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Boosting the Solar Cell Efficiency by Flexo-photovoltaic Effect?

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The photovoltaic effect in p−n junctions has been widely studied and used to work as renewable energy sources for portable devices and various appliances. Due to the band gap energy of semiconductors in p−n junctions, carriers are excited by light and then are separated by an internal electric field built in the interface of the junctions, so that the light can be efficiently absorbed and converted into electricity. Nevertheless, the open-circuit voltage is limited by the band gap energy of the semiconductors. The bulk photovoltaic (BPV) effect, caused by the asymmetric distribution of photoexcited carriers in momentum space, can generate a large photovoltage under uniform illumination, which is far beyond its band gap of the corresponding semiconductor. However, the power generation efficiency is very low due to the unusually low short-circuit current, and the materials that exhibit the BPV effect are generally wide-band-gap noncentrosymmetric materials. Yang *et al.*[1] reported the flexo-photovoltaic (FPV) effect in which the BPV effect can be induced by strain gradients in any semiconductor through the flexoelectric effect. The authors claimed that the strain gradients create very large photovoltaic currents from centrosymmetric single crystals.

A silicon-made atomic force microscopy (AFM) tip with a typical radius size of only 8 nm was pressed on a single crystal with a size of more than 0.5 cm × 0.5 cm with a thickness of more than 0.5 mm to induce strain gradients on the bulk materials. They claimed "the current increases by more than a factor of 100 when the loading force increased from 1 to 18 μN" (actually, from Figure S12A, the current increased by only 3.39 times when the force increased from 1 to 15 μN). The nanosized AFM tip was treated as an ideal rigid spherical indenter, and the Hertzian model was applied to calculate the strain and strain gradient in order to confirm this AFM tip could generate the flexoelectric effect in bulk materials. The author claimed that the flexo-photovoltaic effect was discovered as the photocurrent has a dependence on crystallographic orientation and the light polarization with an amplitude of less than 2 pA. Above all, they believed this FPV effect played a dominating role in the increased photocurrent under strains.

Here, we focus on four aspects to discuss the data, mechanisms, and conclusions presented in Yang's paper and clarify some facts. First, the experimental design is unreasonable as many other issues involved are not properly addressed when the authors drew the conclusions. Second, the physical models adopted for the calculation analysis are irrational, and the results are based on unrealistic assumptions that far exceed the properties of any materials known. Third, the proposed physical model is based on speculation, and the experimental results do not fully support the physical model. Fourth, the statements made in the discussions and conclusions sections are misleading. Therefore, there are many questions and doubts to be clarified, and many statements need to be corrected. We provide some advice on both experimental methods and theoretical models toward the exact quantification of the FPV effect, which are fundamental and critical, to avoid misleading the scientific community and the public readers by the work from Yang and co-authors.

More details are elaborated as follows.

The Unreasonable Experimental Measurement and Design. Flexoelectricity effect is a coupling effect between electric polarization and strain gradient in centrosymmetric material, which was discovered several decades ago. Studies of flexoelectricity in solids have been scarce due to the extremely small magnitude of this effect in bulk samples.[2,3] The current studies are mainly focused on materials/structures at the nanoscale as the large strain gradients in nanomaterials can lead to a strong flexoelectric effect. Strain gradients are inversely proportional to size, so thin films are the obvious place to look for flexoelectric effects.[4] Because whenever the thickness exceeds some critical value, the materials may relieve the stress by a formation of misfit dislocations or by twinning,[5] whether the materials are single crystals or not. Yang *et al.* applied a point force exerted by the tip of a custom-made photoelectric atomic force microscope on the bulk materials with a size of more than 0.5 cm × 0.5 cm with a thickness of more than 0.5 mm to induce strain gradients on the bulk materials. Yang *et al.* did not try to do any experiment to verify whether the flexoelectric effect has been induced or not or measure the strength of the flexoelectric effect induced by the strains. Such important data are missing, and we cannot conclude that the AFM tip can generate the flexoelectric effect on these materials. Every material and every sample is different, including various Young's modules, surface roughness, defects, and it is inappropriate to guess that the effect can be obtained by comparing with other papers unless it has been verified experimentally. However, the polarization induced by the applied force has never been measured and verified.

A conductive AFM probe was employed for both applying pressure and acting as a conductive electrode. Such a design involves many complicated problems and errors. Smooth surfaces, even those polished, are never perfectly flat on a microscopic scale due to asperities. They are rough, with sharp or rugged projections (Figure 1a,b). Single crystals are never atomically flat after the processes of manufacturing and cutting.

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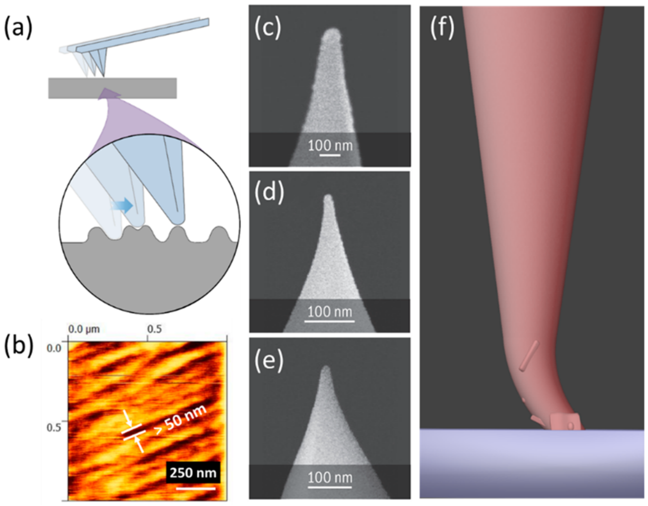

Figure 1. Contact issue of pressing an AFM tip on the surafce of bulk materials. (a) Contact situations of AFM tips when they are pressed to contact the surface of bulk materials. The AFM tips can be located at different positions. The shape, contact area, and angle of the AFM tip can be very different under different forces. (b) Surfaces of single crystals are not perfectly smooth (provided by the authors in Figure S7). The surfaces are rough on both nanoscale and microscale. (d–f) Scanning electron microscopy images of AFM tips from the vendor.[9] AFM tips can have different geometries.

