

Piezo-phototronic effect on optoelectronic nanodevices

Rongrong Bao, Youfan Hu, Qing Yang, and Caofeng Pan

Optoelectronic nanoscale devices have wide applications in chemical, biological, and medical technologies. Improving the performance efficiency of these devices remains a challenge. Performance is mainly dictated by the structure and characteristics of the semiconductor materials. Once a nanodevice is fabricated, its efficiency is determined. The key to improving efficiency is to control the interfaces in the device. In this article, we describe how the piezo-phototronic effect can be effectively utilized to modulate the band at the interface of a metal/semiconductor contact or a $p-n$ junction to enhance the external efficiency of many optoelectronic nanoscale devices such as photodetectors, solar cells, and light-emitting diodes (LEDs). The piezo-phototronic effect can be highly effective at enhancing the efficiency of energy conversion in today's green and renewable energy technology without using the sophisticated nanofabrication procedures that have high cost and complexity.

Introduction

The performance of optoelectronic nanoscale devices is primarily dictated by the structure and the characteristics of the semiconductor materials used in these devices. Extensive efforts have been made to improve the overall efficiency of the devices.^{1–5} Interface band engineering in particular plays a key role in improving the efficiency. Radiative recombination occurs at the interface, and device efficiency is dependent on the quality and band structure at the interface.

The piezo-phototronic effect was first proposed in 2010 and demonstrated in optoelectronic nanoscale devices (please also see the Introductory article in this issue⁶) in order to enhance the performance of devices based on piezoelectric nanowires (NWs).^{7–9} Compared to other traditional techniques, the piezo-phototronic effect with three-way coupling among piezoelectric, semiconductor, and photonic properties in noncentrosymmetric semiconductor materials can serve as an effective means of tuning charge separation, transport, or recombination to optimize the performance of the device.^{10,11} Moreover, although piezo-phototronic devices use traditional piezoelectric materials, the piezo-phototronic effect affects the band structure in such a way that the device efficiency is much higher than that for traditional devices constructed from the same materials. In addition, the efficiency can be tuned even after the device has been fabricated.

Further, the dependence of the intensity of a NW array-based light-emitting diode (LED) on external strain would open a new window for mapping strain when this system is used as an optical signal-based pressure sensor (so-called electronic skin). Human tactile sensation has always been a challenge to reproduce in artificial intelligence and robotics, due to the difficulty of obtaining pressure sensor arrays that have high spatial resolution, have a rapid response, are flexible, and can be integrated on a large scale. Such nanoscale pressure sensitive LED arrays based on the piezo-phototronic effect could provide a solution to this problem. The output signal is electroluminescence light that can be easily integrated with on-chip photonic technologies for fast data transmission, processing, and recording.

In this article, we review recent work on improving the luminous efficiency and intensity of NW-based photodetectors, solar cells, and LEDs through the piezo-phototronic effect. First, we introduce the basic principle of the piezo-phototronic effect and the materials used in piezo-phototronic devices. We discuss improvements in the performance of a number of piezo-phototronic NW-based photodetectors, solar cells, and LEDs to show its general impact. Finally, we demonstrate an optical signal-based pressure sensor for the fast mapping of strain at the micrometer scale based on light emission intensity

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tuning by the piezo-phototronic effect. These studies not only clarify the fundamental science behind piezo-phototronic optoelectronic nanoscale devices, but also provide information for new applications of piezo-phototronic devices.

Basic principle and materials for piezo-phototronic devices

Two-way coupling between the piezoelectric effect and semiconducting properties plays a remarkable role in the piezotronic effect under applied strain. In contrast to the piezotronic effect, the piezo-phototronic effect modulates the optoelectronics process to the targeted nanosystem, resulting in a complicated three-way coupling among piezoelectric, semiconducting, and photoexcitation characteristics.^{12–17} Besides the well-known coupling of semiconductors with piezoelectric materials for optoelectronics, the coupling between the semiconductor and the photon excitation process also informs the field of optoelectronics, and between piezoelectricity and photon excitation informs the field of piezo-phototronics.⁸

One-dimensional nanoscale semiconductor structures that show the piezo-phototronic effect are ideal materials for fabricating tunable optoelectronic devices; these include NWs of ZnO, GaN, and CdS.^{18–22} Of these potential candidates, ZnO is the best choice because it has excellent biocompatibility, is environmentally friendly, and can be conveniently grown on arbitrarily shaped substrates.

