Enhancing Photocurrent of Radially Polarized Ferroelectric BaTiO₃ Materials by Ferro-Pyro-Phototronic Effect

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HIGHLIGHTS
We present a new method to realize photocurrent enhancement in BaTiO₃ materials

The fabricated device enables fast sensing of 365-nm light illumination

The principle relies on the ferro-pyro-phototronic effect of BaTiO₃
Enhancing Photocurrent of Radially Polarized Ferroelectric BaTiO$_3$ Materials by Ferro-Pyro-Phototronic Effect

Kun Zhao,$^{1,2}$ Bangsen Ouyang,$^{1,2}$ and Ya Yang$^{1,2,3,*}$

SUMMARY
The pyro-phototronic effect has been utilized to modulate photoexcited carriers, to enhance the photocurrent in semiconducting nanomaterials. However, most of these materials have low pyroelectric performances. Using radially polarized ferroelectric BaTiO$_3$ materials with a pyroelectric coefficient of about 16 nC/cm$^2$K, we report a dramatic photocurrent enhancement due to ferro-pyro-phototronic effect. The fabricated device enables a fast sensing of 365-nm light illumination with a response time of 0.5 s at the rising edge, where the output current-time curve displays a sharp peak followed by a stable plateau. By applying a heating temperature variation, the output current peak can be enhanced by more than 30 times under a light intensity of 0.6 mW/cm$^2$. Moreover, the stable current plateau can be enhanced by 23% after utilizing a cooling temperature variation, which can be well explained by ferro-pyro-phototronic-effect-induced energy band bending.

INTRODUCTION
Over the past decade, investigations of photocurrent in ferroelectric materials have attracted particular attention related to the use of polarization-induced inner electric field to achieve the effective separation of photo-generated charges (Grinberg et al., 2013; Choi et al., 2009; Cao et al., 2012). Recent advances about enhancement of photocurrent in ferroelectric materials include large stain gradients (Chu et al., 2015), nanostructures on the ferroelectric material surface (Spanier et al., 2016), and electric field control over domain structures (Yang et al., 2010). There has been no report about temperature variation dependence of photocurrent in ferroelectric materials, despite its importance for developing light-heating coupled device applications. Pyro-phototronic effect is based on the related three-way coupling among semiconductors, pyroelectricity, and photoexcitation, which has been utilized to enhance interfacial charge transfer for improving the photovoltaic performances of ZnO nanowire-based solar cells and photodetectors (Zhang et al., 2016; Wang et al., 2017). However, it has remained a challenge to achieve larger modulation of photocurrent in the reported semiconducting ZnO nanowire since it has a low pyroelectric performance with a corresponding pyroelectric coefficient of about 1.5 nC/cm$^2$K (Yang et al., 2012). As a result, it is necessary to exploit the other pyroelectric materials for enabling the next generation of high-performance pyroelectric-photovoltaic devices. Some ferroelectric materials can have much better pyroelectric performance than ZnO nanowires, such as Pb(Zr,Ti)O$_3$ (Vats et al., 2016; Guo et al., 2007; Ko et al., 2016; Zhang et al., 2017), BaTiO$_3$ (Ban and Alpay, 2003), and LiNbO$_3$ (Savage, 1966; Weis and Gaylord, 1985), where BaTiO$_3$ is a prototypical lead-free ferroelectric material with a moderate Curie temperature ($T_c = 120^\circ$C) (Dubourdieu et al., 2013). Moreover, these ferroelectric materials also have dramatic photovoltaic performances under short-wavelength light illuminations (Ichiki et al., 2004; Paillard et al., 2016). Instead of using semiconductor materials, a pyroelectric effect-induced inner electric field in ferroelectric materials can be also utilized to enhance the separation of electrons and holes induced by light illumination. Herein, the related three-way coupling among ferroelectric materials, pyroelectricity, and photoexcitation can be termed as the ferro-pyro-phototronic effect, as illustrated in Figure 1A. The fundamental issues of the pyroelectricity dependence of photocurrent in ferroelectric materials, and of the possible enhancement of photocurrent by heating or cooling temperature variations, become crucial.