The grooves on the surface of the crystal are as wide as 50 nm (Figure 1b), and the tip radius is only 8 nm. In such a small scale range, the contact of two objects is the contact of microcontact points scattered on the contact surface, and the number of contact points would be quite different each time at different sites and could gradually increase as the pressure increases. On the other hand, apexes of AFM tips have irregular shapes (Figure 1b–d) and would deform unpredictably at various forces from undefined directions. So the real contact area cannot be determined. In addition, from the vendor's information, the cantilever has a thickness of 4 μm, a width of 30 μm, and a length of 125 μm; the AFM tip is made of n-type silicon coated with platinum; the typical radius of the tip is only 8 nm, and the Pt-coated resulting tip radius is <30 nm, with a total tip height of 12–18 μm, which is extremely flexible at this scale. The Young's modulus of bulk silicon is 130–188 GPa;[6] in fact, it is much smaller at the nanoscale[7] and 209–218 GPa for TiO_2 (provided by the authors). Obviously, the nanoscale silicon tip is "softer" than the bulk TiO_2; therefore, when it touches a bulk single-crystal TiO_2, the tip would have a strain and deformation much larger than that of the bulk TiO_2 in this experiment. The tip cannot be pressed vertically on the rough surface of the materials; in most cases, there is always an angular relationship between the directions of the force and the contact surface, which would easily cause the probe to deform, bend, slide, and buckle (Figure 1f), which will significantly increase the contact area even under the elastic region of materials.

It is interesting to find that the spikes have been observed at the transition states when the applied force was increased (Figure 1C,D in Yang's paper). This would be caused by triboelectric effect, which demonstrates that the contact area may have been greatly changed when the force was increased. In Yang's paper, it is said that the tip is not seriously damaged, but it is still insurmountable that the tip is elastically deformed. Above all, the contact area could be greatly increased at various forces due to the deformation of the probe. Therefore, the dominating role in the current enhancement is still open to doubt. The AFMs have different geometries and sizes and have different types of deformation (Figure 1c–e). The authors oversimplified

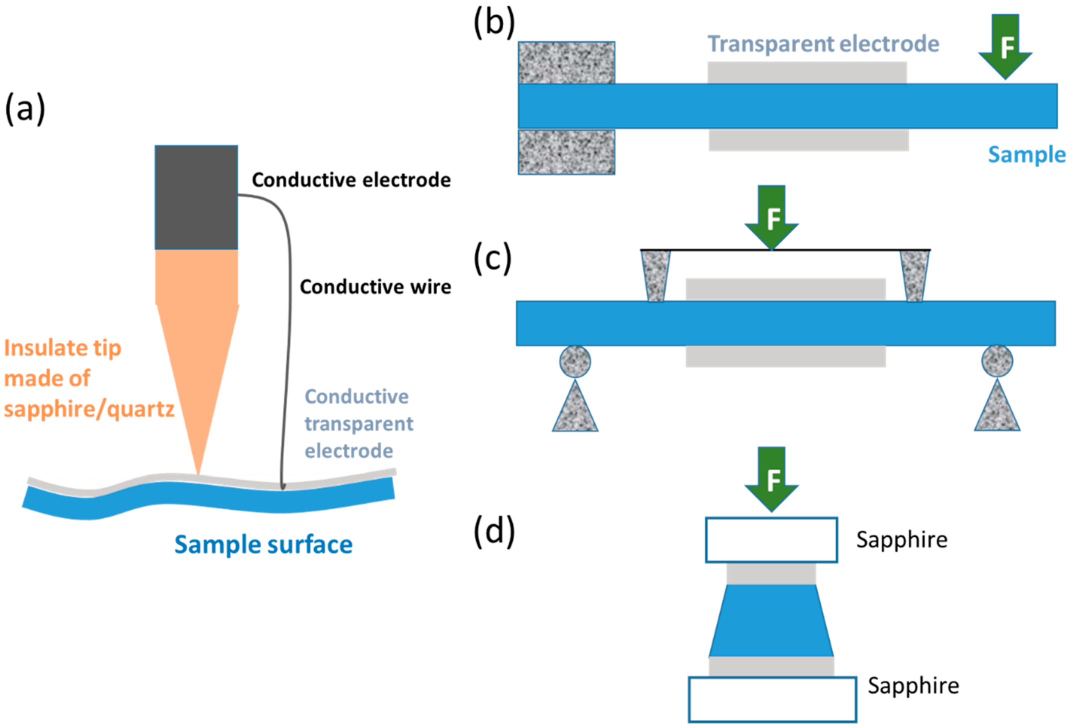

Figure 2. Schematics of suggested flexoelectric experimental setups for measurements of flexo-photovoltaic effect on bulk materials. (a) Measurement using an AFM tip for creating large local strains. (b–d) Methods for creating strains by cantilever bending (b), four-point bending (c), and pyramid compression (d).[10]

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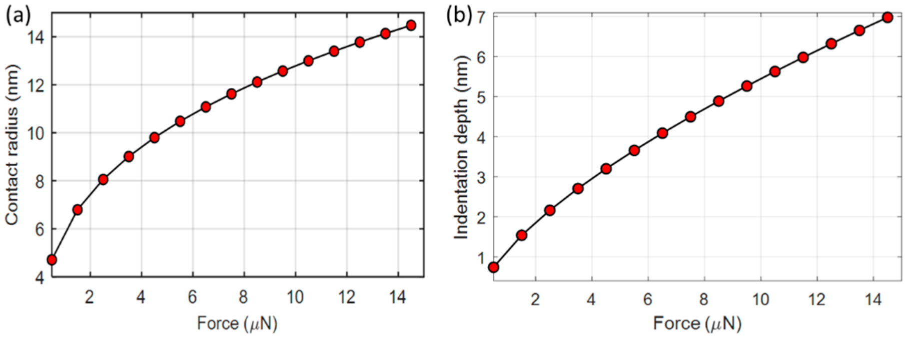

Figure 3. Contact radius (a) and indentation depth (b) dependence on the different applied forces.

the issues involved, and the problems that are raised have not been carefully and reasonably ruled out and avoided. In such experiments, applying external force by a conductive probe is not the right choice.

Second, at the nanoscale, the contact resistance will greatly change under various forces due to the change of geometry as a result of the applied mechanical stress. At the nanoscale, materials have a high value of electrical resistance, and the resistance would be less for a larger size or cross-sectional area.[8] When a larger force is applied on the tip, the resistance decreases significantly, with the probe firmly attached to the surface of bulk materials, which allowed more electrons to flow. The effect of contact resistance has been ignored in the discussion by the authors.

