nature portfolio

Peer Review File

Strongly enhanced shift current at exciton resonances in a noncentrosymmetric widegap semiconductor

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Overall, the work offers an interesting examination of how exciton effects impact nonlinear optical response, which has the potential to contribute to the field of optoelectronic and photovoltaic technologies. However, several aspects need clarification or improvement to strengthen the paper's arguments and conclusions.

(1) Z1,2 exciton has much stronger absortion than Z3 (Fig. 1e), but why is photocurrent by Z1,2 exciton aborption much smaller than that by Z3(Fig. 1f)? What is the spectra of the light source like? Is it considered in the photocurrent spectra?

(2) In Figs. 3b and 3c, obvious n=2 Rydberg exciton absorption was detected by the photocurrent measurement. Why is it not shown in the absorption spectra?

(3) In Fig. 3d, when temperature is below 50 K, it seems that the responsivity of the exciton shift current decreased slightly. How is this explained?

(4) The author is required to give the calculation of the scissor operator as well as in stating whether it affects the absorption spectrum and exciton effects?

(5) Have exciton effects been considered in the displacement current and linear optical response (Fig. S8)?

(6) Incomplete writing of colour scale headings (Fig. S13f)

(7) Why do strain-free and -0.1 % strained CuI have exactly the same distribution of exciton envelope functions in k-space? (Fig. S13)

Reviewer #2 (Remarks to the Author):

The authors report a new study of the nonlinear photocurrent generation in CuI films. In particular, they find strong enhancement of the photocurrent generated when the laser is resonant with an exciton. Through careful polarization analysis they confirm the response is due to shift current. Via measurements of strained and unstrained films, they further show the response can be enhanced by increasing the net shift-vector. This is very nice work showing for the first time a shift current response from an exciton, a highly non-trivial result. I have only a few minor comments.

1) The authors claim in a few places, this might be useful for devices. While there was originally much hope for this, it is clear that, at least for energy recovery, the shift current cannot, in the end, be that useful. The problem is the need to generate both large voltages and large currents to extract high power. (see: arXiv:2211.15124). I suggest the authors remove this claim. However, it is true the nonlinear responses could be useful for ultrafast and polarization-sensitive detectors. Having said this, given the fundamental nature of this work, I think its best to stick to the importance of the discovery.

2) On line 133, page 7, it is stated that the photocurrent is measured with polarization at theta=0,90, but it is not clear what this angle is measured with respect to (crystal, contact etc) .

Reviewer #3 (Remarks to the Author):

In the manuscript titled "Gigantic shift current at exciton resonances in a noncentrosymmetric widegap semiconductor", the authors investigate experimentally the photocurrent generation in thin films of CuI. As their main findings, they report a substantial contribution to the current from excitonic states, which they attribute to an excitonic shift current based on the amplitude, sign, energy dependence, and polarization dependencies, as well as supported by ab-initio calculations.

The bulk photovoltaic effect describes the creation of a DC current under light irradiation which resonantly excites states across the bandgap, a fairly well-known nonlinear phenomenon which has recently received a lot of renewed attention after it was discovered that certain features of the band structure topology can enhance it. In non-magnetic systems and in response to linear polarized light, it is commonly believed that the BPVE originates entirely due to a mechanism called the shift current, which contains as a major ingredient the interband shift vector, a quantum geometric two-band quantity.

The present manuscript adds to this body of work by documenting and characterizing in substantial detail how the shift current is altered and enhanced due to the creation of bound excitonic states. The experimental aspects of the work, including sample creation, measurement, elimination of error sources and the identification of the signal as a nonlinear effect due to excitonic resonances, are explained well and convincingly substantiate the claims made in the abstract. Most importantly, the measured data is of high quality, enabling a straightforward analysis.

The ab-initio calculations seem ok, although an elaborate calculation like GGA+BSE is always difficult to judge in its entirety. I do not see any problems with the overall line of reasoning, even though I cannot be but surprised that the calculation seems to accurately reproduce the entire signal, which is usually not the case. In particular, when calculating the shift current, one normally needs to carefully choose the broadening factor (lifetime) to match the width (and thus height) of the narrow resonances. Which values were chosen in the present case? Similarly, if the thin film has low disorder, resonant scattering is expected to dominate the signal. Is there a particular reason why we can expect the signal seems to originate mostly (entirely?) from intrinsic (band structure) effects?

Let me also point out that the theory discussion, which seems to be added most recently, does not read as well as the remainder of the main text, and is somewhat disjointed from the flow of the previous discussion. I suggest to firstly motivate better what pieces of information gain can be sensibly expected from the calculation, but also to mention which parts of the excellent agreement between theory and experiment should be considered accidental or input dependent.

Secondly, I recommend to simplify the discussion of the shift vector and exciton properties in the strained case. This last point is relevant also because it has been pointed out (

10.1038/s41567-021-01465-z, 10.1103/PhysRevResearch.4.013209) that -yes- the shift current contains the shift vector, but it is not determined solely by it. For this reason, if the current level of detail is kept, there are additional matrix elements which also need to be examined. As far as I see it, the main reason for the large change of the excitonic shift current is the fact that the exciton is strongly localized in momentum at the Gamma point, which is one of the few momentum locations where the integrand contributes basically zero unless strain is applied: The crucial feature is the symmetry breaking, not the exact distribution of the shift vector.

One last note regarding the title, I'd advise to change the adjective "gigantic", which somehow implies that the shift current observed in CuI is much larger than in comparable (any?) other materials, which is not true. I suggest to use "strongly enhanced" instead, which - looking at Fig. 3 - accurately captures the observations.

In summary, this work provides a valuable contribution to the field of bulk photovoltaic responses. I think the manuscript would fit the scope of Nature Communications after the authors have improved the theory discussion and adjusted the title as detailed above.

