Supplementary Text

1. Phenomenological derivation of circular photogalvanic effect response from polar domain walls formed in Ta$_2$NiSe$_5$:

The general phenomenological equation of CPGE response in the dipole order is given by Ref. (30) of the main text:

$$ j^{\text{CPGE}}_{\lambda}(\omega = 0) = i\gamma_{\lambda\mu}(\vec{E} \times \vec{E}^*)_{\mu} $$ (1)

The surface of any system breaks inversion symmetry. Near the polar domain walls the symmetry is reduced to $C_1$ which is a gyrotropic point group with the $\gamma$ tensor given by:

$$ \gamma = \begin{pmatrix} \gamma_{xx} & \gamma_{xy} & \gamma_{xz} \\ \gamma_{yx} & \gamma_{yy} & \gamma_{yz} \\ \gamma_{zx} & \gamma_{zy} & \gamma_{zz} \end{pmatrix} $$ (2)

Thus, CPGE under normal incidence is allowed. $j^{\text{CPGE}}$ in this system will be given by,

$$ j^{\text{CPGE}} = i \begin{pmatrix} \gamma_{xx} & \gamma_{xy} & \gamma_{xz} \\ \gamma_{yx} & \gamma_{yy} & \gamma_{yz} \\ \gamma_{zx} & \gamma_{zy} & \gamma_{zz} \end{pmatrix} (\vec{E} \times \vec{E}^*) $$ (3)

In the geometry shown by figure S6, and following analysis by Ref. (39) of the main text, we can write:

$$ j^{\text{CPGE}} \propto \begin{pmatrix} \gamma_{xx} & \gamma_{xy} & \gamma_{xz} \\ \gamma_{yx} & \gamma_{yy} & \gamma_{yz} \\ \gamma_{zx} & \gamma_{zy} & \gamma_{zz} \end{pmatrix} \begin{pmatrix} \cos(\alpha) \sin(2\theta) \sin(\phi) \\ \sin(\alpha) \sin(2\theta) \sin(\phi) \\ \sin(2\theta) \cos(\phi) \end{pmatrix} $$ (4)

$$ \propto \begin{pmatrix} \gamma_{xx} \cos(\alpha) + \gamma_{xy} \sin(\alpha) \sin(2\theta) \sin(\phi) + \gamma_{xz} \sin(2\theta) \cos(\phi) \\ \gamma_{yx} \cos(\alpha) + \gamma_{yy} \sin(\alpha) \sin(2\theta) \sin(\phi) + \gamma_{yz} \sin(2\theta) \cos(\phi) \\ \gamma_{zx} \cos(\alpha) + \gamma_{zy} \sin(\alpha) \sin(2\theta) \sin(\phi) + \gamma_{zz} \sin(2\theta) \cos(\phi) \end{pmatrix} $$ (5)

For normal incidence $\phi = 0$, thus

$$ j^{\text{CPGE}} \propto \begin{pmatrix} \gamma_{xz} \sin(2\theta) \\ \gamma_{yz} \sin(2\theta) \\ \gamma_{zz} \sin(2\theta) \end{pmatrix} $$ (6)

Now for a polar domain wall oriented in the opposite direction to this (-a axis i.e., $-\hat{x}$ direction in the lab frame) will have its $\gamma'$ tensor in relation to this as:
\[ \gamma' = M_x \gamma M_x^{-1} = \begin{pmatrix} \gamma_{xx} & -\gamma_{xy} & -\gamma_{xz} \\ -\gamma_{yx} & \gamma_{yy} & \gamma_{yz} \\ -\gamma_{zx} & \gamma_{zy} & \gamma_{zz} \end{pmatrix} \] 

(7)

Thus, the opposite polar domain wall will have its \( j'^{CPGE} \) given by

\[ j'^{CPGE} \propto \begin{pmatrix} -\gamma_{xz} \sin(2\theta) \\ \gamma_{yz} \sin(2\theta) \\ \gamma_{zz} \sin(2\theta) \end{pmatrix} \]

(8)

Which is equal and opposite to the \( j^{CPGE} \) from the polar domain wall oriented in the +a axis or the +\( \hat{x} \) direction in the lab frame. Averaging over the excitation spot will lead to sampling an equal number of both orientations of the polar domain walls, leading to a total zero \( j^{CPGE} \) from this process.