Last but not least, the choice of material for the AFM tip is irrational, and it does not match the physical model proposed by the author. As discussed above, Young's modulus of silicon for the AFM tip is much smaller than those of the single-crystal materials. The hardness of silicon is similar to those for the measured crystals (Mohs hardness values are ~6−6.5). So the AFM tip has a strain much higher than that at the surface of crystals. The physical model becomes more complex if the two materials both deform greatly. The Si-made AFM tip cannot be treated as an ideal spherical indenter assumed by the authors, and the authors cannot simply use the Hertzian contact model to calculate the strain gradient distribution. To induce larger strain gradients, harder materials such as sapphire or quartz should be used.

Above all, the authors did not have a good assessment of problems of the experimental design. To exactly quantify the measuring of the FPV effect, we have some advice below for the experimental setup. First, an insulated tip made of extremely hard materials, like sapphire or quartz, is used to press on the surface of the crystals. If the contact area is not fixed or well-controlled at various forces, the real contact area cannot be analyzed, and the contact issue is hard to be ruled out. Therefore, a conductive layer is coated at the top of the insulating tip to work as a conductive electrode. A conductive transparent electrode is coated on the sample surface. In this case, this AFM tip can be treated as an ideal spherical indenter, and the contact area would not increase as the applied force increases. Also, some other methods can be used for measuring the polarization on bulk materials (Figure 2b−d). To measure the dependence of crystal orientation, it is suggested to be conducted on the same device rather than two different devices. Alternatively, it is suggested to measure the photocurrent of the two devices first to make sure that originally they have the same photocurrent direction, and then after applying a force, one of their photocurrent directions has been reversed, whereas the other crystal has a different crystallographic orientation. This is important data to verify that the reverse of the photocurrent is indeed caused by the force not because of sample difference.

The Irrational Calculation and Analysis. To demonstrate that the strain gradients can be large enough to induce the flexoelectric effect, the distribution of strain gradients under the applied force was calculated by employing the Hertzian model by the authors. However, this violates the basic assumptions of the Hertzian theory, which leads to many errors and problems.

First, it violates one of the basic assumptions in the Hertzian theory that the contact area should be very small compared with the geometrical dimensions of two contact bodies ($a \ll R_1$ and R_2).[11] This will be numerically demonstrated in the following. By employing the Hertz theory, according to the material constants provided in the SCI, with $E_{\mathrm{TiO_2}} = 210$ GPa, $E_{\mathrm{Si}} = 190$ GPa, $\nu_{\mathrm{TiO_2}} = 0.28$, and $\nu_{\mathrm{Si}} = 0.26$, the radius of the sphere used by the author is 10 nm, and the contact radius and indentation depth are computed under different applied forces. The contact radius is

$$a = \left(\frac{3FR_0}{4E^*}\right)^{1/3}$$

and the indentation depth d is

$$d = \left(\frac{9F^2}{16R_0E^{*2}}\right)^{1/3}$$

where

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}$$

and R_0 is the radius of the sphere, E_1 and E_2 are the elastic modulus of the sphere and the plane, respectively, and ν_1 and ν_2 are the Poisson ratios associated with each body. The curves *versus* the applied force are shown in Figure 3. It can be seen that the contact radius is about 4.8 nm when $F = 1$ μN, and the contact radius is 12.8 nm when $F = 10$ μN, which is even larger than the radius of the AFM tip; this is contrary to the actual situation. Therefore, the contact area between the tip and substrate for the applied force cannot be evaluated by employing the Hertzian contact theory, and the strain cannot be estimated, as well.

Second, by assuming the tip is an ideal spherical indenter as the authors claim, the giant stress on the 10 nm radius of the silicon made tip is 1−2 orders higher than the fracture modulus of silicon.[7] This does not fit another basic assumption of Hertzian theory that the strain is small and within the elastic

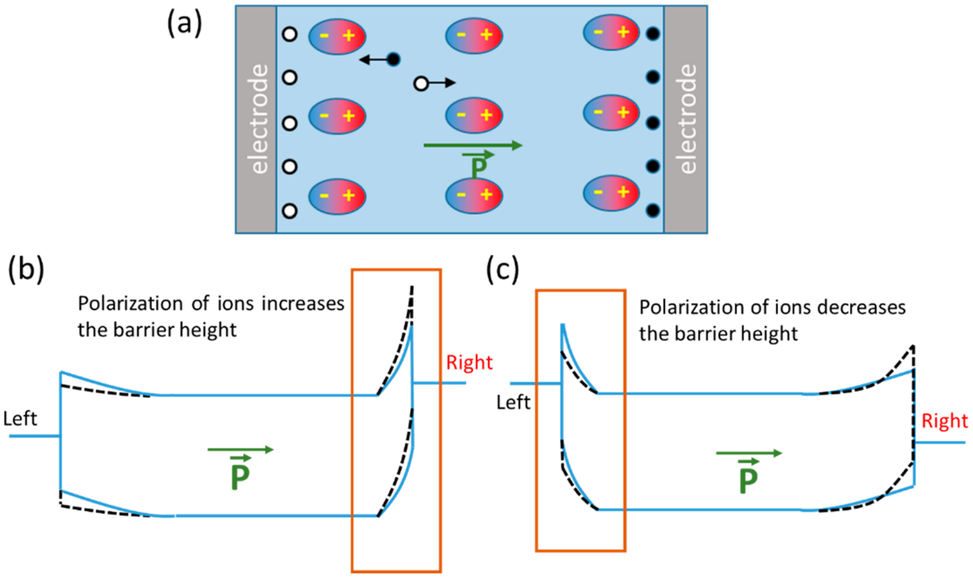

Figure 4. Influence of polarization on photocurrent. (a) Schematic illustration of the mechanism for photovoltaic effect in ferroelectric materials.[21,22] (b,c) Schematic energy band diagram for illustrating the polarization of ions on the barrier height when the right contact is reversely biased (b) and when the left contact is reversely biased (c). The polarization ions have an asymmetric effect on the two end contacts of Schottky junction.

limit. The silicon and the crystal cannot tolerate the stress, and they will break and become damaged. The authors provide the facts that both the tip and crystals have no obvious damage, which is contrary to the reasoning above. This demonstrates that the model proposed by the authors does not fit the real situation at all. On the other hand, the tip would more likely to release the stress by bending or buckling with a much larger contact area and a formation of misfit dislocations or by twinning.