Response to Reviewers' comments

Manuscript #: NCOMMS-23-54508A-Z

Paper title: Gigantic shift current at exciton resonances in a noncentrosymmetric widegap semiconductor

Reviewer #1

Overall, the work offers an interesting examination of how exciton effects impact nonlinear optical response, which has the potential to contribute to the field of optoelectronic and photovoltaic technologies. However, several aspects need clarification or improvement to strengthen the paper's arguments and conclusions.

Reply: All of the authors cordially thank the reviewer for providing his/her invaluable time to make an in-depth review of our paper. We are grateful to the reviewer for the positive feedback and recognition of the significance of this study. We also thank the insightful comments and suggestions necessary to improve our manuscript. In the following, we have responded to all these comments one by one and revised the manuscript accordingly. The revised parts in the resubmitted manuscript are indicated by red characters.

Comment 1: Z1,2 exciton has much stronger absortion than Z3 (Fig. 1e), but why is photocurrent by Z1,2 exciton aborption much smaller than that by Z3(Fig. 1f)? What is the spectra of the light source like? Is it considered in the photocurrent spectra?

Reply: We appreciate this important question. First, we note that the photocurrent spectra shown in Fig. 1f have been normalized by the intensity of the light source, whose spectrum is shown in Fig. R1. The light source spectrum is rather monotonous, and the intensities at the Z_3 exciton energy (~3.7 eV) and the $Z_{1,2}$ exciton energy (~3.05 eV) are not much different. This implies that the smaller photocurrent from the $Z_{1,2}$ exciton is not related to the normalization process.

We speculate that there are two possible reasons why the Z_3 exciton contributes to a much stronger shift current enhancement than the $Z_{1,2}$ exciton. One is related to the degeneracy in the

valence bands. In the $Z_{1,2}$ exciton states, two degenerate bands, the light-hole and heavy-hole bands, contribute to the shift current generation with opposite signs, and they are almost canceled out for the strain-free state, as explained in detail in response to the 4th comment of the Reviewer #3 as well as the theory part of the revised manuscript. On the other hand, the Z_3 exciton is free from such a cancelation of shift current associated with the band degeneracy, which might lead to a stronger shift current enhancement. The other possibility is related to the Fano resonance. The $Z_{1,2}$ exciton transition is located below the bandgap, whereas the Z_3 exciton transition is located within the continuum band. When a discrete quantum state coexists with a background continuum state like the Z_3 exciton, the interference between the two states can lead to an enhanced response as well as the phase shift in the discrete state, known as the Fano resonance, which might contribute significantly to the enhancement of the shift current. In the present study, we mainly focus on the shift current from the $Z_{1,2}$ exciton that is isolated from the continuum state. The shift current from excitons coexisting with the continuum state (Z_3 exciton) is beyond the scope of this study, and we would like to refrain from discussing it in detail in the present paper, although it is an important issue for the future. In the revised manuscript, we have inserted the following remark in the caption for Fig. 1e: "The spectra are obtained at the incident light polarization angle $\theta = 0$ and 90 degrees, and normalized by the light intensity."

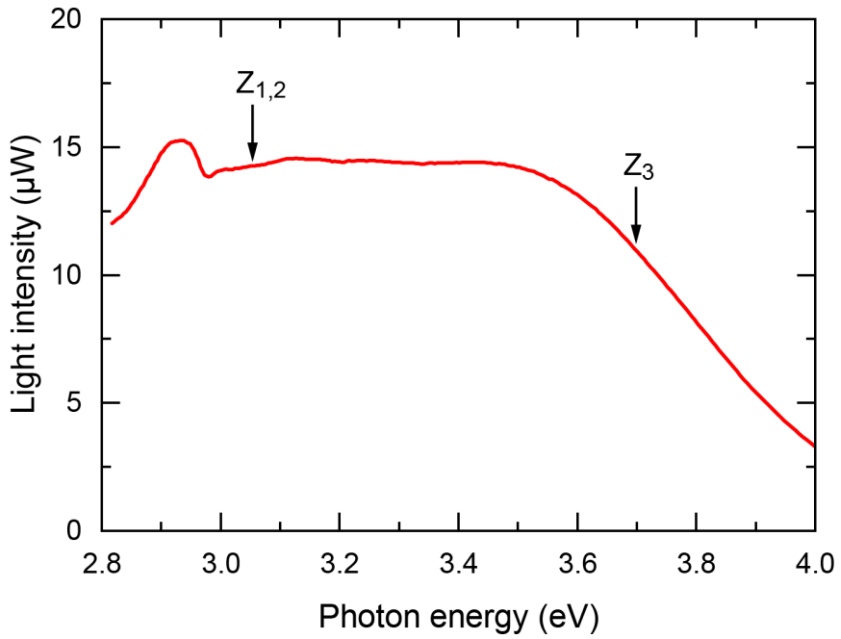

Fig. R1: Spectrum of the light source employed for the measurement of photocurrent spectra. The energies of $Z_{1,2}$ and Z_3 excitons are denoted by the arrows.

Comment 2: In Figs. 3b and 3c, obvious n=2 Rydberg exciton absorption was detected by the photocurrent measurement. Why is it not shown in the absorption spectra?