In this work, we utilized the temperature-variation-induced ferro-pyro-phototronic effect in radially polarized BaTiO$_3$ film with a pyroelectric coefficient of about 16 nC/cm$^2$K to enhance the photocurrent of the device under 365-nm ultraviolet (UV) light illumination. The photocurrent of polarized BaTiO$_3$ film exhibits a sharp current peak followed by a stable current plateau as well. Under a light intensity of 0.6 mW/cm$^2$, the output current peak can be significantly enhanced by more than 30 times by applying an external heating.
temperature variation. Moreover, the stable photocurrent plateau can be increased by 23% after using an external cooling temperature variation, which can be well explained by ferro-pyro-phototronic-effect-induced energy band bending at the interfaces between BaTiO3 and indium tin oxide (ITO) electrodes. These results present a major step toward the exploitation of pyroelectric-photovoltaic devices for energy scavenging and self-powered sensing applications.

RESULTS

Fabrication of Radially Polarized BaTiO3 Device

Figure 1B is a schematic diagram of a radially polarized BaTiO3 device under UV light illumination, wherein the transparent ITO on the surface of a BaTiO3 film was utilized as electrodes. The BaTiO3 precursor nanowires were synthesized by an electro-spinning method with a large area of 32 cm x 32 cm, as displayed in Figure 1C. The obtained BaTiO3 precursor nanowires have diameters less than 500 nm (Figures 1D and S1A). To remove the organic materials on the surfaces of BaTiO3 nanowires, the fabricated samples were sintered at 1,200 °C in 6 hr. The corresponding X-ray diffraction patterns (Figure S1B) indicate that the BaTiO3 nanomaterials after being sintered at 1,200 °C have an orthorhombic phase. The BaTiO3 precursor nanowires after being sintered are changed to BaTiO3 nanoparticles with diameters ranging from 300 nm to 1.5 μm (Figures S1C and S1D). Good dispersion of the BaTiO3 nanoparticles can be found after
an effective mechanical lapping (Figures S1E and S1F). The BaTiO3 film can be obtained by sintering the extruded nanowires-polyvinyl alcohol (PVA) mixtures under a pressure of 9 MPa; the corresponding SEM image of the BaTiO3 film exhibits a good connection between the adjacent BaTiO3 particles. A laser engraving method was utilized to fabricate planar ITO electrodes on the surface of BaTiO3 film (Figure 1E). A high voltage was applied between the two planar ITO electrodes to realize the radial polarization of the BaTiO3 film. Figure 1F is a photograph of the fabricated device with 10 pairs of engraved ITO electrodes, the device having a diameter of about 25 mm and a thickness of about 1 mm.

Photovoltaic and Pyroelectric Performances of Radially Polarized BaTiO3 Device

Figures 2A and 2B illustrate the measured output voltage (A) and current (B) signals of the device (N = 10) under individual light illumination and heating and cooling conditions. (C and D) Comparison of the measured output voltage (C) and current peak (D) signals of the different devices with different ITO electrode pair numbers. (E) Measured output voltage and current peak signals of the device (N = 10) under different temperature variation rates. (F) Calculated pyroelectric current coefficients of the device (N = 10) under different temperature variation rates. See also Figures S2–S11.
output voltage and current signals can be observed when a cooling temperature variation was applied. The effect of ITO electrode pair number on the performance of device has been also investigated by designing different electrode pair numbers ranging from 2 to 10 (Figure S2). The comparisons of the output voltage and current peaks of these devices are displayed in Figures 2C and 2D by the analysis of measured voltage/current-time data (Figures S3–S6). A slight increase of output voltage under light illumination or heating/cooling conditions can be observed (Figure 2C). Moreover, the output photovoltaic current exhibits a dramatic increase from 18.3 nA to 38.1 nA on increasing the ITO electrode pair number, although a small variation can be seen for pyroelectric current.