The authors mistakenly ignored the deformation of the AFM tip when they calculate the ratio of the increase of the contact area under different loading forces. From this equation (Supporting Information, p9)

$$F = \frac{3}{4}E^{*}R^{1/2}d^{3/2} \text{ and } d = \frac{a^2}{R}$$

the authors took it for granted that R and E^* do not change, and $\frac{F_f}{F_i} = \left(\frac{a_f}{a_i}\right)^3$; therefore, they concluded that the ratio was independent of the materials' properties. However, in this formula, both d and R are strongly related to the materials' properties. According to Young's modulus for Si, TiO_2, and $SrTiO_3$, especially considering the shape and size of the materials, the Si-made AFM tip is at the nanoscale, and the single crystals are at centimeter scale; Si is relatively "soft" compared to the crystals. The geometry of the AFM tip changes under the giant stress, and the tip will have irregular and unpredictable deformations, as well. Therefore, the calculation of how the contact area changes as the applied force increases is not reliable. The authors did not fully analyze the mechanical properties of the materials and did not estimate the geometry change of the AFM tip; the calculated value of the contact area change is largely underestimated in their calculation. The influence of the contact area change in current cannot be overlooked. Another error has also been made in the equation listed in section S4; this is different from another reference,[12] in which the distance l between the electrodes is missing, and the correct expression is[13]

$$V_{OC} = I_{SC}l/(G_d + G_{ph})$$

The current density calculation is not reliable. First, the geometry of each AFM tip is different (Figure 1d−f); many factors such as contact angle, shape, and surface morphology of crystals would lead to the significant difference of the contact area when the materials are contacted (Figure 2a), and the actual contact area cannot be estimated. Second, when the external force is applied, the giant pressure would result in the geometry change, and the change of the contact area is also not achievable. Although the calculation processes are not provided by the authors, no matter how they calculate the values, the values are not worthy of trust unless they can find a way to measure the real value of the contact area and track its changes when the force was increased. Third, the authors employed a wrong physical model to calculate the contact area change. The value is greatly underestimated, and the calculated current density will certainly be magnified, remarkably larger than its real value. Therefore, the calculated data of the current density are not worthy of being dependable. The authors cannot claim the current density has 3 orders of magnitude of enhancement, which is significantly amplified.

The article is lack of direct and strong evidence that "FPV" effect plays a leading role in the increase of the photocurrent. The authors calculated the relative contribution of the "FPV" effect on the total photocurrent but unreasonably ignored all other factors (Figure S14), for example, the contact resistance change, the shape change, reflection/absorption, and many more. The authors unfairly assume the "FPV" effect must have been induced and it must be the only reason for the growth of current. The authors overlook the contribution from the Schottky junction, and there is no strong evidence to totally rule out all other possibilities that would contribute to the increase of photocurrent. This calculation significantly magnified the contribution of the "FPV" effect, which is inappropriate. In short, the strength of the flexoelectric effect induced in these bulk materials is really unknown.

Above all, the authors did not use a correct model to calculate the contact area change and the spatial distributions of strain and strain gradients. As the flexible probe would deform, bend, or buckle, the contact area calculated by this model is greatly underestimated. The contact area still plays an important role in photocurrent, but the influence cannot be evaluated in this experimental design by using the simple physical model employed by the authors. On the other hand, according to the mechanical properties mentioned above, an AFM tip should have a much higher strain than the bulk materials. Their results show that the strain at around $z = 5$ nm and right beneath the surface is as large as 50%, which is definitely not realistic (section S2, Figure S4). The calculated strain and strain gradients based on false assumptions were largely amplified, extremely higher than the real value of the data. To quantify the FPV effect, it is suggested to use the nonconductive hard materials such as sapphire to press the surface and coat a layer of transparent conductive material on the surface to fix the contact area. In this way, the Hertzian model can be used, the tip can be treated as an ideal spherical indenter, and the current density can be calculated accurately.

The Unsupported Physical Model. Flexoelectricity is a coupling effect between electric polarization and strain gradient. The strain gradient breaks its inversion symmetry and results in the piezoelectric effect in centrosymmetric materials.[14] The bulk photovoltaic effect is inherent only in piezoelectric and ferroelectric crystals[15] and relies on the polarization-induced internal electric field (Figure 2). The polarity induced by strains and strain gradients should modulate the characteristics of the two end contacts in an asymmetric or opposite manner.[16−20] In general, the negative polarization charges and hence the negative potential induced at the semiconductor side can result in increased local barrier heights, whereas the positive polarization charges and hence the positive potential can result in decreased local barrier heights (Figure 4b,c). Consequently, the current shows a different modulation effect by the polarization charges (*i.e.*, the current decreases at positive external bias and increases at a negative bias). However, from Figure S12, as the force increases, the current increase in nearly the same trend at both negative bias and positive bias. Considering the flexibility of the nanosized silicon tip and less than 20 times improvement of the current, it is very likely that the enhancement is caused by the increase of the contact area and the decrease of the contact resistance, which is very similar to the piezoresistive effect. This can be easily explained by the equation of the resistance R:

$$\mathrm{R} = \frac{\rho L}{A}$$

where L is its length, A is the cross-sectional area, and ρ is the conductivity. After a larger force is applied, the contact area increases (as discussed in section 1), and the length of the tip and the thickness of the crystal also decrease due to the extremely high pressure, so that the contact resistance decreases. The experimental results demonstrate that the "FPV" effect has no polarity of induced charges; this is contradictory to the proposed physical model by the authors, and it is still doubtful that the "FPV" effect caused the enhancement of current.