Reply: We appreciate this question. As the reviewer points out, the n=2 Rydberg exciton was clearly observed in the shift current spectra, whereas it is indiscernible in the absorption spectra. The situation is the same for the result of first-principles calculations including exciton effects shown in Fig. 4c and 4d. We consider that one possible reason is that the small signal from the Rydberg exciton is pronounced in shift current spectra due to the opposite signs of shift currents from exciton and continuum states. In contrast, in the absorption spectra, the tiny absorption peak from the Rydberg exciton may be hidden by the absorption tail of the continuum state due to their same sign. The impact of Rydberg excitons on shift current has been scarcely investigated so far, both experimentally and theoretically, and is an important future issue needed for a deeper understanding of exciton shift current. In the revised manuscript, we have inserted the following statement: "Note that the n=2 Rydberg exciton state is clearly observed only in the shift current spectra in both experiments and calculations. This is perhaps because the small signal from the Rydberg exciton is pronounced in shift current spectra due to the opposite signs of shift currents from exciton and continuum states."

Comment 3: In Fig. 3d, when temperature is below 50 K, it seems that the responsivity of the exciton shift current decreased slightly. How is this explained?

Reply: We appreciate this comment. We expect that shift current is actually nearly constant below 50 K, and the slight decrease might be attributed to uncertainties in the normalization process. As described in the Method section, we converted the observed shift current (J^{shift}) to shift current conductivity (σ) using the following relation,

$$\sigma = \frac{3}{\sqrt{6}} \frac{\alpha}{(1-e^{-\alpha d})(1-R)wE_0^2} J^{\mathrm{shift}}, \quad (1)$$

where α is the absorption coefficient, R the reflectance, E_0^2 the light intensity, d the film thickness, and w the diameter of the optical spot. This conversion is necessary because the

absorption and reflectance are strongly enhanced at exciton resonances and are highly temperature dependent, as shown in supplementary Fig. S7. Since the CuI thin film used for shift current measurements had electrodes attached to it, we used a different thin film for the measurement of α and R at each temperature. Although the two films were fabricated under the same conditions, they can have slight differences in absorption and reflectance at low temperatures because the optical responses at exciton resonances are very sensitive to the crystallinity of the samples. Suppose the difference in σ between 30 K and 50 K is solely due to the underestimation of the absorption coefficient, 2.5 % of correction is necessary at $Z_{1,2}$ exciton energy (8.0 % at Z_3 exciton energy), which is a reasonably small correction. In the revised manuscript, we have inserted the following sentence: "Note that the slight decrease in shift current conductivity below 50 K may be due to uncertainties in the absorption and reflectance used for the conversion from the observed photocurrent to conductivity."

Comment 4: The author is required to give the calculation of the scissor operator as well as in stating whether it affects the absorption spectrum and exciton effects?

Reply: We appreciate this comment. We obtain a band gap value of 2.12 eV from the one shot G0W0 calculations, which is about 1 eV smaller than the experimental value. To better compare with the experimental absorption spectrum, we made a scissor correction by applying an overall shift of 2.08 eV on the conduction band energy to match the experimental band gap and then solved the Bethe-Salpeter equation for excitons. The scissor shift leads to an overall shift of the kinetic energy of the electron-hole pair and is described by a constant shift in the diagonal part of the BSE Hamiltonian matrix elements in numeric. Such shift leads to a constant shift of all exciton eigenenergies and the absorption spectrum. We therefore do not expect any qualitative changes to the absorption spectrum and exciton effects. In the revised manuscript, we have inserted the following sentences in the Methods part: "We obtain a band gap value of 1.032 eV from the GGA calculation. To better compare with the experimental absorption spectrum, we made a scissor correction by applying an overall shift of 2.08 eV on the conduction band energy to match the experimental band gap (3.112 eV) and then solved the Bethe-Salpeter equation for excitons. The scissor shift leads to an overall shift of the kinetic energy of the electron-hole pair and is described

by a constant shift in the diagonal part of the BSE Hamiltonian matrix elements in numeric. Such shift leads to a constant shift of all exciton eigenenergies and the absorption spectrum."

Comment 5: Have exciton effects been considered in the displacement current and linear optical response (Fig. S8)?

Reply: We appreciate this question. Shift current and linear optical responses shown in Fig. S8 were calculated in the independent particle approximation without considering exciton effects. This is because the calculation employing the Bethe-Salpeter-Equation (BSE) method deals with all the Coulomb interactions between photoexcited electrons and holes, making the calculations and the interpretation of the results quite complex. The purposes of calculating the shift vector and linear optical response shown in Figs. S8 and S11 are to understand why the shift current from excitons has an opposite sign to that from the continuum state and why the exciton shift current is quite sensitive to strain. From these calculations without considering the exciton effects, we could reveal that the competition of the shift current from the two degenerate bands leads to such non-trivial exciton shift current responses. In the caption for Fig. S8 in the revised supplementary information, we have added the following remark: "In these calculations, we have not incorporated exciton effects to simplify the calculations and bring out the essence of the underlying physics."

Comment 6: Incomplete writing of colour scale headings (Fig. S13f)

Reply: We appreciate the reviewer for pointing out the incompleteness of the figure. We have revised Supplementary Fig. S13 as shown in Fig. R2.