2. **Theoretical formalism of QCPGE response using density matrix formalism**

We adopt a two-level description of the QCPGE phenomenon described by the Feynman diagram in figure 4(B) of the main text. We assume that bulk inversion symmetry is present in the system and there are two discrete levels indexed by definite parity g and u separated by a gap, \( \Delta \). These may be understood to be Wannier representations of two bands in a crystal. The equation of motion for the density matrix is the Liouville operator:

\[ i\hbar \dot{\rho} = [H, \rho] \]

(9)

We will break the Hamiltonian \( H \) into a static term \( H_o \) (the system) and a driving term \( V(t) \) (the fields). We will work with a two-state system with a ground state ‘1’ with energy \( \varepsilon_1 \) and a single excited state \( 2 \) with energy \( \varepsilon_2 \). Then resolving the various components of \( \rho \) we can write,

\[ i\hbar \rho_{\mu'\nu'} = (\varepsilon_\mu - \varepsilon_\nu)\rho_{\mu\nu} + V_{\mu'\nu}(t)\rho_{\mu'\nu} - \rho_{\mu'\nu}V_{\nu'\nu}(t) \]

(10)

We start from a zeroth order density matrix:

\[ \rho^{(0)} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \]

(11)

representing the ground state and integrate the equation of motion to second order in the driving fields. Since the response vanishes averaged over a mixed state where both states 1 and 2 have equal occupation number, any response comes from an asymmetry in the initial occupation numbers, and it is useful to propagate from the initial density matrix:
\[ \rho^{(0)} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]  

We are interested in the nonlinear mixing of harmonic optical fields, so we write:

\[ V(t) = V_+ e^{-i\omega t} + V_- e^{i\omega t} \]  

(13)

and calculate the response to second order in the fields isolating the bilinear terms involving the product \( V_+ V_- \). This gives a static field by integrating the optical fields and is responsible for a static (d.c.) current. We will couple the light to matter using the vector potential in the velocity gauge.

Since the system has bulk inversion symmetry, in the eigenstate basis the dipole operators are purely off diagonal. Specifically,

\[ \mathbf{v}_\alpha = \begin{pmatrix} 0 & v_\alpha^* \\ v_\alpha & 0 \end{pmatrix} \]  

(14)

The electric quadrupole/magnetic dipole coupling has even parity, so it is purely a diagonal operator

\[ \mathbf{m}_{z\gamma} = \frac{-i\hbar}{2\Delta} \begin{pmatrix} z v_\gamma + v_\gamma^* z & 0 \\ 0 & z v_\gamma^* + v_\gamma z \end{pmatrix} \]  

(15)

To evaluate the \( z \) operator we transform to the velocity representation using,

\[ z_{\mu\nu} = \frac{-i\hbar}{\varepsilon_\mu - \varepsilon_\nu} \langle \mu | v_z | \nu \rangle \]  

(16)

which gives explicitly,

\[ \mathbf{m}_{z\gamma} = \frac{-i\hbar}{2\Delta} \begin{pmatrix} 0 & -v_\gamma^* v_\gamma - v_\gamma v_\gamma^* \\ v_\gamma^* v_\gamma + v_\gamma v_\gamma^* & 0 \end{pmatrix} \]  

(17)

Since the scalar \( v \)'s commute we can write this as,

\[ \mathbf{m}_{z\gamma} = \frac{-i\hbar}{2\Delta} \begin{pmatrix} v_\gamma^* v_\gamma - v_\gamma v_\gamma^* & 0 \\ 0 & v_\gamma^* v_\gamma + v_\gamma v_\gamma^* \end{pmatrix} \]  

(18)

When the driving field is applied for a long time, we look for solutions oscillating at the frequency of the field \( \omega \),

\[ i \dot{\rho}_{21} = \Delta \rho_{21} + [V_+]_{21} e^{-i\omega t} - \rho_{22} [V_+]_{21} e^{-i\omega t} \]  

(19)

Setting \( \rho_{11} = -\rho_{22} = 1 \) and isolating terms rotating at \( e^{-i\omega t} \) we get:

\[ \rho^{(1)}_{21}(\omega) = -\frac{v_\alpha}{\Delta - \hbar \omega} A_\alpha(\omega) e^{-i\omega t} \]  