The open-circuit V_{OC} is the integration of photovoltage of both conventional photovoltaic effect caused by the Schottky junction V_{photo} (Figure S14) and the "FPV" effect V_{FPV}:

$$V_{\mathrm{OC}} = V_{\mathrm{photo}} + V_{\mathrm{FPV}}$$

If it is true as it was claimed that, for noncentrosymmetric materials with a large photoconductivity, the resultant V_{FPV} is very small, then $V_{\mathrm{OC}} \approx V_{\mathrm{photo}}$, and the value of V_{OC} remains constant. Thus, for the same device, the direction of the photocurrent would not be changed under the same value of V_{OC} and the photocurrent would have no dependence on the crystallographic direction. Interestingly, the experimental data show some conflicting results. The data presented in Figure S12C suggests that the V_{OC} shifts from positive to negative, which contradicts the results of Figure S12A,B,D in which V_{OC} remains the same, and this could not be explained. In addition, for the $\mathrm{TiO_2}$, it is suggested that the BPV effect reversed an original negative current into the opposite (Figure 1D,F), then V_{FPV} should be much larger than V_{photo} and in an opposite sign, so that the BPV effect could generate a photovoltage that could shift the V_{OC} from positive to negative. However, the measured V_{OC} remained the same (Figure S12B). The current can not change its direction without changing the direction of the voltage. What's more, under the flexoelectric effect, the materials will be polarized when they are subject to an inhomogeneous deformation. The larger forces will produce greater strain gradients, resulting in a larger polarization by the flexoelectric effect. From the results presented by the authors, the photovoltage generated by the BPV effect should increase as the force increases. If the current has increased by a factor of 100 by increasing the strains, then the voltage caused by the strain-induced polarization should be changed greatly, but their experimental results show that the V_{OC} is independent of the force. All of these data could not explain how the photocurrent significantly increased without any change of voltage and polarization from the flexoelectric effect.

The authors claim the photocurrent cannot merely be attributed to a Schottky contact because the observed PV effect depends on crystallographic orientation. However, two different samples were used, and it was assumed that the sample with the (100) face is analogous to the (001) face in all other respects. This assumption is weak; there are many dissimilarities, as well, for example, the different properties of different samples manufactured at different conditions with different surface states or have different doping concentration, defects concentration, and so on. However, the reverse direction of photocurrent is just because of the Schottky junction or other factors rather than the "FPV" effect. From Figure S14A in the Supporting Information, we could find that $\mathrm{TiO_2}(001)$ originally generated positive photocurrent by the Schottky contact; from Figure 1 and Figure S12, $\mathrm{TiO_2}(100)$ may naturally produce negative photocurrent by the Schottky contact. In this case, we could not conclude that the "BPV effect" changes the direction of the current. The hypothesis that the BPV effect is the origin of this photocurrent enhancement is unconvincing as it stands.

The authors commit a fallacy of oversimplification. They attribute all the enhancement of current to the FPV effect (Figure S14), which is, of course unreasonable. There are several major factors contribute to the enhancement of current other than the "FPV" effect, such as contact area, resistance, internal electric field, band gaps, absorption/reflection, and many more. It is worth noting that the applied stress influences the band gap. These are all ignored by the authors. The data of the relative contribution of the "FPV" effect on the total photocurrent are ineffective and somehow misleading. In addition to the effect of force on flexoelectricity and BPV effect, the authors should also consider the effect of flexoelectric on the Schottky junction, which produces a piezoelectric effect that affects the energy bands or junction barrier, similar to the piezo-phototronic effect.[23] This is quite different from the BPV effect. The light polarization dependence of photocurrent cannot demonstrate the relative contribution to the photocurrent enhancement. Therefore, it is fallacious reasoning unless other possible causal explanations have been considered, evaluated, and ruled out. Without solid evidence, the flexo-photovoltaic effect is not responsible for the improved current by pressing the tip onto the surface of the sample.

The authors did not use the proposed model to explain why the nanoscale area range of strain gradient could have such a giant influence on the photocurrent by the conventional PV effect. Even though the authors overestimate the strain gradients by using the unconscionable model, the affected area is still below 100 nm. Considering the photovoltage does not change as the force increases (Figure S12 in Yang's paper), it is still open to doubt that whether this extremely small area affected by the local stress can generate a strong polarization to reverse the flowing direction of all photoexcited carriers (Figure 1F in Yang's paper). The authors have not given any explanation of these experimental results for why the photocurrent can be greatly improved without any change of polarization.

Yang *et al.* pointed out that the light polarization dependence of the short-circuit photocurrent is the fingerprint feature of the BPV effect. However, the amplitudes of the sine waves are only 1−2 pA for various materials, which is extremely small as compared with the total photocurrent (55 pA, Figure 4C in Yang's paper), so the results show that the measured photocurrent does not have a strong dependence on light polarization at all. A typical signal of strong light polarization dependence of short-circuit photocurrent is shown in Figure 5.[24−26] Normally, if the measured current is strongly dependent on the light polarization, the baseline should be close to 0. As the photocurrent has low dependence on light polarization, it is hard to determine that the photocurrent is mainly generated by the FPV effect. The dominating role on the photocurrent should not be the FPV effect.

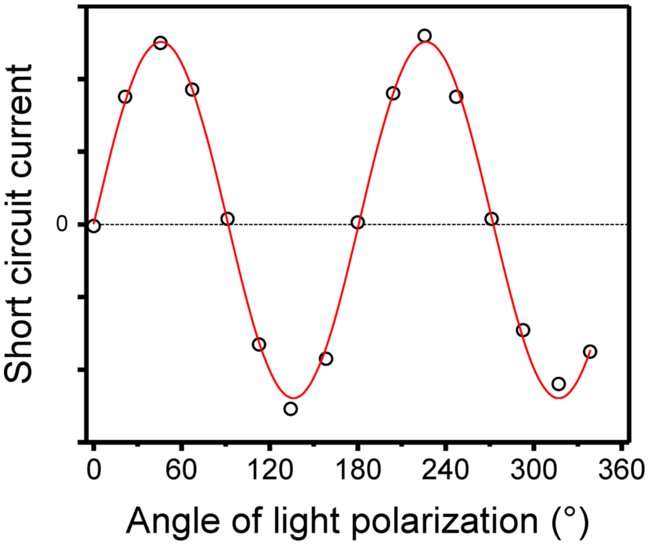

Figure 5. Typical signal of light polarization dependences of short-circuit current. The sine waves oscillate between zero or close to zero. Otherwise, the signals have low dependence of light polarization.

Yang *et al.* claimed the governing mechanism of the photocurrent is the FPV effect and derived the equation for the measured photocurrent as

$$I_{\mathrm{FPV}} = \frac{\pi}{2} I_0 (A_Z + B_Z \cos 2\alpha)$$

and the current should be determined by A_Z and B_Z. From Figure 3 and 4 in Yang's paper as the I_{FPV} has a small dependence of α and the amplitudes of the sine wave are very small, then

$$B_Z \ll A_Z$$

however, from the expressions of A_Z and B_Z, this is impossible.