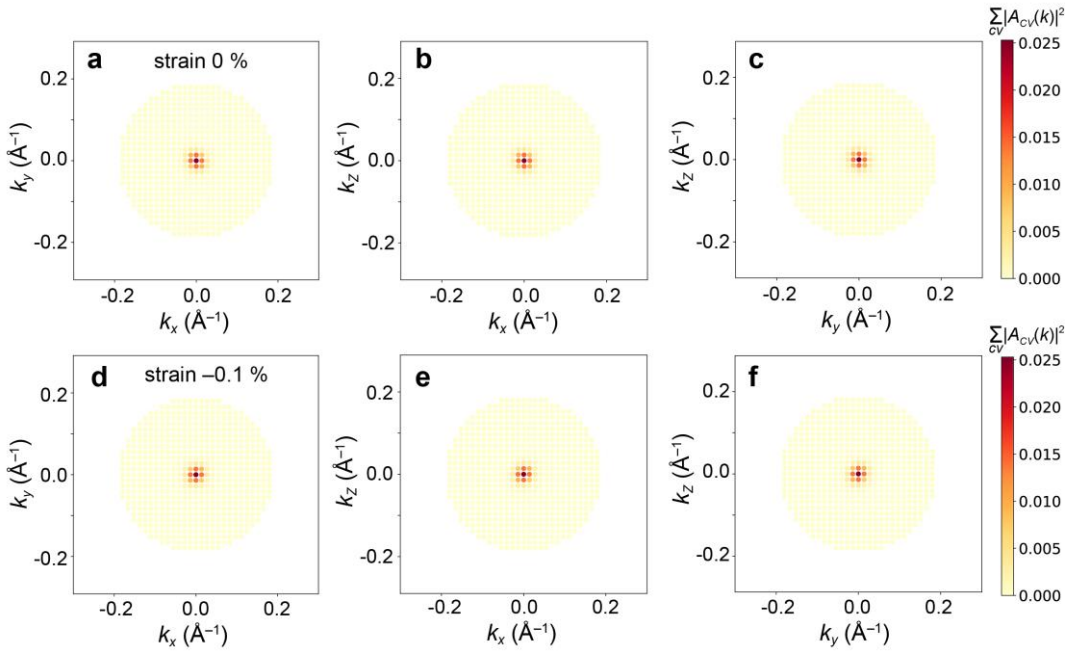

Fig. R2: Revised Fig. S13

Comment 7: Why do strain-free and -0.1 % strained CuI have exactly the same distribution of exciton envelope functions in k-space? (Fig. S13)

Reply: We appreciate this comment. The distribution of exciton envelope functions in k-space is basically determined by the band dispersion of the compound. Although the −0.1 % strain causes the lifting of the degeneracy between the light-hole and heavy-hole bands at the Γ-point, the resulting energy splitting (~3 meV) is much smaller than the bandgap (3.1 eV) and has a negligible influence on the k-space distribution of excitons. In fact, the exciton resonance peaks in the calculated linear optical spectra shown in Fig. 4d are almost unchanged by −0.1 % strain. On the other hand, shift current, which directly reflects the Berry connection of each electron band, is very sensitive to symmetry breaking and the associated small degeneracy lifting. In the revised Supplementary Note 12, we have added the following sentences: "Note that the distribution of exciton envelope function is almost unchanged between the strain-free and −0.1 % strained states. This is because the exciton distribution is basically determined by the band dispersion, and the band structure modulation induced by the −0.1 % strain is negligible for exciton states because the strain-induced band splitting (~3 meV) is much smaller than the bandgap (3.1 eV)".

Reviewer #2

The authors report a new study of the nonlinear photocurrent generation in CuI films. In particular, they find strong enhancement of the photocurrent generated when the laser is resonant with an exciton. Through careful polarization analysis they confirm the response is due to shift current. Via measurements of strained and unstrained films, they further show the response can be enhanced by increasing the net shift-vector. This is very nice work showing for the first time a shift current response from an exciton, a highly non-trivial result. I have only a few minor comments.

Reply: All of the authors cordially thank the reviewer for providing his/her invaluable time to make an in-depth review of our paper and positive feedback. We are very grateful to the reviewer for acknowledging the most important significance of this study, which is the first demonstration of a shift current response from an exciton, a highly non-trivial result. We also thank the constructive comments and suggestions necessary to improve our manuscript. In the following, we have responded to all these comments one by one and revised the manuscript accordingly. The revised parts in the resubmitted manuscript are indicated by red characters.

Comment 1: The authors claim in a few places, this might be useful for devices. While there was originally much hope for this, it is clear that, at least for energy recovery, the shift current cannot, in the end, be that useful. The problem is the need to generate both large voltages and large currents to extract high power. (see: arXiv:2211.15124). I suggest the authors remove this claim. However, it is true the nonlinear responses could be useful for ultrafast and polarization-sensitive detectors. Having said this, given the fundamental nature of this work, I think its best to stick to the importance of the discovery.

Reply: We appreciate this important suggestion. As the reviewer points out, shift current is potentially useful for sensing devices because of its ultrafast and polarization-sensitive natures, but it still has critical drawbacks when used in energy harvesting devices, particularly its small current magnitude. Moreover, the significance of this work is the first clear experimental demonstration of exciton shift current, which is important from a fundamental physics rather than applied standpoint. In the revised manuscript, we have changed the abstract and introduction

section to better emphasize the significance of this study from the fundamental research viewpoint as follows.

The sentence in the abstract "The present results reveal that the exciton effect can significantly improve the responsivity of the nonlinear photovoltaic effect, which offers a promising route for developing next-generation optoelectronic devices." is changed to "The present study reveals the crucial role of excitons in enhancing the shift current magnitude and its strain sensitivity, and will open a novel route for efficient manipulation of nonlinear optical effects."

The sentence in the introduction section "Shift current intrinsically possesses high robustness against carrier localization due to scattering and trapping as well as ultrafast responsivity to pulsed light due to the geometric origin[10-12], which are of crucial importance for photovoltaic and optoelectronic applications" is changed into "Shift current intrinsically possesses high robustness against carrier localization due to scattering and trapping as well as ultrafast responsivity to pulsed light due to the geometric origin[10-12], which have attracted significant interest both from fundamental and technological perspectives."

The sentence in the introduction section "These results indicate that excitons that do not involve free electron-hole pair have a potential for enabling high photovoltaic performance below the bandgap spectral region as well as ultrasensitive detection of external stimuli through the nonlinear shift current process." is changed into "These results indicate that excitons dramatically increase the magnitude and strain sensitivity of shift current, which will promote establishing deeper insight into light-matter interaction in the nonlinear regime. "

Comment 2: On line 133, page 7, it is stated that the photocurrent is measured with polarization at theta=0,90, but it is not clear what this angle is measured with respect to (crystal, contact etc) .