(20)
We now down-convert this to a static term in the density matrix using the $m$ to couple to a driving field at $e^{i\omega t}$. This operator is diagonal in the band basis, and we are looking for a static response. Therefore,

$$0 = \Delta \rho_{21}^{(2)}(\omega = 0) + [V_-]_{22} e^{i\omega t} \rho_{21}^{(1)} - \rho_{21}^{(1)} [V_-]_{11} e^{i\omega t} \quad (21)$$

which is solved to give,

$$\rho_{21}^{(2)}(\omega = 0) = \frac{i\hbar}{\Delta^2} \frac{(v^*_z v'_y - v^*_y v'_z)v_\alpha}{\Delta - \hbar\omega} A_\alpha(\omega)A_y(-\omega) \quad (22)$$

Similarly,

$$\rho_{12}^{(1)}(\omega) = -\frac{v^*_\alpha}{\Delta + \hbar\omega} A_\alpha(\omega)e^{-i\omega t} \quad (23)$$

$$\rho_{12}^{(2)}(\omega = 0) = -\frac{i\hbar}{\Delta^2} \frac{(v^*_z v'_y - v^*_y v'_z)v^*_\alpha}{\Delta + \hbar\omega} A_\alpha(\omega)A_y(-\omega) \quad (24)$$

Reciprocity requires $\rho_{21}(\omega) = \rho_{12}^*(\omega)$ which holds here.

The induced current is given by:

$$j_\delta(\omega = 0) = \text{Tr}[\rho^{(2)} v_\delta] \quad (25)$$

Which explicitly gives,

$$j_\delta(\omega = 0) = \frac{i\hbar}{\Delta^2} \left[ \frac{(v^*_z v'_y - v^*_y v'_z)v_\alpha v^*_\delta}{\Delta - \hbar\omega} \right. \left. - \frac{(v^*_z v'_y - v^*_y v'_z)v^*_\alpha v_\delta}{\Delta + \hbar\omega} \right] \left( iq_z A_\alpha(\omega)A_y(-\omega) \right) \quad (26)$$

Here the spatial dispersion $iq_z$ has been restored. Simplifying the above equation, we have,

$$j_\delta(\omega = 0) = -\frac{\hbar}{\Delta^2} \left[ \frac{(v^*_z v'_y - v^*_y v'_z)v_\alpha v^*_\delta}{\Delta - \hbar\omega} \right. \left. - \frac{(v^*_z v'_y - v^*_y v'_z)v^*_\alpha v_\delta}{\Delta + \hbar\omega} \right] \left( q_z A_\alpha(\omega)A_y(-\omega) \right) \quad (27)$$
So, the response matrix is purely imaginary, and the two terms have different resonant denominators. We want the part of this expression that is antisymmetric under $\alpha \leftrightarrow \gamma$ which gives the CPGE contribution.

Ignoring terms that are symmetric under $\alpha \leftrightarrow \gamma$ we get,

$$j_\delta(\omega = 0) = -\frac{\hbar}{\Delta^2} \left[ \frac{v_z v_\delta^* v_\alpha^*}{\Delta - \hbar \omega} + \frac{v_z^* v_\gamma^* v_\alpha^*}{\Delta + \hbar \omega} \right] (q_z A_\alpha(\omega) A_\gamma(-\omega))$$ (28)

The factor depending on the subscripts $\alpha$ and $\gamma$ can be written as a real and imaginary part,

$$v_\gamma^* v_\alpha = \text{Re}[v_\gamma^* v_\alpha] + i \text{Im}[v_\gamma^* v_\alpha] = U_1 + i U_2$$ (29)

where $U_2$ is the term antisymmetric under exchange $\alpha \leftrightarrow \gamma$. This gives:

$$j_\delta(\omega = 0) = -\frac{\hbar}{\Delta^2} \left[ \frac{v_z (U_1 + i U_2) v_\delta^*}{\Delta - \hbar \omega} + \frac{v_z^* (U_1 - i U_2) v_\delta}{\Delta + \hbar \omega} \right] (q_z A_\alpha(\omega) A_\gamma(-\omega))$$ (30)