By the BPV effect, the increase of the applied force leads to larger strain gradients, resulting in local centrosymmetry breaking; hence it is expected that this will lead to a large BPV effect and a larger current. Excellent linearity was found between the output charge *versus* applied force.[27] However, the measured results in this paper do not follow the trend. The proposed model cannot well explain the experimental result of why the current tends to have a saturation limit as the force grows. Instead, the study[28] of the influence of contact area on current density shows that the current at small contact areas is comparatively more variable and area-dependent. There is a plateau in current or current density when the geometric contact area grows to a relatively large value, which is very consistent with the experimental results in the article (Figure 1e and Figure S13 in the article).

Above all, the measured results cannot verify that the flexoelectric effect and BPV effect have been induced, and the enhancement of photocurrent is mainly caused by the "FPV" effect.

Logical Errors and Misleading Statements. There are many claims, statements, and conclusions in the article that are not correct, misleading, and have logical errors.

The authors present inconsistent data in the article: from the data provided,[29] we can read the short-circuit current values I_{SC} are 0.75 pA and 2.55 pA under the force of 1 and 15 μN, respectively, which is increased by only 3.39 times when the loading force was increased by a factor of 15. This is different from the values shown in Figure 1C,E. Similarly, for other materials, we did not find there is much improvement for I_{SC} measured under the forces (Table 1). The claim from the authors that the values have increased by 2 or 3 orders of magnitude is not real.

The calculation of the current density has a lot of uncertainties because the real contact area is not measured and it is hard to obtain the current density in such an experimental design as the tips always have irregular shapes and unpredictable deformation under extremely high pressure. It is tricky to divide a small current by another indeterminate tiny value of the contact area to get a large current density value. Against the claim that the "FPV" effect can create very large photovoltaic currents, we only find current values are just at the scale of nA or even pA level. Regardless of the use of large or small probes, the value is still quite small. Therefore, it is inappropriate to claim it generates very large photocurrent by the BPV effect or the large photovoltage as claimed in Yang's paper.

The authors gratuitously assume that the current density has a linear relationship with the contact area and arbitrarily think that if it is because of contact issue then "the contact area should also increase 100 times to have an increase of the current density by more than a factor of 100". However, no evidence is stated to support the linear relationship between contact area and

Table 1. Enhancement of Current as the Applied Force Increases[a]

	Index	Force / Current (A)	Force / Current (A)	Improvement (times)
AFM tip	Fig. S12 A	1μN	15μN	3.39
		-7.53E-13	-2.55E-12	
	Fig. S12 B	1μN	9μN	10.64
		-2.28E-12	-2.43E-11	
	Fig. S12 C	0.5μN	13μN	20.05
		1.94E-11	3.88E-10	
Micro-indenter	Fig. S12 D	1N	10N	7.99
		-1.75E-10	-1.40E-09	
	Fig. S13	1N	7N	7.80
		-3.69E-11	-2.88E-10	
	Fig. S14 A (⌀=10 μm)	0 N	6 N	7.40
		8.10E-14	6.00E-13	
	Fig. S14 A (⌀=50 μm)	0 N	6 N	4.23
		1.63E-13	6.89E-13	
	Fig. S14 A (⌀=50 μm)	0 N	6 N	2.14
		4.17E-13	8.92E-13	

[a] The data are provided by the author.[29] The improvements of photocurrent are less than 20 times.

photocurrent. It is more likely that the bending or buckling of the AFM tip will greatly increase the contact radius, and the changes of the contact area and contact resistance will greatly improve the current output when the contact area grows from a radius of several nanometers to tens of nanometers.

The authors conclude that the efficiency of solar cells can be improved by the "BPV effect" based on little information that the photocurrent has been enhanced by pressing the AFM tip. As we know, the efficiency depends on many factors: the band structure, reflection/absorption, short-circuit current, open-circuit voltage, defects, and many more. An array of indenters will influence the reflection and absorption, and the extremely high pressure on the materials would cause defects, like mismatch, dislocation, twinning, and many other defects. It has many negative impacts on the solar cell performance and lifetime. Bulk photovoltaic effect unusually provides extremely large photovoltage, but the current is unusually low. The open-circuit voltage presented in Yang's paper is still below its band gap (Figure S12), and its current is at nA scale; there is no information provided to demonstrate that an extremely large current can be obtained by using a large-scale tip or arrays of nanotips and little evidence to show that the efficiency of solar cells could be improved by the "FPV" effect.

Solar cells are operated under illumination from sunlight, which is incoherent and polychromatic; however; in Yang's work, locally strained single crystals of $SrTiO_3$, TiO_2, and Si were illuminated under a coherent and monochromatic (405 nm wavelength) polarized laser light. The experimental test results under incoherent, polychromatic, and relatively weak diffuse sunlight are required to prove that BPV (FPV) solar cells actually exceed the Shockley−Queisser efficiency limit in the standard condition. There is no solid evidence to prove the claim that the "FPV" effect is "free from the thermodynamic Shockley−Queisser limit".[30] Actually, the efficiency of BPV exceeding the Shockley−Queisser limit has already been shown to be invalid.[31]

Overall, the experimental results and proposed mechanisms cannot explain the 30 errors and concerns:

(1) The authors have not provided direct evidence to prove the flexoelectric effect has been induced and any data about the strength of the flexoelectric effect induced by the AFM tip. The polarization caused by the flexoelectric effect has not been measured and verified.

(2) The authors have not provided strong evidence to prove the bulk photovoltaic effect has been induced. The light polarization dependence of photocurrent is really very weak compared with the total photocurrent, which does not fit the typical signals of BPV effect.

(3) The data in Figure S12 and Figure 1C does not match! From Figure S12, the $\underline{I_{SC}}$ is only increased by about 3 times when the loading force was increased by a factor of 15. The short-circuit currents I_{SC} do not exhibit 2 or 3 orders of magnitude improvement.

(4) It is inappropriate to use a conductive AFM tip for applying the external force. This will cause significant contact issues and induce many uncertainties. The influence of contact issues cannot be ruled out.

(5) The actual contact area at various forces is not achievable due to asperities.

(6) The AFM tips have irregular shapes and would have unpredictable deformations, and the real contact area is not achievable.

(7) The impact of contact area change on the current is underestimated considering the mechanical properties of the AFM tip. The calculation of the contact area change is based on an unrealistic assumption. There is not sufficient evidence to prove the Schottky junction is not the main origin of the current enhancement.