Reply: We appreciate this comment. We have not explicitly described the definition of light polarization direction in the original manuscript, although it is illustrated in Fig. 1d. The $\theta = 0$ and 90 degrees correspond to the polarization directions parallel to the $[11\bar{2}]$ and $[\bar{1}10]$ axes, respectively. In the revised manuscript, we have added the following description of the light polarization directions: "The measurements were performed at the incident polarization angle $\theta =$ 0 and 90 degrees, corresponding to the polarization directions parallel to the $[11\bar{2}]$ and $[\bar{1}10]$ axes, respectively, as illustrated in Fig. 1d."

Reviewer #3

In the manuscript titled "Gigantic shift current at exciton resonances in a noncentrosymmetric widegap semiconductor", the authors investigate experimentally the photocurrent generation in thin films of CuI. As their main findings, they report a substantial contribution to the current from excitonic states, which they attribute to an excitonic shift current based on the amplitude, sign, energy dependence, and polarization dependencies, as well as supported by ab-initio calculations.

The bulk photovoltaic effect describes the creation of a DC current under light irradiation which resonantly excites states across the bandgap, a fairly well-known nonlinear phenomenon which has recently received a lot of renewed attention after it was discovered that certain features of the band structure topology can enhance it. In non-magnetic systems and in response to linear polarized light, it is commonly believed that the BPVE originates entirely due to a mechanism called the shift current, which contains as a major ingredient the interband shift vector, a quantum geometric two-band quantity.

The present manuscript adds to this body of work by documenting and characterizing in substantial detail how the shift current is altered and enhanced due to the creation of bound excitonic states. The experimental aspects of the work, including sample creation, measurement, elimination of error sources and the identification of the signal as a nonlinear effect due to excitonic resonances, are explained well and convincingly substantiate the claims made in the abstract. Most importantly, the measured data is of high quality, enabling a straightforward analysis.

Reply: All of the authors cordially thank the reviewer for providing his/her invaluable time to conduct an in-depth review of our paper and positive feedback. We are very grateful that the reviewer deeply understands the significance of this work and appreciates the high quality and reliability of the experimental results. We also thank the insightful and constructive comments and suggestions. In the following, we have responded to all these comments one by one and revised the manuscript accordingly. The revised parts in the resubmitted manuscript are indicated by red characters.

Comment 1: The ab-initio calculations seem ok, although an elaborate calculation like GGA+BSE is always difficult to judge in its entirety. I do not see any problems with the overall line of reasoning, even though I cannot be but surprised that the calculation seems to accurately reproduce the entire signal, which is usually not the case. In particular, when calculating the shift current, one normally needs to carefully choose the broadening factor (lifetime) to match the width (and thus height) of the narrow resonances. Which values were chosen in the present case?

Reply: Thank you for this important question. As the reviewer points out, the peak height and width of the exciton resonances are very sensitive to the broadening factor. We set the broadening factor at 5 meV in the ab-initio calculations shown in this paper. This value was chosen so that the calculated linear optical spectrum reproduces the experimental result at the $Z_{1,2}$ exciton resonance. Figures R3a and b show experimental and calculated linear optical spectra. The calculated spectrum with a broadening factor (η) of 5 meV reproduces well the peak height and width of the $Z_{1,2}$ exciton resonance. We used the same broadening factor for the calculation of the shift current spectrum as shown in Fig. R3d, which also reproduces well the experimentally observed shift current peak from the $Z_{1,2}$ exciton state shown in Fig. R3c. In the revised manuscript, we have added the following sentence in the Methods section: "In the calculations, we set the broadening factor at 5 meV so that the calculated linear optical spectrum reproduces the experimental result at the $Z_{1,2}$ exciton resonance (see Supplementary Note 13)." We have also added Fig. R3 as Fig. S14 and noted the determination of the broadening factor in Note 13 in the revised supplementary information.