There are two methods to grow large-area arrays (a few millimeters) of ZnO NWs. The first is vapor–solid growth, which vaporizes ZnO powder in the presence of carbon on a prepatterned substrate (e.g., GaN, Si) upon the introduction of an Au catalyst. The growth temperature is approximately 900°C, and the growth quality of ZnO NWs can be regulated by pressure in the growth tube furnace. With this method, ZnO NWs have fewer defects. ZnO NW arrays can also be grown by a low-temperature hydrothermal method.²³ These arrays, when compared with their vapor–solid grown counterparts, are more beneficial to the practical piezo-phototronic photoelectric devices because of their simpler growth conditions and prepatterned substrates, for example, flexible substrates patterned by photoresist, which cannot withstand high temperature. An oxygen plasma treatment while operating the device can reduce structural defects in ZnO NWs grown by this method.

Piezo-phototronic effect in photodetector devices

At the core of a piezo-phototronic device are internal piezoelectric polarization charges, which were induced by an applied strain, located at the interface with a metal contact. These charges tune the charge transport/separation process at the contact. Here, we introduce piezo-phototronic optoelectronic devices that can use this built-in piezoelectric field to modulate the carrier generation, separation, transport, and recombination processes at the interface to enhance the photoelectric process. The piezo-phototronic effect also influences the

sensitivity of the photodetectors based on NWs. By changing the strain and stimulating the light intensity, the Schottky barrier height in the device can be modulated, which provides a window into the physical mechanisms of the piezo-phototronic effect, the optical effect, and semiconductor properties in piezo-phototronic photodetector devices.^{24–32}

It has been shown that the responsivity of CdSe NW photodetectors (PDs) can be enhanced by the piezo-phototronic effect due to Schottky barrier height tuning through the piezopotential at the NW/metal electrode interface of the device⁸ (**Figure 1a**). The piezo-phototronic effect under compressive strain increases the internal electric field of the Schottky barrier and assists in the separation of photoexcited electron–hole pairs, resulting in an increase in the photocurrent. Pan et al. reported a UV photodetector array, consisting of 32×40 pixels based on vertically aligned ZnO NWs²⁶ (**Figure 1b**), that is a single piezo-phototronic effect photodetector sensor. Each pixel is composed of ZnO NWs and Au nanopatterns that form a Schottky contact. By introducing the piezo-phototronic effect, the strain-induced piezoelectric polarization charges effectively enhance the performance of the UV PD array by 700% in photoresponsivity, 600% in sensitivity, and 280% for the detection limit.²⁶