(8) The suspected triboelectric signals have been observed at the transition states when the applied force increased, suggesting that the contact area has been changed greatly when the force increases, and the contact issue is significant and cannot be ignored.

(9) The contact resistance will greatly decrease as the force increases due to the change of geometry under the giant mechanical stress, but this has been not taken into consideration by the authors.

(10) The authors picked up the silicon-made AFM tip to induce large strain gradient in bulk materials. The silicon is soft compared to the other materials (TiO_2, $SrTiO_3$), and nanoscale silicon is very flexible. The AFM tip will have much more strains than the bulk materials. The large strain gradient cannot be achievable by using the silicon-made AFM tips.

(11) The authors have not provided evidence that the photocurrent of the TiO_2 sample with a (001) face has been reversed by the BPV effect. The TiO_2 sample with a (001) face without force originally has a different direction of photocurrent.

(12) It is unreasonable to assume the silicon-made AFM tip is an ideal spherical indenter, as the AFM tip has a larger strain than that of the bulk materials according to the mechanical properties of materials.

(13) The Hertz theory model employed by the authors is not suitable for this case as it violates one of the basic assumptions—the contact area is not much smaller than the geometrical dimensions of the two contact bodies.

(14) By using Hertz theory, the calculated radius of the contact area under the applied force can be larger than the AFM tip radius (10 nm), which is unrealistic.

(15) By assuming the AFM tip is ideal indenter, the tip has such giant stress which is much larger than the material limit of silicon, the AFM tip will break and damage. This does not fit the real situation.

(16) The radius change of an elastic sphere R and the displacement d are all strong depend on the properties

of the materials; however, the authors thought they remain unchanged under various forces. Therefore, the calculation of the ratio of increase of the contact area with the loading force is wrong.

(17) The calculation of strain and strain gradient has been greatly magnified based on an unrealistic assumption (the AMF tip is an ideal indenter) and an unfit physical model Hertzian theory. They cannot be utilized to show the strain gradient is large enough to induce the flexoelectric effect.

(18) The current density calculation is definitely not reliable. The real contact area cannot be achieved.

(19) The relative contribution of the "FPV" effect on the total photocurrent is significantly magnified. All other factors that lead to the enhancement of photocurrent were ignored by the authors when they calculated the results, which is, of course unconvincing.

(20) Under the flexoelectric effect, the materials have a polarization voltage at a large force and would cause the open-circuit voltage V_{OC} change, but the V_{OC} remains constant in most materials measured, which does not fit the proposed physical model.

(21) The V_{OC} data from different materials are conflicting with each other. The V_{OC} of Si shifts at various forces, but the V_{OC} of other materials do not shift at all. The data have no consistency, and the results cannot demonstrate their mechanisms.

(22) The experimental results show that the BPV effect is a symmetric effect on the two end contacts of the Schottky junction, but this does not fit the physical model.

(23) The data presented are not able to show that the signals are mainly from the BPV effect.

(24) The authors did not explain why the extremely small size scale of strain gradients (<10 nm) could have such a giant influence on the photocurrent and its photocurrent for large size (0.5 cm) bulk materials.

(25) The photocurrent quickly reaches a saturated value as the force increases. This cannot be well explained by the proposed mechanism in this article, but this could be well explained by other models.

(26) Not just the BPV effect, but some other effects also have some dependence on light polarization. This is not the fingerprint of the BPV effect. The extremely low dependence of light dependence cannot support the physical model, instead this may be caused by absorption and other effects.

(27) Even some of the photocurrent might come from the BPV; it is still unknown how much it contributes.

(28) It is said that the "FPV" effect can create very large photovoltaic currents, but we only find the current at the nA or pA level. It is tricky to divide a small number by another indeterminate small number, as the contact area cannot be evaluated.

(29) There is little information about the BPV effect on the efficiency of solar cells. The current is low, and the photovoltage is still below the band gap energy. Many factors such as reflection, mismatch, dislocation, and other defects would destroy the performance and lifetime of devices.

(30) There is no evidence to prove the observed "FPV" effect is free from the thermodynamic Shockley−Queisser limit.

In summary, although Yang *et al.* did notice that the measured current was increased as the applied force increases. However, the current only has less than 20 times improvement (Table 1) rather than 2−3 orders of magnitude as claimed. The enhancement of current has been hugely exaggerated. Other factors that lead to the enhancement of current have not been addressed with either solid evidence or careful evaluation. The experimental results cannot support the proposed physical model proposed by the authors. The experiment setup goes against the basic assumptions of the physical models employed by the authors, and the calculation results of strain and strain gradients are untrustworthy. This cannot prove the flexoelectric effect has been introduced. The two TiO_2 samples originally have different current directions as they are different samples (Figure 1D and Figure S14A); this was generated without applying force. The measured photocurrent signals have an extremely low dependence on light polarization with an amplitude of only 2 pA, compared to total photocurrent, and the center of the sine wave is far away from zero, which does not fit the BPV model. The 30 major questions and concerns obviously go against the claims made by the authors, which cannot be explained by using their model. The whole article is full of errors, problems, and misleading claims from the beginning to the end, including the experimental design, computational analysis, physical models, statements, and conclusions, which are quite misleading to the readers. Although the proposed mechanism may somehow be realized, definitely the presented experimental results by the authors did not provide any valid evidence to prove the existence of the flexoelectric effect and BPV effect, and the enhanced current is mainly due to the "FPV" effect. Therefore, it is critical to point out the errors, problems, and concerns, so that the researchers would not be misled by the paper. We also propose some strategies to accurately measure the bulk photovoltaic effect under strains.

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REFERENCES

(1) Yang, M. M.; Kim, D. J.; Alexe, M. Flexo-Photovoltaic Effect. *Science* **2018**, *360*, 904−907.

(2) Zubko, P.; Catalan, G.; Tagantsev, A. K. Flexoelectric Effect in Solids. *Annu. Rev. Mater. Res.* **2013**, *43*, 387−421.

(3) Majdoub, M. S.; Sharma, P.; Cagin, T. Enhanced Size-Dependent Piezoelectricity and Elasticity in Nanostructures Due to the Flexoelectric Effect. *Phys. Rev. B* **2008**, *77*, 125424.

(4) Lu, H.; Bark, C.-W.; Esque de los Ojos, D.; Alcala, J.; Eom, C. B.; Catalan, G.; Gruverman, A. Mechanical Writing of Ferroelectric Polarization. *Science* **2012**, *336*, 59−61.