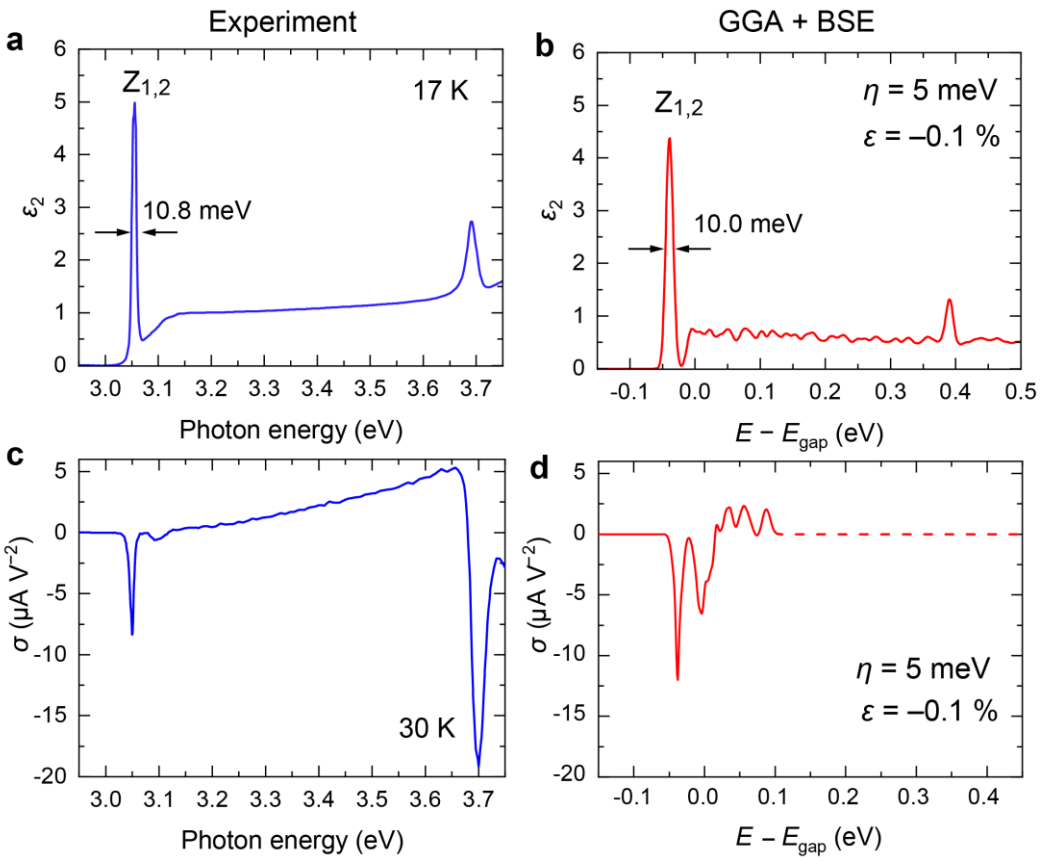

Fig. R3: (Added as the revised supplementary Fig. S14) Imaginary part of the dielectric constant obtained from the experiment at 17 K (**a**) and *ab initio* calculations including exciton effects (**b**). Excitation spectra of shift current conductivity obtained from the experiment at 30 K (**c**) and *ab initio* calculations including exciton effects (**d**). In these calculations, the broadening factor (η) and epitaxial strain (ε) are set at 5 meV and −0.1 %, respectively.

Comment 2: Similarly, if the thin film has low disorder, resonant scattering is expected to dominate the signal. Is there a particular reason why we can expect the signal seems to originate mostly (entirely?) from intrinsic (band structure) effects?

Reply: Thank you for this comment. As the reviewer points out, the optical response at exciton resonances is significantly affected by resonant scattering when the sample is less disordered. Most of the studies on resonant exciton scattering have been done in high-quality GaAs quantum wells, in which the linewidth of exciton resonance is typically below 1 meV (J. Hegarty *et al.*, Phys. Rev. Lett. **49**, 930 (1982), G. Kocherscheit *et al.*, Phys. Rev. B **68**, 085207 (2003)).

Although we believe the quality of our thin films to be the best in halids, the exciton linewidth is 10 meV, about one order of magnitude broader than that in GaAs quantum wells. Thus, we consider that the resonant scattering is still not dominant in our thin films. In fact, the theoretical calculations without consideration of the scattering effect are consistent well with the experimental results just by assuming the broadening factor, as shown in Fig. R3. Therefore, the present calculations considering only intrinsic effects capture the essence of underlying physics. However, if the sample quality is further improved, the effect of resonant scattering will be more pronounced and must be taken into account, which is an important issue for the future.

Comment 3: Let me also point out that the theory discussion, which seems to be added most recently, does not read as well as the remainder of the main text, and is somewhat disjointed from the flow of the previous discussion. I suggest to firstly motivate better what pieces of information gain can be sensibly expected from the calculation, but also to mention which parts of the excellent agreement between theory and experiment should be considered accidental or input dependent.

Reply: We appreciate this important suggestion. One of the most important motivations for the theoretical calculations is to elucidate the mechanism of the opposite signs between the exciton shift current and interband shift current. The exciton shift current is considered to originate from the transfer of the spectral weight partly from the continuum state in the noninteracting system to the exciton resonance below the bandgap (T. Morimoto and N. Nagaosa, Phys. Rev. B **94**, 035117). Therefore, the exciton and interband shift currents are expected to have the same sign, but this is not the case in the present CuI thin films. The *ab initio* calculations considering the exciton effect shown in Fig. 4c reproduce the negative exciton shift current and positive interband shift current. The agreement between theory and experiment is not only in the sign but also in the magnitude of the exciton shift current and the appearance of the n=2 Rydberg exciton state. In the calculation, the input parameters are only two: the broadening factor (η) of the exciton resonance and epitaxial strain (ε). As explained in response to the reviewer's first comment, we set η at 5 meV so that the calculated linear optical response reproduces the experimental result (Figs. R3a and b). The ε is set at −0.1 %, which is experimentally verified from optical spectra (Supplementary Note 9).

Therefore, we could obtain surprisingly excellent agreement between theory and experiment both in the linear and shift current responses only by setting these two parameters to reasonable values.

We further performed the calculations of the k-space distributions of the shift vector to provide a more intuitive understanding of the negative sign of the exciton shift current (Figs. 4e-h). They reveal that the two degenerate bands contribute oppositely to the shift current generation near the absorption edge (Figs. 4e-h), and under epitaxial strain, the splitting of the degenerate bands at the Γ-point and the strong localization of the exciton wavefunction in the momentum space result in the negative shift current at the exciton resonance.

We have revised the manuscript to clarify the purpose of the theoretical calculations, which is described in detail in the response to the reviewer's next comment.

Comment 4: Secondly, I recommend to simplify the discussion of the shift vector and exciton properties in the strained case. This last point is relevant also because it has been pointed out (10.1038/s41567-021-01465-z, 10.1103/PhysRevResearch.4.013209) that -yes- the shift current contains the shift vector, but it is not determined solely by it. For this reason, if the current level of detail is kept, there are additional matrix elements which also need to be examined. As far as I see it, the main reason for the large change of the excitonic shift current is the fact that the exciton is strongly localized in momentum at the Gamma point, which is one of the few momentum locations where the integrand contributes basically zero unless strain is applied: The crucial feature is the symmetry breaking, not the exact distribution of the shift vector.