The pyroelectric performance of radially polarized BaTiO$_3$ device with 10 ITO electrode pairs was systematically investigated by measuring the output current and voltage signals under different temperature variation rates. The corresponding temperature variation distribution and temperature-time curves can be recorded by using an infrared thermometer (Figures S7 and S8). The output voltage and current signals of the device were measured under different temperature variation rates (Figures S9 and S10). Under a cooling temperature variation rate of $-1.14$ K/s, the output current is about $-35.27$ nA, whereas the output current is about 29.26 nA under a heating temperature variation rate of 1.25 K/s. By analysis of these data, it can be found that both the output voltage and current signals scale linearly with the temperature variation rate, as illustrated in Figure 2E. The pyroelectric current coefficient can be described as $P_C = I/(A \cdot dT/dt)$, where $I$ is the pyroelectric current, $A$ is the electrode area, and $dT/dt$ is the temperature variation rate (Lang, 2005). Under the cooling temperature variation conditions, the corresponding pyroelectric current coefficient can be calculated to be about 16 nC/cm$^2$K (Figure 2F), which is 10 times larger than that of the reported ZnO nanowires (1.5 nC/cm$^2$K). Moreover, it is 7.6 times larger than that of the reported Ag/BTO/Ag device with a vertical structure (2.1 nC/cm$^2$K) (Ma and Yang, 2017). The pyroelectric current coefficient decreases with increasing temperature, which is associated with a lower polarization intensity under a higher temperature. Moreover, the BaTiO$_3$ has a Curie temperature of 120°C (Dubourdieu et al., 2013), and there is no spontaneous polarization if the temperature is larger than 120°C. Thus the pyroelectric current coefficients exhibit a slight decrease under the heating temperature variation conditions, as displayed in Figure 2F. Meanwhile, we calculated the pyroelectric current coefficient of the device with different numbers of ITO electrodes, showing that the electrode effective area of the device decreases with an increase in the number of electrodes. The pyroelectric current coefficient exhibits a slight increase with an increase in the number of ITO electrodes under the same temperature variations (Figure S11).

Photocurrent Enhancement of Radially Polarized BaTiO$_3$ Device

The heating-induced pyroelectric effect has been utilized to enhance the UV light response. Since the silver electrode is opaque to UV light, the fabricated Ag/BTO/Ag device exhibited only pyroelectric effect and did not show photovoltaic effect (Ma and Yang, 2017). Ferro-pyro-phototronic effect utilizes a temperature variation-induced pyroelectric electric field to modulate photoexcited carriers for enhancing photocurrent in ferroelectric materials owing to the coupling among ferroelectric material, pyroelectricity, and photoexcitation. BaTiO$_3$ is a ceramic material with a low carrier concentration and a high pyroelectric coefficient. There is no obvious screening effect of photo-excited carriers on the pyroelectric polarization of BaTiO$_3$. As a comparison, ZnO nanowire is a semiconductor with relatively higher carrier concentration and lower pyroelectric coefficient (Yang et al., 2012), which may result in a significant screening effect. Figure 3A depicts the output current signals of the device under different UV light illuminations, where the output current increases with increasing intensity of UV light. As presented in Figure 3B, a sharp current peak followed by a stable plateau can be seen under simultaneous light illumination and heating temperature variation. The current peak increases with increasing light intensity, whereas the stable current plateau is smaller than that of individual UV light illumination. Figure 3C illustrates the output current data under simultaneous light illumination and cooling temperature variation, indicating that the current plateau can be effectively enhanced by the cooling temperature variation. The corresponding output voltage signals of the devices under individual UV light illumination and simultaneous light-temperature variation also exhibit similar changing tendency (Figure S12). To compare the change of photocurrent under different conditions, the output current peak signals of the device in Figures 3A–3C are displayed in Figure 3D, indicating that a heating temperature variation can be utilized to enhance the output current peak signals of the device. Under a light intensity of about 0.6 mW/cm$^2$, the photocurrent of the device under simultaneous UV light illumination and heating temperature variation can be enhanced by more than 30 times when compared with the photocurrent of the device under individual light illumination (Figure S13). The enhancement ratio of photocurrent decreases with increasing light intensity. In Figure 3D, the current value of $I_2$-$I_1$ (light + cooling) is larger than that of $I_2$-$I_1$ (light + heating), which is associated with
the larger pyroelectric coefficients under cooling conditions (Figure 2F). The output photocurrent plateau signals of the devices under the different conditions are displayed in Figure 3E, indicating that a cooling temperature variation can be used to enhance the photocurrent plateau. The enhancement ratio increases with decreasing light illumination intensity (Figure S13B), whereas the corresponding photocurrent can be enhanced by about 23% under a light intensity of 0.6 mW/cm². Because both peak current and plateau current signals generated by the light illumination are small at the low light intensity (0%–15%), the current peak and plateau enhancement ratios are large. With the increase of the light intensity, both peak current and plateau current signals generated by the light illumination are slowly increased, so the enhancement rate tends to be saturated.

