Enhanced Photo-electric Response of p-n Heterointerface on Ordered ZnO Nanowires/Polyaniline Films

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Abstract. In this paper, a p-n heterojunction structure of ZnO nanowires/Polyaniline (Z NWs/PANI) nanocomposites was synthesized by layer-by-layer. Since the PANI plays p-type hole-transporting material (p-HTM), it is contributed to separate the photo-generated electron-hole pairs. The Z NWs were synthesized by the sol-gel method and the aqueous solution method. Compared to the commercial ZnO particles, the as-grown Z NWs array was composed of hexagonal wurtzite nanorods which grew in preferential c-axis [0001] direction. The Z NWs have the abundant oxygen vacancy defects, which can trap more photo-generated electrons under the UV illumination or excite more trapped electrons in the oxygen vacancy levels into the conduction band under the Blue illumination. It is hoped that the present work may provide an efficient and applicable method to develop photoelectric response with excellent performance.

1. Introduction
Semiconductor-based photoelectric application has attracted considerable attention as a promising material for dealing with solar cells [1], photocatalysis [2] and photodiodes[3]. Among various semiconductors used for photoelectric application, ZnO nanomaterials have received enormous interest in exclusive electrical, catalytic, electronic and optical properties due to their wide band gap (3.3eV), low power threshold sand high exciton binding energy (~60meV) as well as their low cost. [4] Many works have reported that ZnO shows even better photoelectric property than WO₃, TiO₂, and so on [5]. Even so, the photoelectric performance of ZnO is still not that satisfying for practical utilization on a large scale, because recombination of photo-generated charge carriers remains a dominant barrier. Thus, it is indeed challenging and significant to prepare ZnO-based materials with a high charge transfer rate and good separation efficiency of electron-hole pairs.

In allusion to the above-mentioned disadvantages, many methods have been developed to decrease the recombination rate of charge carriers in ZnO. [6] Especially, defect-related mediation has drawn much interest because not only are defects effective to modulate the activity of the photoelectric response but also defects are universal in material.[7] Despite the controversy concerning the role of photo-generated charge carriers whereas localized bulk ones usually serve as recombination sites.[8] We have also, in our previous work[9-10], demonstrated that defects on the outer surface of a ZnO film can remarkably boost the photoelectric response in UV and Blue illumination. However, the defects in the subsurface exhibit inferior promoting capability to the photoelectric response, subject to the fact that the surface defects can form recombination centre levels in the forbidden energy gap. Thus, it is considered that the p-n heterointerface between ZnO and PANI can promote to reduce the recombination rate of the photo-generated electron-hole pairs. [11-12]

Recently, combination of inorganic semiconductor with conjugated polymer for enhanced photoelectric response is an emerging area of research. The conducting polymers, which are the
excellent hosts for the trapping of the carriers of the semiconducting nanomaterias, have substantial π-electrons through the polymeric chain. PANI has drawn more attention as a promising material for microelectronic devices due to unique electrical, optical, photoelectric properties and good environmental stability. PANI is extensively used as p-type material which could be deposited by various techniques such as wet, chemical, and electrophoretic methods on n-type semiconducting electrodes for p-n heterostructure devices. Moreover, this polymer, which can behave like a p-type semiconductor, is an excellent hole transporting material. Nevertheless, both surficial defects and PANI can act as active sites and charge separation centers, but knowledge about the interaction (synergistic or antagonistic) of the two is still lacking.

In the present work, we developed a facile route to prepare p-n heterointerface, oxygen vacancy ($V_o$) mediate ZnO nanowires by the screen printing and the sol-gel method. The fabricated films are played remarkably enhanced photoelectric response under the UV illumination and the Blue illumination, due to the synergic effect between defects and PANI. The coupling mechanism was investigated systematically. It is hoped that the present work may open a strategy for designing a high performance and high stability photoelectric response for practical applications.

2. Experiment

2.1 Materials

Commercial PANI (average size 1 μm) and ZnO (average size 80nm) were used. Other chemicals used in the experiment were of analytically pure grade.