Reply: We thank the reviewer for this important suggestion. We agree with the reviewer that the crucial feature is the symmetry breaking from cubic to rhombohedral due to strain. The current discussion based on the shift vector distribution is intended to provide a heuristic picture of the strain effects. In fact, our analysis of the matrix elements confirms the vital role of broken symmetry as demonstrated in the following.

To understand the effects of strain, we analyze the partial sum of the terms (let us call them the generalized oscillation strengths), which appear in the sum-over-state expression in our shift current calculation. In particular, let us consider the oscillation strength term

$$\sum_{S} \frac{X_S^b \Pi_{Sj}^a X_j^{c,*}}{(\hbar\omega - E^S + i\eta)(\hbar\omega - E^j - i\eta)},$$

where E^S is the exciton energy of state S, X_S^b is the excitonic dipole matrix elements of state S along b direction in the Cartesian coordinate, and Π_{Sj}^a is the inter-exciton velocity matrix elements between state S and j along the a direction. This term has a dominant contribution to the shift current due to its resonance structure in the denominator. In Fig. R4 below, we show the partial sums for fixed j indices with large contributions.

For the cubic case, we indeed find cancellations from different j states which leads to small shift current at 3.07 and 3.11 eV. In contrast, due to the strain-induced symmetry lowering, the cancellation is incomplete for the strained CuI and we observe a large shift current at those two energies.

While the symmetry lowering is crucial to the strain dependence of the exciton shift current, the symmetry argument alone is not enough to get insight into the opposite sign of shift current between the exciton and continuum states. As the reviewer noted, shift current is not determined solely by the shift vector, but it is a good quantity to roughly estimate the sign of the shift current. The distribution of shift vector shown in Figs. 4e-h provides an intuitive picture of this non-trivial sign change in shift current. The distribution indicates that the shift currents from the degenerate two bands cancel each other near the Γ-point in the strain-free state, whereas the negative-sign component dominates under compressive strain, which is reflected in the sign and magnitude of exciton shift current due to the strong exciton localization near the Γ-point. Thus, we consider that the above discussion based on the shift vector distribution is helpful for readers in understanding the underlying mechanism of the strain-dependent shift current in CuI thin films.

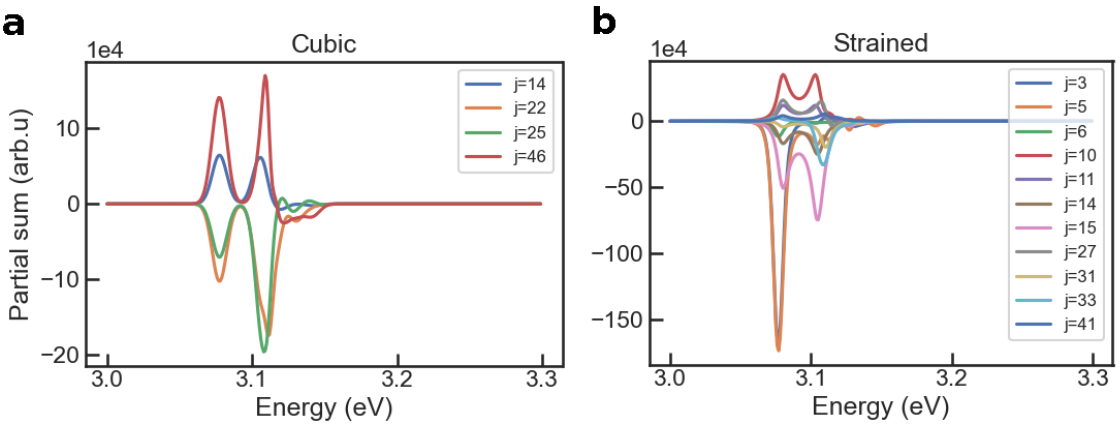

Fig. R4: Calculated partial sum of the generalized oscillation strengths for cubic (strain-free) (**a**) and rhombohedral (compressive strained) (**b**) CuI.

In the revised manuscript, we have totally rewritten the theory part to clarify that the symmetry reduction and the strong localization of exciton are essential for the large negative enhancement of exciton shift current. The following is the revised manuscript regarding the theoretical calculations:

"It is considered that exciton shift current originates from the transfer of the spectral weight partly from the continuum state in the noninteracting system to the exciton resonance below the bandgap[17]. Therefore, the exciton and interband shift currents are expected to have the same sign in general, but this is not the case in the present CuI thin films. We examined the mechanism for the opposite signs between exciton and interband shift currents from first-principles calculations. The generalized gradient approximation (GGA) was employed for band-structure calculations, and exciton effects in linear and nonlinear optical responses were computed by solving the Bethe-Salpeter equation (BSE)[18, 19] (Methods). The calculations were performed for a strain-free state and −0.1 % strain (very small compressive strain) states. As discussed later, it is revealed that our thin films are subjected to tiny strain, and symmetry reduction associated with the strain is crucial for the strong enhancement and its sign of the exciton shift current.