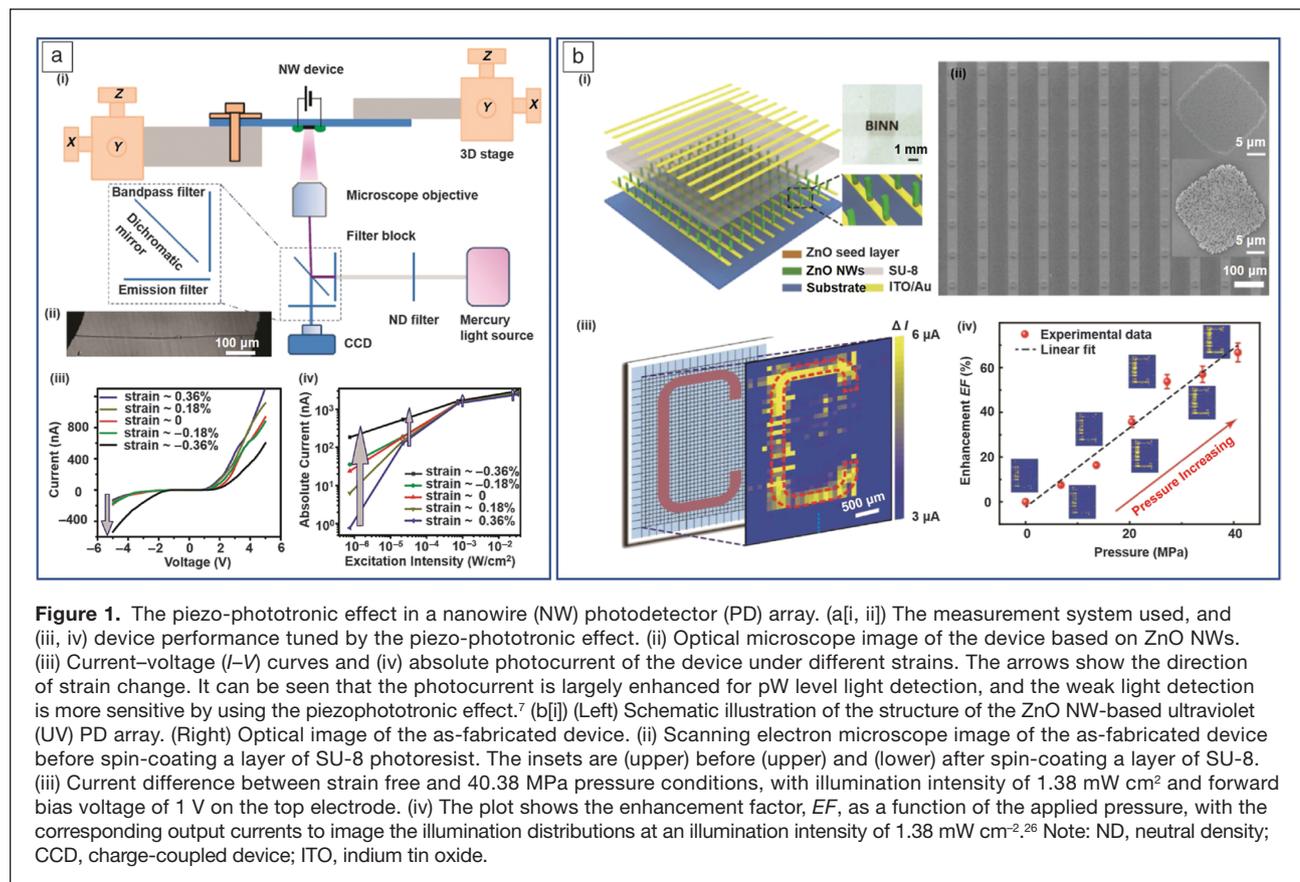
Piezo-phototronic effect in solar-cell devices

During charge-carrier separation and transport in solar cells, the device efficiency can be regulated by the energy band at the semiconductor/semiconductor or semiconductor/metal interface of the device, which can be reduced by the piezo-phototronic effect. In this section, we discuss the influence of the process and principle of the piezo-phototronic effect on the efficiency of solar-cell devices based on piezo NWs, and performance improvements in NW solar-cell array devices.^{33–40}

Pan et al. demonstrated a new *n*-CdS/*p*-Cu₂S coaxial NW-based photovoltaic device. The performance of the devices were controlled via the piezo-phototronic effect. A schematic of the device structure is shown in **Figure 2a**.³³ The piezo-phototronic effect could be used to control electron–hole pair generation, transport, separation, or recombination, thus enhancing the efficiency of the devices as high as 70%. As shown in **Figure 2b**, the piezo-phototronic effect of a ZnO NW array can be used as the driving force to promote the separation and transport of carriers by adjusting the band structure at the heterojunction in the core–shell NW.³⁵ The efficiency of this flexible *n*-ZnO/*p*-SnS core–shell NW array solar cell can be effectively improved up to 37.3% under moderate vertical pressure by applying the piezo-phototronic effect. The results of this research show the potential of piezo-phototronics for high-performance large-scale flexible solar-cell applications.