Writing this over a common denominator $\Delta^2 - (\hbar \omega)^2$ and isolating the $U_2$ term gives,

$$j_\delta(\omega = 0) = -\frac{\hbar \omega}{2\Delta^2} \left[ (v_z v_\delta^* + v_z^* v_\delta)(v_\alpha^* v_\gamma^* - v_\alpha^* v_\gamma) \right] (q_z A_\alpha(\omega) A_\gamma(-\omega))$$ (31)

Or in terms of electric fields:

$$j_\delta(\omega = 0) = -\frac{\hbar}{2\omega \Delta^2} \left[ (v_z v_\delta^* + v_z^* v_\delta)(v_\alpha^* v_\gamma^* - v_\alpha^* v_\gamma) \right] (q_z E_\alpha(\omega) E_\gamma(-\omega))$$ (32)

This is a current along the $\delta$ direction driven by circular polarization in the plane described by $\alpha - \gamma$ indices including the first dispersive correction in $q_z$. The prefactor is purely imaginary, odd in $\omega$, antisymmetric under $\alpha \leftrightarrow \gamma$ and linear in $q_z$. This resonant lineshape is plotted in Figure 4(D) of the main text (where a phenomenological damping term has been included) showing the antiresonant lineshape. Restoring units at this point to give the physically measured response function (and denoting the number density with $n$ and setting $\omega_o = \Delta/\hbar$),

$$j_\delta(\omega = 0) = -\frac{n}{2} \left( \frac{e^3}{\hbar^2} \right) \left[ (v_z v_\delta^* + v_z^* v_\delta)(v_\alpha^* v_\gamma^* - v_\alpha^* v_\gamma) \right] (q_z E_\alpha(\omega) E_\gamma(-\omega))$$ (33)
The function is antisymmetric on exchange $\alpha \leftrightarrow \gamma$ and odd in $\omega$ but symmetric under combined exchange and frequency inversion. It is odd under twofold rotation $C_{2z}$ which, if present, would exclude this form of CPGE. The left side is a static current: it is odd under inversion and odd under time reversal. The driving terms $q_z \left( E_\alpha(\omega)E_\gamma(-\omega) - E_\alpha(-\omega)E_\gamma(\omega) \right)$ are also odd under inversion and odd under time reversal. Thus, the response function has to be even under inversion and even under time reversal. One sees immediately that it is indeed even under inversion. Under time reversal the matrix elements are conjugated but $\omega \mapsto -\omega$ so the expression is also even under time reversal. This means that the response function is zero exactly at $k = 0$ where the Hamiltonian is real, but it turns on as an even function of $k$. Therefore, although forbidden exactly at $k = 0$, it is present when integrated over nonzero-momentum (complex) Bloch states with a time-reversal invariant population.

3. **Calculation of surface CPGE response using density matrix formalism**

We present a detailed derivation for the diagram shown in figure 4(C) of the main text for surface contribution to CPGE. A different process occurs if we consider a dipole coupling to the driving fields and insert the $q$ dependence in the outgoing current vertex. Note that one has to make the substitution $q_z \mapsto i\kappa$ in order to exponentially localize the response to the surface of the material. In that case we will have to examine the imaginary part of the resonant expressions, which can then be found using the substitution $\omega \mapsto \omega + i\eta$. As before the density matrix to first order in the fields is perturbed.

\[
\rho_{21}^{(1)} = -\frac{v_\alpha}{\Delta - \hbar\omega} A_\alpha(\omega) \\
\rho_{12}^{(1)} = -\frac{v_\alpha^*}{\Delta + \hbar\omega} A_\alpha(\omega)
\]  

\[(34)\]  

\[(35)\]

The difference is that since the outgoing field has only diagonal matrix elements in this basis, we need to extract the second order shift to the population $\rho_{11}^{(2)}$ instead of a second order coherence $\rho_{21}^{(2)}$. So, for example:

\[i\rho_{11} = 0 = [V, \rho^{(1)}] - \frac{i\rho_{11}}{\tau}\]  

where the zero-time derivative holds in the driven steady state. This gives the population shift to second order in the fields:

\[
\rho_{11}^{(2)} = -i\tau \left[ \frac{v_\alpha^* v_\beta}{\Delta + \hbar\omega} - \frac{v_\alpha v_\beta^*}{\Delta - \hbar\omega} \right] A_\alpha(\omega) A_\beta(-\omega)
\]  