Figures 4a and 4b show the spectra of shift current conductivity (σ) and linear dielectric constant (ε_2) calculated without including the exciton effect for strain-free and −0.1 % strain states (more detailed strain dependences of σ and ε_2 are shown in Supplementary Fig. S8). The shift current conductivity exhibits a negative peak near the band edge, but the peak is broad and very small, not consistent with the experimental results. Then, we examined exciton effects by performing GGA+BSE calculations, as shown in Figs. 4c and 4d. The linear dielectric constant exhibits two clear peaks corresponding to the $Z_{1,2}$ and Z_3 exciton resonances. By setting the broadening factor to 5 meV, the peak height and width of the $Z_{1,2}$ exciton resonance are well reproduced (Supplementary Note 13 and Fig. S14). The shift current conductivity calculated using the same broadening factor shows a small positive peak in the strain-free state at the $Z_{1,2}$ exciton resonance, and the peak is strongly enhanced in the negative direction at −0.1 % strain. The spectrum under strain also exhibits an additional negative peak near the main peak corresponding to the n = 2 Rydberg exciton and positive sign in the continuum state. All these features of the calculated shift current spectra under −0.1 % strain are very consistent with the experimental result. The consistency is not only in the signs but also in their magnitudes (Supplementary Note 13 and Fig. S14). Note that the n=2 Rydberg exciton state is clearly observed only in the shift current spectra in both experiments and calculations. This is

perhaps because the small signal from the Rydberg exciton is pronounced in shift current spectra due to the opposite signs of shift currents from exciton and continuum states.

The above results suggest that the strain is crucial for the exciton shift current in CuI. The presence of strain in the present CuI thin films on CaF_2 substrates is verified by the reflectance spectrum, which shows two peaks at the $Z_{1,2}$ exciton resonance that indicate the split of the lh and hh bands due to symmetry lowering from cubic to rhombohedral structure by strain (Supplementary Fig. S9). The strain value estimated from the band splitting (3 meV) is about −0.1 % (Supplementary Fig. S10 and Table S1). This strain is due to the mismatch of the thermal expansion coefficient between CuI and CaF_2 (CuI: 1.6×10^{-5} K^{-1}, CaF_2: 1.8×10^{-5} K^{-1}), inducing about −0.1 % strain at low temperatures.

Hereafter, we discuss the reason for the high strain sensitivity of the exciton shift current based on a momentum-space distribution of the shift vector. Although shift current is not determined solely by shift vector[35,36], it is a good quantity to roughly estimate the sign of shift current. Figures 4e-h display the distribution of shift vector around the Γ-point on the k_x-k_y plane at $k_z = 0$ (4e and g) and k_a-k_z plane (4f and h), where k_x (or k_y) lies within the film plane, k_z is along the out-of-plane direction, and k_a is within the k_x-k_y plane as denoted in (4e and g) (see more details in Supplementary Fig. S11). The shift vector is calculated at the energy of the top of the negative peak as denoted in the inset of Fig. 4a ($E = E_{peak}$). In these calculations, exciton effects are not included to simplify the calculations and extract the essence of the underlying physics. In the strain-free state, shift vector in the k_x-k_y plane is positive while negative in the k_z direction (Figs. 4e and f). The anisotropic shift vector distribution is related to the degeneracy of the valence bands at the Γ-point, where the degenerate two bands have opposite contributions to the shift vector (see Supplementary Note 11 and Fig. S12 for more details). Thus, the integral of the shift vector around the Γ-point cancels out to nearly zero. When the strain is applied, the degeneracy is lifted by the symmetry reduction, and the shift vector becomes finite near the Γ-point (it is negative in compressive strain), as shown in Figs. 4g and h.

Excitons in CuI are strongly localized in the momentum space near the Γ-point, as shown in Supplementary Fig. S13. Therefore, shift current from the $Z_{1,2}$ exciton is expected to reflect the integrated shift vector around the Γ-point, nearly zero at strain-free and large negative value under compressive strain. This agrees well with the result of extensive first-principles calculations considering all electron-hole interactions shown in Fig. 4c. The present theoretical calculations

indicate that the symmetry reduction due to strain and strong localization of exciton in the momentum space play a crucial role in the large negative enhancement of shift current at the $Z_{1,2}$ exciton resonance observed in the experiment."

We have also added the following references in the revised manuscript.

35. Ahn, J., Guo, G.-Y., Nagaosa, N., & Vishwanath, A. Riemannian geometry of resonant optical responses. *Nat. Phys.* **18**, 290-295 (2021).

36. Kaplan, D., Holder, T., & Yan, B. Twisted photovoltaics at terahertz frequencies from momentum shift current. *Phys. Rev. Research* **4**, 013209 (2022).

Comment 5: One last note regarding the title, I'd advise to change the adjective "gigantic", which somehow implies that the shift current observed in CuI is much larger than in comparable (any?) other materials, which is not true. I suggest to use "strongly enhanced" instead, which - looking at Fig. 3 - accurately captures the observations.

Reply: We thank the reviewer for this thoughtful suggestion. In the revised manuscript, we have changed the title as follows, "Strongly enhanced shift current at exciton resonances in a noncentrosymmetric widegap semiconductor".

Comment 6: In summary, this work provides a valuable contribution to the field of bulk photovoltaic responses. I think the manuscript would fit the scope of Nature Communications after the authors have improved the theory discussion and adjusted the title as detailed above.

Reply: We thank the reviewer again for encouraging and constructive comments. As described in the above responses to your comments, we have revised the title and theoretical part of the manuscript. We now believe that the revised manuscript fits the scope of Nature Communications.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

In this article, the authors showed the generation of nonlinear photocurrent can be achieved by excitons within CuI. The enhancement from excitons onto the shift current was demonstrated experimentally and theoretically. In the revised manuscript, the concerns raised by the initial reviewers have been adequately addressed, and numerous beneficial additions have been made to the article. It now sufficiently demonstrates the significant role of excitons in the nonlinear photovoltaic response of low-dimensional materials. We recommend that the paper be accepted for publication.

Reviewer #3 (Remarks to the Author):

In the revised manuscript, the authors address the comments and suggestions of all three references in detail. The additions to the experimental section, and the new theory section present a considerable improvement for the overall line of argument, and in terms of presentation and clarity.

I have no further remarks beyond the ones mentioned in the previous report and recommend publication in its current form.