Figure 3. Photocurrent Enhancement of Radially Polarized BaTiO₃ Device
(A) Measured output current signals of the device under 365-nm UV illumination with different light intensities, where \( I_1 \) is the current peak, \( I_{1-1} \) is the current plateau.
(B and C) Measured output current signals of the device under simultaneous light illumination with different intensities and temperature variations with a heating temperature change rate of 1.25 K/s (B) and a cooling temperature change rate of −1.08 K/s (C), where \( I_2 \) and \( I_3 \) are the current peaks and \( I_{2-1} \) and \( I_{3-1} \) are the current plateaus.
(D and E) Comparison of the measured output current peak (D) and plateau (E) signals of the devices under the different light intensities.
See also Figures S12–S15.
To evaluate the UV light detection sensitivity of the device, both the responsivity $R = I_{\text{ph}}/(PS)$ and specific detectivity $D^* = R/(2e \cdot I_{\text{dark}}/S)^{0.5}$ were calculated by using the experiential data in Figure 3D, where $I_{\text{ph}}$ is the photocurrent, $P$ is the incident light intensity, $S$ is the effective irradiated area, and $e$ is the electronic charge (Zheng et al., 2016; Dhar et al., 2016). Under a light intensity of 0.6 mW/cm$^2$, the calculated responsivity values of the device under individual light illumination and simultaneous light-heating conditions are $2.3 \times 10^{-7}$ A/W and $71.7 \times 10^{-7}$ A/W, respectively (Figure S13C). They are 2.8 and 117.5 times larger than those of the reported Ag/BTO/Ag device in the coupled lighting and heating conditions ($6.1 \times 10^{-8}$ A/W) (Ma and Yang, 2017). The corresponding specific detectivity values of the device under individual light illumination and simultaneous light-heating conditions are 11.9 Jones and 378.8 Jones, respectively. When compared with individual light illumination, the heating-induced ferro-pyro-phototronic effect leads to a huge enhancement of both the responsivity and the specific detectivity by more than 30 times under a light intensity of 0.6 mW/cm$^2$, although the enhancement ratio can be decreased with increasing light intensity (Figure S13D). We also investigated the response time of the device to UV light illumination (Figure S14), clearly showing that the fabricated device exhibits a good photoresponse component with a rise time of 0.5 s and a fall time of 0.2 s, where the time was calculated between 10% and 90% of the photocurrent signal when the UV light was turned on and off, respectively. We also measured the stability of device under more than 240 cycles in 24 hr (Figure S15), where a constant output voltage peak of about 0.62 V in all cycles indicates an excellent stability for the fabricated device.

**The Mechanism for the Enhancement of Photocurrent Plateau**

To identify the effect of ferro-pyro-phototronic effect on the photocurrent plateau further, we measured photocurrent signals of the device under individual light illumination ($81.8$ mW/cm$^2$), heating (1.25 K/s), and simultaneous light-heating conditions, as displayed in Figure 4A. It can be seen that the photocurrent under simultaneous light-heating condition is not simple superposition of the photocurrent signals under individual light and heating conditions. When compared with individual light illumination, the photocurrent plateau can be decreased due to the coupling of light and heating. When compared with individual light and cooling conditions, the coupling enhancement (“1 + 1 > 2”) of photocurrent plateau can be clearly observed when simultaneous light and cooling were applied on the device, as illustrated in Figure 4B. The output voltage signals of the device exhibit a similar change (Figure S16). However, according to Figures 4A and 4B, the illumination peak current is 50 nA and the pyroelectric peak currents are 29.3 nA and –36 nA under the heating and cooling conditions, respectively. The measured total peak current values are 71 nA (<50 nA + 29.3 nA) and 0.2 nA (<50 nA – 36 nA) under light + heating and light + cooling conditions, respectively. Therefore the relationship between the total peak current and the individual current is not a simple additive one.