The piezo-phototronic effect in NW LED devices

The efficiency of carrier injection, recombination, and light extraction are decisive factors controlling light emission from semiconductors. The piezo-phototronic effect can enhance the performance of LEDs, as has been shown for different LED



structures.^{41–52} We introduce research for improving the emission light intensity and efficiency of three types of single NW-based LEDs through the piezo-phototronic effect.

A single NW inorganic hybrid p - n junction LED is schematically shown in **Figure 3a**. This LED was fabricated by manipulating an n -type ZnO wire on a p -type GaN film doped with Mg. The emission light intensity and injection current at a fixed applied voltage were enhanced by a factor of 17 and 4, respectively, upon application of a compressive strain of 0.093% along the a -axis.⁴² A vertical single-wire n -ZnO NW grown on a GaN substrate LED device is shown in **Figure 3b**.⁹ The UV light emitted from the single-wire LED under different applied strains was recorded by a charge-coupled device (CCD), and simultaneously, the corresponding light intensities were obtained. The emission intensity increased significantly with increasing compressive strain. When the c -axis was under a compressive strain of -0.149% , the emission intensity was enhanced approximately $9\times$ in magnitude compared to the unstrained case.

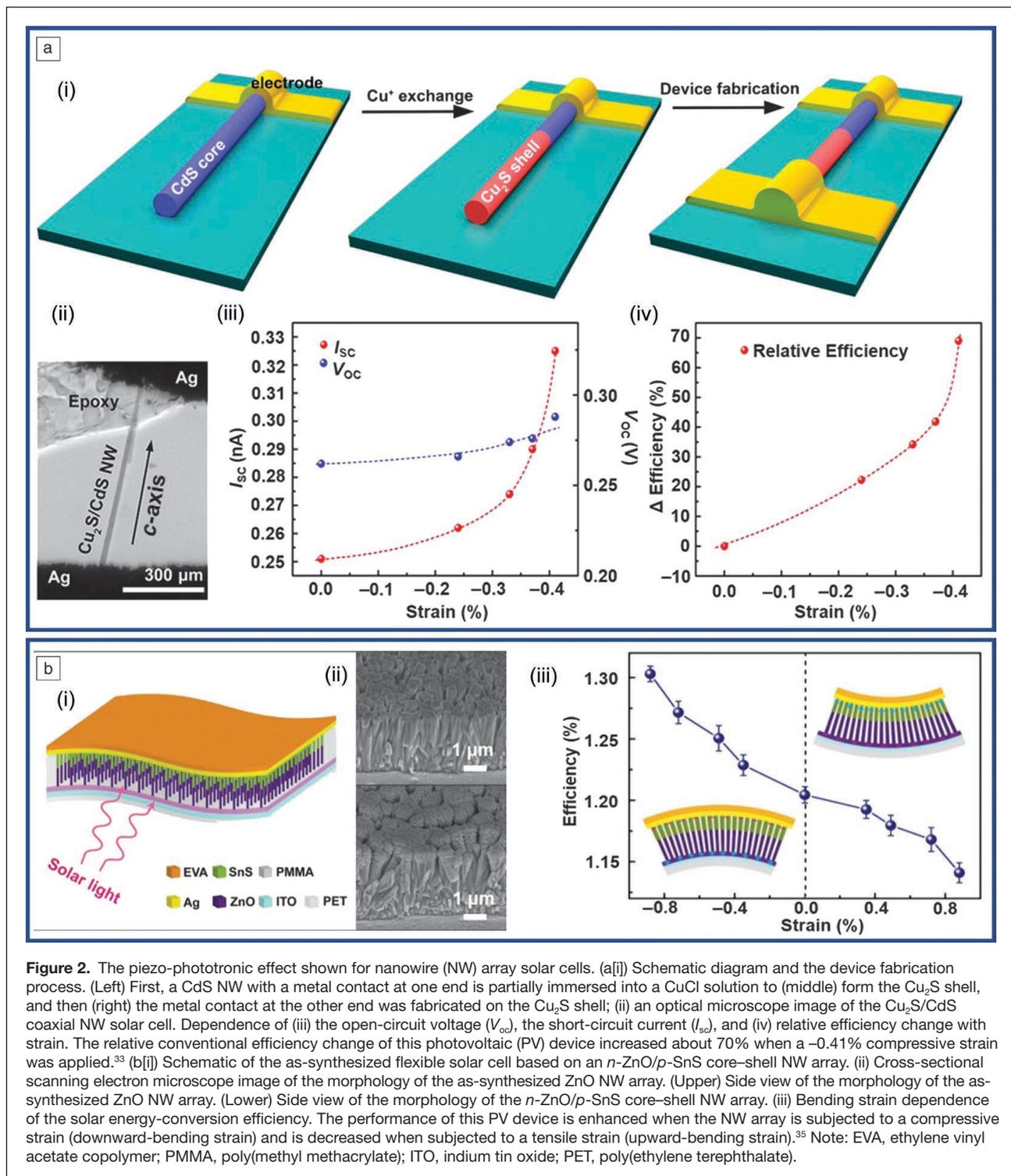
A piezo-phototronic effect-modulated n -ZnO NW/poly(3,4-ethylenedioxythiophene):poly(styrene)sulfonate (PEDOT:PSS) LED array based on a flexible transparent indium tin oxide (ITO)/poly(ethylene terephthalate) (PET) substrate was recently reported.⁴⁵ The vertical ZnO NW array grew on the a prepatterned flexible PET substrate by the hydrothermal method. The piezocharge produced by compression pressure

