd}{\lambda}$, where $\lambda$ is the wavelength, $d$ is the thickness of the layer, while $n$ and $k$ are the real and imaginary part of the complex refractive index. One can see that as an atomically thin monolayer (very small $d$), the reflectance and absorbance of 1T’ MoSSe are not very strong. This is similar as in monolayer graphene [9, 10], where a large amount of (97%) light transmit through graphene due to its single atomic thickness. In our system, the effective thickness of JTMDs is also very small, and the light can easily trespassing the system without significant absorption or reflection. This is different from 3D bulk materials or thick films. Of course, the total reflectance and absorbance would be stronger if monolayer 1T’ JTMDs are stacked. Hence, we suggest to use monolayers or few layers to serve as photocurrent devices. But actually, the absorbance of photons by electron interband transition is not a disadvantage: this is the mechanism of conventional semiconductor photodetectors. As for the reflection problem, it can be resolved, or at least eased, by proper optical designing of the device.
Supplementary Figures

Supplementary Figure 4: The phase diagrams with in-plane strain for all six JTMDs, in analogy to Figure 3(c) in the main text.
Supplementary Figure 5: A test on the $k$-mesh convergence of the SC conductivity of MoS$\text{Te}_2$. Two $k$-mesh of $2251 \times 4501$ and $1601 \times 3201$ in the first BZ give nearly identical results.
Supplementary Figure 6: As discussed in the main text, an out-of-plane electric field can trigger topological transition in 1T’ JTMDs. Here we show this effect on MoSSe. S atoms are on the top layer while Se atoms are on the bottom layer. For the electric field, a positive value indicate that the its direction is from the top to the bottom. The topological transition happens with $E \approx -0.12 \text{ V/Å}$. Similar to the in-plane strain effect as in the main text, $\sigma_{xx}^z$ and $\sigma_{yz}^z$ flip direction upon the topological phase transition.
Supplementary Figure 7: An out-of-plane electric field can also trigger topological phase transition in 1T’ WSeTe. Se atoms are on the top layers while Te atoms are on the bottom layers. For the electric field, a positive value indicates that its direction is from the top to the bottom. The topological phase transition happens with $E \approx -0.58 \text{ V/A}$. All four components of the SC conductivity flip direction upon the topological transition.
Supplementary Figure 8: The SC conductivity of MoSSe and WSTe when changing the Fermi Level. Similar to MoSTe in the main text, the SC conductivity also jumps to a significant positive or negative value when the Fermi level is slightly inside the CB or VB.
Supplementary Figure 9: The $k$-specified contribution $\text{SC}(k)$ and $\text{CC}(k)$ to the SC and CC conductivities as defined in the main text. Here shows how $\text{SC}(k)$ and $\text{CC}(k)$ of MoSTe change with Fermi level $E_f$, in consistency with the discussions in the main text (Figure 6b).
Supplementary Figure 10: The peak values of the second harmonic generation (SHG) susceptibility $\chi^{xy}$ for 1T’ JTMDs. As a comparison, the peak value of the SHG susceptibility of 2H MoS$_2$ is on the order of 1 nm$^2$/V.
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