This behavior for the enhancement of photocurrent plateau in Figure 4B can be well understood due to the effect of ferro-pyro-phototronic effect on the energy band structures of the device, as depicted in Figures 4C–4F. The energy-level diagram showing the valence and conduction energies of each component material in the BaTiO$_3$ device is depicted in Figure 4C. The device has a structure of ITO/BaTiO$_3$/ITO, which can be regarded as a BaTiO$_3$ layer sandwiched between two back-to-back Schottky barriers at the interfaces. After the BaTiO$_3$ layer was polarized, the negative and positive polarized charges can increase and decrease the Schottky barrier height at the two BaTiO$_3$/ITO interfaces, respectively. As displayed in Figure 4D, the UV light illumination-induced electron and hole pairs can be effectively separated by the left Schottky barrier to produce the observed photocurrent signals. When the device is heating, the polarized charges of the BaTiO$_3$ layer can be decreased, resulting in the reduction of the left Schottky barrier height. Moreover, the right Schottky barrier height can be increased due to the decrease of positive polarized charges in BaTiO$_3$, as depicted in Figure 4E. The reduction of left Schottky barrier height will weaken the effective separation of light-induced electron-hole pairs, and the increased Schottky barrier height at the right interface is detrimental to the flow of electrons from BaTiO$_3$ to the right ITO electrode, resulting in the decrease of photocurrent plateau in Figure 4A. However, when the device is cooling, the polarized charges of BaTiO$_3$ layer can be increased, resulting in the increase of the left Schottky barrier height, which is more effective to separate the light-induced electron-hole pairs, as illustrated in Figure 4F. The decrease of right Schottky barrier height will further promote the flow of electrons from BaTiO$_3$ to the right ITO electrode. As a result, the photocurrent plateau can be effectively enhanced by the coupling of light and cooling in the device.

**DISCUSSION**

In summary, we have demonstrated how to utilize ferro-pyro-phototronic effect to realize a dramatic photocurrent enhancement in radially polarized ferroelectric BaTiO$_3$ materials with a pyroelectric coefficient of about...
16 nC/cm²K by coupling light illumination and cooling temperature variation. Under 365-nm light illumination, the fabricated BaTiO₃ device delivers a sharp current peak followed by a stable current plateau as well. When compared with individual light illumination, the output current peak signals of the device can be enhanced by more than 30 times by using the coupling of light and heating under a light intensity of 0.6 mW/cm². Moreover, the stable output current plateau can be enhanced by 23% due to the coupling of light and cooling, which can be well explained by ferro-pyro-phototronic-effect-induced band bending at the interfaces of BaTiO₃ and ITO electrodes. Our results reveal the role of ferro-pyro-phototronic effect in ferroelectric BaTiO₃ photodetectors, which has potential applications in improving the output performances of optoelectronic devices based on ferroelectric materials such as solar cells and photodetectors.
METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information includes Transparent Methods and 16 figures and can be found with this article online at https://doi.org/10.1016/j.isci.2018.04.016.

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AUTHOR CONTRIBUTIONS
Y.Y. conceived the idea of ferro-pyro-phototronic effect and supervised the research. K.Z. and B.O. carried out the device fabrication and the performance measurement; K.Z. and Y.Y. analyzed the data and co-wrote the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Figure S1: Characterization of BaTiO$_3$ precursor nanowires, nano-BaTiO$_3$ and BaTiO$_3$ films, related to Figure 1.

(A) SEM image of the BaTiO$_3$ precursor nanowires with the low magnification.
(B) XRD patterns of the prepared and pure BaTiO$_3$ nanoparticles.
(C and D) SEM images of the obtained BaTiO$_3$ nanowires with the low (C) and high (D) magnifications.
(E and F) SEM images of the obtained BaTiO$_3$ nanoparticles with the low (E) and high (F) magnifications.
(G and H) SEM images of the BaTiO$_3$ films sintered at 1200 ºC with the low (G) and high (H) magnifications.
Figure S2: Schematic illustrations of the device's size, related to Figure 2.

(A-E) The device's size with the engraved ITO electrode number of 2 (A), 4 (B), 6 (C), 8 (D) and 10 (E).
Figure S3: Measured output voltage (under a loading resistance of 50 MΩ) and output current signals of the device (ITO electrode number, N=2) at forward connection under light, heating and cooling states, related to Figure 2.

(A and B) Measured output voltage (A) and current (B) signals of the device under illumination of 365 nm light with the light intensity of 81.8 mW/cm².

(C and D) Measured output voltage (C) and current (D) signals of the device under a heating temperature variation with the temperature changing rate of 0.52 K/s).

(E and F) Measured output voltage (E) and current (F) signals of the device under a cooling temperature variation with the temperature changing rate of -0.44 K/s.
Figure S4: Measured output voltage (under a loading resistance of 50 MΩ) and output current signals of the device (ITO electrode number, N=4) at forward connection under light, heating and cooling states, related to Figure 2.