on the NW LED array reduces the barrier height for hole transport and leads to better balance between electron and hole currents in the LED device. As shown in **Figure 3a**, the luminescence intensity of the LED increases linearly with compressive stress on the surface of the device. The piezo-phototronic effect tuning Si-based LED arrays can be obtained by grown ZnO NW arrays on the p -Si substrate.⁴⁹ When the device was under compressive strain, the light emission of this Si-based LED increased with a maximum value at a compressive strain of 0.15–0.2%, and then decreased. This progress is attributed to strain-induced piezopolarization charges, which could regulate the energy band diagrams at the p - n junction and lead to an increase in light-emitting performance.

Piezo-phototronic arrays for pressure sensor applications

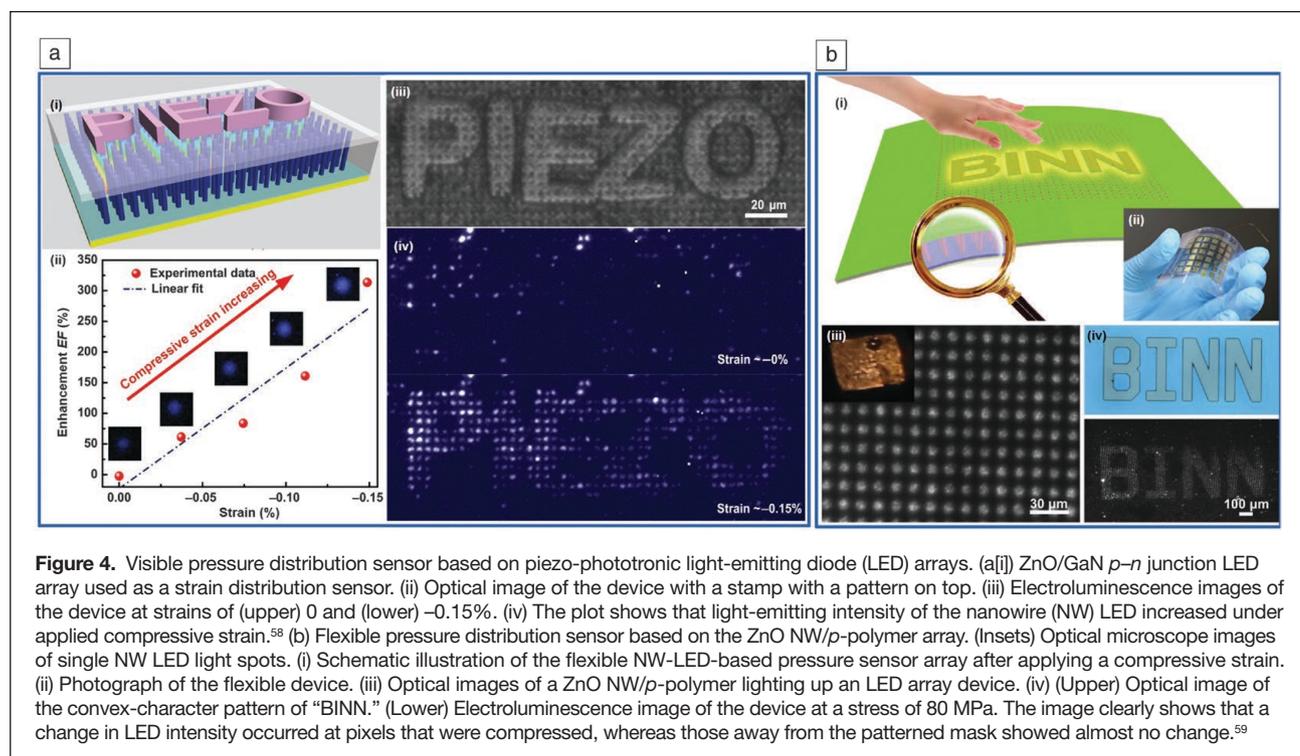
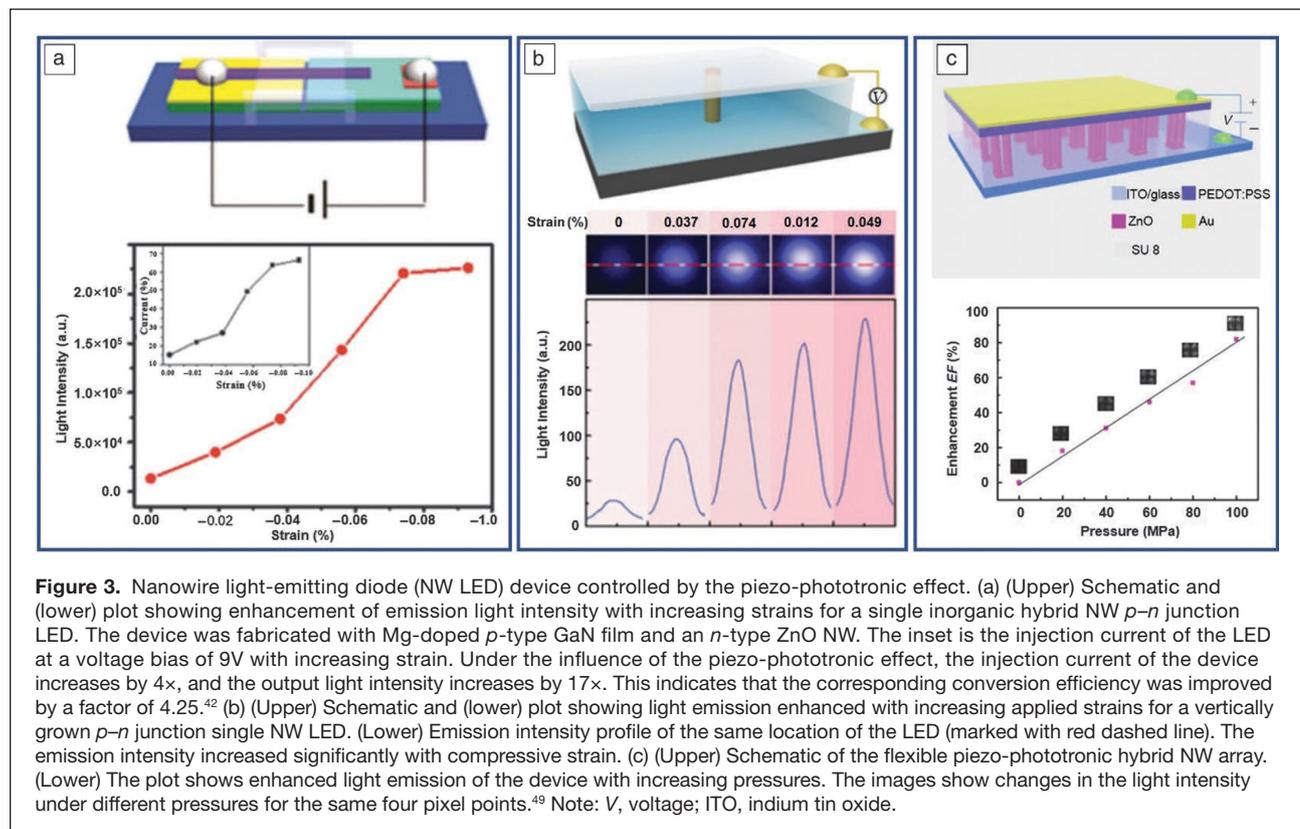
Most pressure sensors are based on resistance sensors or capacitive sensor arrays, which require time to read out the pressure distribution from the whole pixel matrix of the device.^{53,54} As discussed in previous sections, the emission intensity of the NW LED dependence on the local strain owing to the piezo-phototronic effect may enable a map of the distribution of pressure with high spatial resolution and fast response by reading the optical signals in parallel.^{55–57}