(36)

Then the outgoing current is generated by the even parity quadrupole operator:

\[
\frac{z v_\delta + v_\delta z}{2}
\]  

(37)

Following through a similar derivation as for the QCPGE part (section S2) we get:

\[
j_\delta = \frac{q_z \tau}{\Delta} (v_\xi^* v_\delta + v_\delta^* v_\xi) \left( v_\alpha^* v_\beta - v_\alpha v_\beta^* \right)
\]

\[
- v_\alpha v_\beta^* \left[ \frac{2i\omega \eta}{(\Delta^2 - (\hbar\omega)^2 + 4(\hbar\omega)^2 \eta^2)} \right] A_\alpha(\omega) A_\beta(-\omega)
\]  

(38)

Here one recognizes the important substitution,

\[
\frac{1}{\Delta^2} \rightarrow \frac{\tau}{\Delta}
\]  

(39)

indicating that this process actually describes an injection rate and is therefore not a coherently driven current. The quantity in brackets (eqn 38) describes a Lorentzian lineshape centered on the resonant frequency. Thus, this process is always present exactly on resonance. This system will not allow a net current in the limit that \( \eta \rightarrow 0 \). The current is an injection current and requires a change of population. It is governed by a population relaxation rate. One can think about this as CPGE coupling to a spatially modulated current.
**Figure S1:** Temperature-dependent resistivity curve of Ta$_2$NiSe$_5$. The resistivity data shows a kink in resistivity at $\sim$323 K showing a second order phase transition from the high temperature orthorhombic phase to the low temperature structural phase.
Figure S2: Room temperature XRD data of Ta$_2$NiSe$_5$. Inset shows the full X-ray diffraction pattern as well as bulk crystals with crystal axis orientations. The crystals are long along the a-axis, that is the Ni chain direction and layered along the b-axis.
Figure S3: High temperature photocurrent data showing no photogalvanic effect. Only polarization independent background current ($I_0$) was observed at temperatures higher than $T_C$. 
Figure S4: Optical image of a device used for laser scanning CPGE measurement in Fig. 2(b) of the main text. Red line shows the laser scanning direction. External d.c. bias is applied via Electrodes 1 and 4, while the photocurrent response of the system is measured between electrodes 2 and 3.
Figure S5: Photocurrent curves for two different devices (from Fig. 3(A) showing opposite value of CPGE under the same conditions. The two devices represent the top and bottom surfaces of a crystal after exfoliation of the crystal, in effect leading to a reversal $q_z \leftrightarrow -q_z$ (see Fig. 3(C)).
Figure S6: Schematic showing arrangement for calculations in section S1. $\theta$ is the angle between the quarter wave plate (QWP)’s fast axis and the incoming laser polarization, $\phi$ is the angle of incidence of the laser beam on the sample, $\alpha$ is the angle of the incidence plane with the x axis. Figure and analysis adapted from Ref. (39) of the main text.
Figure S7: Schematic showing possible arrangements of the domain wall polarization. The arrangement of Ta dipoles being in the same direction at the domain walls results in a non-zero total polarization along the $+a$ or the $-a$ directions. Section S4 details the resultant CPGE response.
Figure S8: Bias dependent, polarization-independent photocurrent $I_0$ (from eqn 1, main text). The polarization independent photocurrent $I_0$ shows a linear change with the bias applied, showing that the device responds to the applied bias, but the PGE shows no effect (Fig. 3(B)).
Figure S9: Photocurrent measurements at two different applied bias values (see Fig. 3(B)): (a) 0 V and (b) 500 mV. The polarization dependent response disappears as the applied voltage is increased beyond 0.3V due to equal population of the valence and conduction band edges, thereby reducing the hybridization parameter $\langle \psi_A^\dagger \psi_B \rangle$ to zero, which in turn restores the $C_2$ symmetry of the system. A broken $C_2$ symmetry is required for a non-zero CPGE response.
Figure S10: Dark current behavior of a typical device as seen in figure S4 under applied bias at room temperature. A double-Schottky barrier type behavior is seen in the device. However, all relevant measurements including the collapse of CPGE due to applied bias were performed in the low current regime (<100 nA) where Joule heating is not considerable enough to cause a phase transition in the system.