Firstly, the ZnO nanoparticle and PANI was structured on the Au interdigital electrode which was preprinted on an alumina substrate via the silk-screen printing. The ZnO paste was printed onto the Au interdigital electrode which had been preprinted on the alumina substrate (Zhuhai Yueke Jinhua Electronic Ceramics CO. LTD., China). After drying, the PANI paste was printed onto the ZnO layer. After the above procedures, a thick porous film was obtained in each case. The schematic diagram of the device is shown in Figure 1. Following the above procedures, ZnO layer and PANI layer were laminated from bottom to top. The [ZnO/PANI] samples are studied labeled as Z/P.

Secondly, the ZnO nanowire and PANI was also synthesized on the FTO. Vertically aligned ZnO nanowires were grown on PANI films via a hydrothermal method. Firstly, 50 mM zinc acetate dehydrate [Zn (CH$_3$COO)$_2$·2H$_2$O] in methanol and ethanolamine was stirred by magic for 1h. The solution was dropped onto the PANI films by dip-coating method. Then, the dip-coating step was repeated four times followed by annealing at 200°C for 2h to yield a thin ZnO seed layer. Finally, hydrothermal growth was carried out at 90°C for 4h in seal bottles with the substrates suspended in an aqueous solution containing 50 mM Zn (CH$_3$COO)$_2$·2H$_2$O) and 50 mM hexamethylenetetramine (HMTA). The schematic diagram of the device is shown in Figure 1. The [ZnO nanowires/PANI] samples are called Z NWs/P.

2.2 Photoconductivity measurement

The photoconductivity of each device in the material library was measured by a homemade photoconductivity measurement platform. All the samples were located in the stainless steel test chamber and tested under the different light sources (UV LED 365 nm, 36 W/m², blue LED 475nm, 11.2 W/m²) with constant specific bias voltage (1v or 0.1v) in dry air conditions (20 °C and below 20% relative humidity) which was controlled by the dry air generator and the mass flow controller. The $I–V$ characteristics were measured under the UV LED array (365 nm, 36 W/m²). The voltage window of 4.5V was employed.

2.3 Characterization

The morphologies of the prepared samples were observed on field-emission scanning microscopy (FSEM, Sirion 200 FEI). The phase identification was carried out on an X-ray diffractometer (X’PertPRO, PANalyticalB.V.) using Cu Kα1 radiation. The chemical states of the samples were characterized by X-ray photoelectron spectroscopy (XPS, VGMultilab2000).
3. Results and discussion

3.1 Characterizations

The morphologies and phase components of the Z/P prepared by the screen-printing technique are shown in Figure1. The top-view of the Z/P identifies the ZnO nanoparticles cover on the PANI in Figure 1. The SEM photograph in Figure 1 shows the cross-section morphology of the Z/P layered structure. The printed film is about 20μm in thickness, in which the ZnO and PANI layers are both 10μm. An apparent interface between two layers is observed, indicating that it is two-layer type heterojunction and is different from the mixture type in a composite system. From the insert of Figure 1, we can see that the films have lots of micro-holes, which are formed due to volatilization of organic component during the heat-treatment process and originated from agglomerated structure in the screen printing phase.

![Figure 1. SEM image of the ZnO/PANI films](image1)

The surface morphologies of the Z NWs and the Z NWs/P films are shown in Figure 2a and Figure 2b. Figure2a shows the SEM image of the Z NWs. It can be seen that the as-grown Z NW hexagonal structure are vertically aligned on the substrate. The average diameter of the nanowires is ~100 nm. The SEM photograph in Figure 2b shows the morphology of the Z NWs/ PANI film. The ZnO nanowires are grown on the PANI films. Figure 2c shows the section of the Z NWs / P film.

![Figure 2. SEM images of (a) Z NWs; (b) Z NWs/P; and (C) section of the Z NWs/P films](image2)

The XRD patterns on Figure 3a illustrate the printed ZnO with the hexagonal wurtzite structure (JCPDS 79-0207), and the substrates of Al₂O₃ (JCPDS 75-1862). As shown in Figure 3b, the peak at
34.5° corresponding to the (002) plane is very sharp, which indicates that the as-grown ZnO nanowires are preferentially grown along the c-axis in a direction almost perpendicular to the substrate surface.