(5) Matthews, J. W.; Blakeslee, A. E. Defects in Epitaxial Multilayers. *J. Cryst. Growth* **1974**, *27*, 118−125.

(6) Hopcroft, M. A.; Nix, W. D.; Kenny, T. W. What Is the Young's Modulus of Silicon? *J. Microelectromech. Syst.* **2010**, *19*, 229−238.

(7) Furmanchuk, A. o.; Isayev, O.; Dinadayalane, T. C.; Leszczynska, D.; Leszczynski, J. Mechanical Properties of Silicon Nanowires. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 817−828.

(8) Cao, Q.; Han, S. J.; Tersoff, J.; Franklin, A. D.; Zhu, Y.; Zhang, Z.; Tulevski, G. S.; Tang, J. S.; Haensch, W. End-Bonded Contacts for

Carbon Nanotube Transistors with Low, Size-Independent Resistance. *Science* **2015**, *350*, 68−72.

(9) Mikromasch Product Catalogue https://www.spmtips.com/pdf_downloads/MikroMasch-Product-Catalogue.pdf (accessed 06/12).

(10) Wang, B.; Gu, Y.; Zhang, S.; Chen, L.-Q. Flexoelectricity in Solids: Progress, Challenges, and Perspectives. *Prog. Mater. Sci.* **2019**, DOI: 10.1016/j.pmatsci.2019.05.003.

(11) Johnson, K. L. *Contact Mechanics*; Cambridge University Press, 1987.

(12) Fridkin, V. M. Bulk Photovoltaic Effect in Noncentrosymmetric Crystals. *Crystallogr. Rep.* **2001**, *46*, 654−658.

(13) Lee, D.; Yoon, A.; Jang, S. Y.; Yoon, J. G.; Chung, J. S.; Kim, M.; Scott, J. F.; Noh, T. W. Giant Flexoelectric Effect in Ferroelectric Epitaxial Thin Films. *Phys. Rev. Lett.* **2011**, *107*, 057602.

(14) von Baltz, R.; Kraut, W. Theory of the Bulk Photovoltaic Effect in Pure Crystals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1981**, *23*, 5590−5596.

(15) Tagantsev, A. K. Piezoelectricity and Flexoelectricity in Crystalline Dielectrics. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *34*, 5883−5889.

(16) Wu, W. Z.; Wen, X. N.; Wang, Z. L. Taxel-Addressable Matrix of Vertical-Nanowire Piezotronic Transistors for Active and Adaptive Tactile Imaging. *Science* **2013**, *340*, 952−957.

(17) Zou, H. Y.; Li, X. G.; Peng, W. B.; Wu, W. Z.; Yu, R. M.; Wu, C. S.; Ding, W. B.; Hu, F.; Liu, R. Y.; Zi, Y. L.; Wang, Z. L. Piezo-Phototronic Effect on Selective Electron or Hole Transport through Depletion Region of Vis-Nir Broadband Photodiode. *Adv. Mater.* **2017**, *29*, 1701412.

(18) Wu, W. Z.; Wang, Z. L. Piezotronics and Piezo-Phototronics for Adaptive Electronics and Optoelectronics. *Nat. Rev. Mater.* **2016**, *1*, 201631.

(19) Wang, Z. L. Progress in Piezotronics and Piezo-Phototronics. *Adv. Mater.* **2012**, *24*, 4632−4646.

(20) Wang, Z. L. Piezopotential Gated Nanowire Devices: Piezotronics and Piezo-Phototronics. *Nano Today* **2010**, *5*, 540−552.

(21) Ji, W.; Yao, K.; Liang, Y. C. Bulk Photovoltaic Effect at Visible Wavelength in Epitaxial Ferroelectric Bifeo3 Thin Films. *Adv. Mater.* **2010**, *22*, 1763.

(22) Zhang, G. H.; Wu, H.; Li, G. B.; Huang, Q. Z.; Yang, C. Y.; Huang, F. Q.; Liao, F. H.; Lin, J. H. New High Tc Multiferroics $KBiFe_2O_5$ with Narrow Band Gap and Promising Photovoltaic Effect. *Sci. Rep.* **2013**, *3*, 01265.

(23) Wang, Z. L.; Wu, W. Z. Piezotronics and Piezo-Phototronics: Fundamentals and Applications. *Natl. Sci. Rev.* **2014**, *1*, 62−90.

(24) Burger, A. M.; Agarwal, R.; Aprelev, A.; Schruba, E.; Gutierrez-Perez, A.; Fridkin, V. M.; Spanier, J. E. Direct Observation of Shift and Ballistic Photovoltaic Currents. *Sci. Adv.* **2019**, *5*, eaau5588.

(25) Nakashima, S.; Hayashimoto, R.; Fujisawa, H.; Shimizu, M. Bulk Photovoltaic Effects in Mn-Doped Bifeo3 Thin Films and the Optical Strains. *Jpn. J. Appl. Phys.* **2018**, *57*, 11UF11.

(26) Choi, T.; Lee, S.; Choi, Y. J.; Kiryukhin, V.; Cheong, S. W. Switchable Ferroelectric Diode and Photovoltaic Effect in Bifeo3. *Science* **2009**, *324*, 63−66.

(27) Lu, J. F.; Lv, J. Y.; Liang, X.; Xu, M. L.; Shen, S. P. Improved Approach to Measure the Direct Flexoelectric Coefficient of Bulk Polyvinylidene Fluoride. *J. Appl. Phys.* **2016**, *119*, 094104.

(28) Rothemund, P.; Morris Bowers, C.; Suo, Z.; Whitesides, G. M. Influence of the Contact Area on the Current Density across Molecular Tunneling Junctions Measured with Egain Top-Electrodes. *Chem. Mater.* **2018**, *30*, 129−137.

(29) Kim, D. J. Data for flexo-photovoltaic effect; http://wrap.warwick.ac.uk/100429/ (accessed 7/5/2019).

(30) Kirk, A. Comment on Flexo-Photovoltaic Effect; https://science.sciencemag.org/content/360/6391/904/tab-e-letters.

(31) Kirk, A. P.; Cardwell, D. W. Reconsidering the Shockley-Queisser Limit of a Ferroelectric Insulator Device. *Nat. Photonics* **2017**, *11*, 329−329.