(A and B) Measured output voltage (A) and current (B) signals of the device under illumination of 365 nm light with the light intensity of 81.8 mW/cm².

(C and D) Measured output voltage (C) and current (D) signals of the device under a heating temperature variation with the temperature changing rate of 0.52 K/s.

(E and F) Measured output voltage (E) and current (F) signals of the device under a cooling temperature variation with the temperature changing rate of -0.44 K/s.
Figure S5: Measured output voltage (under a loading resistance of 50 MΩ) and output current signals of the device (ITO electrode number, N=6) at forward connection under light, heating and cooling states, related to Figure 2.

(A and B) Measured output voltage (A) and current (B) signals of the device under illumination of 365 nm light with the light intensity of 81.8 mW/cm².

(C and D) Measured output voltage (C) and current (D) signals of the device under a heating temperature variation with the temperature changing rate of 0.52 K/s.

(E and F) Measured output voltage (E) and current (F) signals of the device under a cooling temperature variation with the temperature changing rate of -0.44 K/s.
Figure S6: Measured output voltage (under a loading resistance of 50 MΩ) and output current signals of the device (ITO electrode number, N=8) at forward connection under light, heating and cooling states, related to Figure 2.

(A and B) Measured output voltage (A) and current (B) signals of the device under illumination of 365 nm light with the light intensity of 81.8 mW/cm².

(C and D) Measured output voltage (C) and current (D) signals of the device under a heating temperature variation with the temperature changing rate of 0.52 K/s.

(E and F) Measured output voltage (E) and current (F) signals of the device under a cooling temperature variation with the temperature changing rate of -0.44 K/s.
Figure S7: Infrared images of the device (ITO electrode number, N=10) at the different heating and cooling temperatures, related to Figure 2. (A-H) Infrared images of the device under different heating states. (I-P) Infrared images of the device under different cooling states.
Figure S8: The cyclic temperature variations and temperature data time interval of the device (ITO electrode number, N=10), related to Figure2.

(A and B) The cyclic temperature variations (A) of the device, where the enlarged curve is displayed in (B) under a heating temperature variation condition.

(C and D) The cyclic temperature variations (C) of the device, where the enlarged curve is illustrated in (D) under cooling condition.
Figure S9: Heating temperature variations and pyroelectric performances of the device (ITO electrode number, N=10), related to Figure 2.  
(A and B) The cyclic change in temperature (A) of the device and the corresponding differential curve (B) in the different heating conditions.  
(C and D) Measured voltage (under the loading resistance of 50 MΩ) (C) and current (D) signals of the device under the corresponding temperature variations in A.
Figure S10: Cooling temperature variations and pyroelectric performances of the device (ITO electrode number, N=10), related to Figure 2.

(A and B) The cyclic temperature variations (A) of the device and the corresponding differential curve (B) in the different cooling conditions.

(C and D) Measured voltage (under the loading resistance of 50 MΩ) (C) and current (D) signals of the device under the corresponding temperature variations in A.
Figure S11: The effect of electrode area on the pyroelectric current coefficients of radially polarized BaTiO$_3$ device, related to Figure 2. The heating and cooling temperature changing rates of 0.52 K/s and -0.44 K/s, respectively.
Figure S12: Measured output voltage signals of the device (ITO electrode number, N=10) under the individual light illumination, the simultaneous light illumination and heating or cooling temperature variations, related to Figure 3. (A) Measured voltage (under the loading resistance of 50 MΩ) signals of the device under 365 nm UV illuminations with different light intensities from 0.6 to 62.2 mW/cm².

(B) Measured voltage (under the loading resistance of 50 MΩ) signals of the device under simultaneous 365 nm UV illuminations with different light intensities from 0.6 to 62.2 mW/cm² and heating temperature variations with a change rate of 1.25 K/s.