The visualized pressure-mapping system was reported with the structure of the ordered ZnO NWs on the prepatterned



p-GaN thin-film sapphire substrate through low-temperature wet chemical methods.⁵⁸ This pressure sensor array composed of *n*-ZnO NW/*p*-GaN had been demonstrated to map distributions of strain/pressure with spatial resolution as high as 2.7 μm , which corresponds to 6350 dpi pixel density (Figure 4a). With compressive strain on the device surface, a negative piezopotential is produced at the local interface of the ZnO/GaN

p-n junction to increase the recombination rate of electrons and holes in the *p-n* junction, leading to enhancement of the light-emission intensity. The pressure distribution is obtained by reading out in parallel at an ultrafast detection speed of 90 ms. As shown in the Figure 4b, in order to be used as an electronic skin, a flexible LED array composed of a *p*-polymer layer and patterned *n*-ZnO NWs with a spatial resolution as high as 7 μm



for mapping pressure has been reported.⁵⁹ The device was prepared on a prepatterned flexible PET/ITO substrate, with a vertically grown n -ZnO NW array as the electron-transport layer and a PEDOT:PSS layer as the hole-transport layer.

The influence of the growth conditions and the morphologies of the ZnO NWs at each pixel on the device pressure measurements ranging from 40 to 100 MPa has also been explored.⁵⁹

Conclusion

The piezo-phototronic effect is a result of three-way coupling among piezoelectricity, photoexcitation, and semiconducting characteristics in noncentrosymmetric semiconductor materials. This can be used to regulate the properties of optoelectronic devices, such as photodetectors, solar cells, and LEDs. This article reviewed the piezo-phototronic effect in NW-based optoelectronic devices, including fundamental science, technology, and important applications. Simulation and experiments proved that the piezo-phototronic effect is an effective way to modulate interface band structure to improve the efficiency of the devices dramatically and universally. On the other hand, the optical signal can be used to map the strain/pressure with ultrafast response and high resolution at the micrometer scale. Recently, research on piezo-phototronic effects has been extended to new materials and devices, such as piezo-phototronic effects on two-dimensional materials and devices and piezo-phototronic effects on NW random lasers. The piezo-phototronic effect can be effectively used for enhancing the efficiency of energy conversion in today's safe, green, renewable energy technologies and as well as in the field of mechanosensing and smart robotics.

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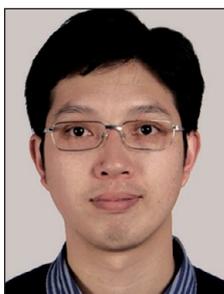


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