![Figure 3](image)

**Figure 3.** XRD patterns of the samples (a) ZnO nanoparticles on Al₂O₃ substrate (b) Z NWs grown on FTO glass

In order to understand the chemical compositions and the defects states of the ZnO, XPS analysis was performed on the ZnO nanoparticles and nanowires. The binding energies of the XPS spectra have been calibrated taking the carbon C 1s peak (285.0 eV) as a reference. As shown in Figure 4a, the XPS survey scans confirm that the ZnO and Z NWs are not doped with other elements. To gain more insight into the oxygen vacancies, the O 1s spectra of the samples are shown in Figure 4b and c. In order to examine the detailed oxygen states, the O 1s spectra are carefully deconvolved into 3 peaks (Oₐ, Oₐb, Oₐc) by using Gaussian fitting. The Oₐ peak at 530.1 ± 0.3 eV is attributed to the O²⁻ ions on the wurtzite structure of the hexagonal Zn²⁺ ion array. The O²⁻ ions are surrounded by zinc atoms with the full supplement of nearest-neighbor O²⁻ ions. The Oₐb peak at 531.4 ± 0.3eV is associated with the O²⁻ ions in the oxygen-deficient regions within the ZnO matrix. The Oₐc peak at 532.3 ± 0.3 eV is usually attributed to chemisorbed oxygen on the surface of the ZnO, such as CO₃²⁻, adsorbed H₂O or adsorbed O₂. The main adsorption type usually is chemisorbed oxygen O₂ on the surface of ZnO in dry air. For better comparison, the relative integrated intensity percentages of the different oxygen species calculated from O 1s fitting peaks are listed in Table 1.

![Table 1](image)

**Table 1.** The relative integrated intensity percentages for the different oxygen species calculated from O 1s fitting peaks of the ZnO and Z NWs

| Sample | Oₐ [%] | Oₐb [%] | Oₐc [%] |
|--------|--------|---------|---------|
| ZnO    | 52.17  | 23.85   | 23.98   |
| Z NWs  | 42.29  | 41.08   | 16.63   |

For the Z NWs, the percentages of Oₐ, Oₐb, and Oₐc are 42.29%, 41.08% and 16.63%. But the percentages of Oₐ, Oₐb, and Oₐc for the ZnO are 52.17%, 23.85% and 23.98%. The change in the intensity of Oₐb peak is connected with the variations in the concentration of oxygen vacancies in ZnO. The increase in the Oₐb percentage of the Z NWs reveals that a high number of oxygen vacancies have been introduced into the ZnO nanowires. The high Oₐb percentage of the Z NWs also indicates that most of the O²⁻ ions are in the oxygen-deficient regions. Since the oxygen vacancies acting as donors in ZnO increase the electron carrier density in the conduction band, the abundant oxygen vacancies result in the degenerate ZnO.
3.2 Photoconductivity property

For clarifying the roles of PANI and defects, we compared the photoresponse of different samples under the UV or Blue illumination. Figure 5 shows the photoconductivity responses of the samples (ZnO, PANI, and Z/P) under a light source of UV LED array (bias at 1V). Also, pure PANI shows a quite low response as compared to the ZnO. In the whole experimental range, the Z/P films demonstrate much higher response than that of the pure ZnO, indicating that the addition of PANI is beneficial to the UV response of the ZnO nanoparticles. Figure 6 shows the effect of the UV irradiation on the current-voltage ($I-V$) characteristics of Z/P configurations. The non-linear curve in Figure 6 exhibits almost symmetric characteristic with an extended plateau suggestive of tunneling conduction through the interface between the ZnO and PANI. This result confirms that the p-n junction was successfully formed.