(C) Measured voltage (under the loading resistance of 50 MΩ) signals of the device under simultaneous 365 nm UV LED illumination with different light intensities from 0.6 to 62.2 mW/cm² and cooling temperature variations with a temperature change rate of -1.08 K/s.
Figure S13: Photocurrent enhancement, responsivity and detectivity performances of the device (ITO electrode number, N=10), related to Figure 3.
(A) Current peak enhanced ratios under the different light illumination intensities due to the ferro-pyro-phototronic effect.
(B) Stable current plateau enhanced ratios under the different light illumination intensities due to the ferro-pyro-phototronic effect.
(C and D) Responsivity and detectivity values (C) under the different light illumination intensities and the corresponding enhanced ratios (D) of responsivities and detectivities by the ferro-pyro-phototronic effect.
Figure S14: Response time of the device (ITO electrode number, N=10), related to Figure 3.

(A-C) The photocurrent (A) and response time including rise time (B) and fall time (C) of the device under the 365 nm illumination with light intensities of 62.2 mW/cm².
Figure S15: Stability test of the device (ITO electrode number, N=10), related to Figure 3. (A and B) Measured output voltage signals of the device under cyclic UV light illuminations (365 nm, 81.8 mW/cm²) for 25 hours (A), where the enlarged curve is illustrated in (B) under a loading resistance of 50 MΩ.
Figure S16: Measured output voltage signals of the device (ITO electrode number, N=10) under different conditions, related to Figure 4.
(A and B) Measured output voltage signals of the device under the individual light illumination, the individual heating (A) or cooling (B) temperature variations, and the simultaneous light illumination and temperature variations.
TRANSPARENT METHODS

Preparation of BaTiO$_3$ nanowires
Tetrabutyl titanate ((C$_4$H$_9$O)$_4$Ti), barium acetate ((CH$_3$COO)$_2$Ba) and acetyl acetone (CH$_3$COCH$_2$COCH$_3$) with a stoichiometric ratio of 1:1:2 and the total mass of 19.89 g were dissolved in 40 ml glacial acetic acid (CH$_3$COOH) at room temperature under a constant stirring with a magnetic stirrer for 2 h. Subsequently, polyvinylpyrrolidone (PVP, Mw ≈ 1300,000) of 1.5 g was added and stirred for 12 h. After that, the mixed solution was delivered in 20 ml plastic syringe which was connected by a stainless steel needle. A positive voltage of 12.66 kV and a negative voltage of -1.68 kV were applied between the metal needle tip and an aluminum foil collector with a distance of 10 cm. The polymer jet was ejected at a constant flow rate of 0.08 mm/min. BaTiO$_3$ nanowires were obtained by annealing the precursor nanowires at 550 °C for 1.5 h at the heating rate of 3 °C/min and 1200 °C for 6 h in air at the heating rate of 5 °C/min and then cooling to room temperature in the muffle furnace.

Preparation of ferroelectric BaTiO$_3$ film
The 0.3 ml PVA-water solution concentration of 2 % was added in BaTiO$_3$ nanowires of 3 g. The sample was grounded in an agate pestle and mortar to produce fine powders. And then, the obtained fine powders were transferred to a stainless steel mould that diameter of 30 mm, and it was compacted into disk-shaped sheets with approximately 30 mm diameter and 1 mm thickness at a pressure of 9 MPa with powder compression machine for 1 min. Afterwards, BaTiO$_3$ ceramic films were obtained by annealing the BaTiO$_3$ films at 650 °C for 1 h at the heating rate of 5 °C/min and 1200 °C for 2 h in air at the heating rate of 10 °C/min in the muffle furnace, followed by natural cooling to room temperature.

Fabrication of the devices
Firstly, a thin layer of ITO film was sputtered on the surface of the prepared BaTiO$_3$ films by a magnetron sputtering system (Beijing jinshengweina technology Co. MSP-820). Moreover, the figures were drawn using CorelDraw X4 and the engraving width is 0.6 mm, and then two radially arrayed ITO electrodes were engraved on the surface of BaTiO$_3$ film by using a laser cutting machine (Universal laser systems, PLS 4.75). Finally, the sample was poled for 30 min under an applied electric field of 2.1 kV/mm in a designed direction at room temperature.

Characterizations and Measurements
The morphology of the nanowires and nanoparticles were characterized using a field-emission scanning electron microscope (Hitachi SU8020). The crystal structure was identified by an X-ray diffractometer (Panalytical X'pert$^3$ powder), which using Cu Kα radiation. The temperature was measured by an infrared thermometer (Optris PI400). The output voltage and current signals of the devices were measured by a low-noise preamplifier (Stanford Research SR560) and a low-noise current preamplifier (Stanford Research SR570), respectively.