We also tested the photoelectric response of Z NWs, Z/P and Z NWs/P on the FTO under UV illumination (bias at 0.1V) in dry air at room temperature as shown in Figure 7. However, the Z NWs/P sample exhibits remarkably improved performance among all the samples, and the response is six times...
than that of Z/P (see Figure 7 in the Supporting Information). Our previous research [9-10] indicated that the photogenerated carriers in the Z NWs/P film have a longer life time and lower recombination rate, and it exhibited a special charge storage property. The special photoelectric response and the charge storage of the Z NWs are attributed to the interconnected conductive path and the different charge state oxygen vacancies distributed in the different regions of the Z NWs. [10] Considering that ZnO has been reported by many works [14-15] to be rather good photoelectric material under light and that the value of the response for Z NWs/P exceeds the simple accumulation of those of Z/P and Z NWs samples, it is reasonable to deduced that there exists a synergic effect between PANI and the defects.

![Figure 7](image.png)

**Figure 7.** Photoconductivity responses of the samples illuminated under a light source of UV LED array

![Figure 8](image.png)

**Figure 8.** Photoconductivity responses of the samples illuminated under a light source of Blue LED array

Based on the XPS result, the abundant oxygen vacancy defects in the ZnO nanowires, whose amount is larger than those in the commercial ZnO particles. Under the blue illumination, more electrons trapped in the oxygen vacancy levels can be excited into the conduction band.[15] Compared to the Z/P sample, the response of the Z NWs/P sample has sharply increased in the beginning (see Figure 8 in the Supporting Information). Based on all the above results, the photoelectric response of Z NWs/P exceeds the simple accumulation of those of Z and Z/P samples. It is reasonable to deduce that there exists a synergic effect between PANI and the defects.

### 3.3 Mechanism analysis

Based on all the above results and discussion, we can depict a probable mechanism of the synergistic effect between PANI and defects accounting for an enhanced photoelectric response. The details are illustrated in Figure 9 and Figure 10. Under the UV light, surficial $V_o$ can act as trapping sites of photo-generated electron as well as active sites,$^{[14-15]}$ both of which are beneficial for photoelectric response. Besides, $(V_o^+, V_o^0)$ are electron donors and are considered to enhance the donor density.$^{[11, 15]}$ PANI has high mobility of charge carriers and excellent transporting capacity of holes. Moreover, this conjugated polymer can theoretically be photoexcited and inject electrons into the conduction band of ZnO,$^{[12]}$ though PANI shows poor photoelectric response by itself (see Figure 5 in the Supporting information). The HOMO and LUMO of PANI match well with the energy band of ZnO as shown in Figure 9a. When irradiated by the UV light, the photo-generated holes transfer from ZnO toward the PANI while electrons from both ZnO and PANI can be effectively trapped by $V_o$ on the surface ZnO, and a good separation of charge carriers can be achieved consequently. An atomics schematic diagram depicting the charge separation process caused by the synergistic effect between PANI and defects is illustrated in Figure 9b.
(a) Proposed photoelectric mechanism according to the band alignment (b) Atomic schematic diagram illustrating the synergistic effect between defects and PANI

**Figure 9.** The probable mechanism under the UV light

Under the Blue light, the photons from the blue illumination can excite more electrons into the conduction band via the defect levels in the Z NWs, and these photoexcited electrons also can be stored in the conduction band for a long time. Moreover, this conjugated polymer can theoretically be photoexcited and inject electrons into the conduction band of ZnO. The proposed photoelectric mechanism according to the band alignment and the atomic schematic diagram illustrating the synergistic effect between defects and PANI are respectively shown in Figure 10a and b.

**Figure 10.** The probable mechanism under the Blue light

4. Conclusions
In summary, organic semiconductor of PANI hybridized inorganic semiconductor of ZnO (ZnO or Z NWs) has been fabricated on Al₂O₃ substrate using screen printing or hydrothermal method. The photocurrent response of the Z/P sample displayed obvious higher than those of the ZnO without hybridization. The formation of p-n heterojunction interface between the p-type polyaniline and n-type ZnO was verified by I-V characteristic. A synergistic effect between PANI and defects is proposed and demonstrated. Moreover, the Z NWS/P has effectively stability defects on the surface and p-n interface, which are of significance for practical applications.

5. References
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