Photo-Electric Response of Polyaniline/ZnO Nanocomposites Based on Inorganic/Organic Heterojunctions

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Abstract. The samples were analyzed and characterized by scanning electronic microscope (SEM) and X-ray diffraction (XRD). The XRD results showed that the diffraction peaks of PANI/ZnO nanocomposites agreed with the pure ZnO. The as-prepared nanocomposites with different amounts of PANI dopants exhibited different sensing properties. When the weight ratio of PANI is 5%, the photoelectric response of nanocomposites to UV light reaches maximum (1938). Compared with ZnO, the response shows 60 times improvement. Additionally, the probable photoelectric response mechanism was also proposed. Firstly, the existence of p-n heterojunctions formed between p-type PANI and n-type ZnO interfaces was confirmed by the IV characteristics. It is believed that the p-n heterojunctions can promote the charge separation and further increase the amount of absorbed negative oxygen ions. Secondly, the highly dispersed states of PANI could suppress the formation of interfacial recombination centers and accelerate p-type hole transporting. The photocurrent of composites is improved significantly. And we hope this work can help for designing more photoelectric materials with the higher response.

1. Introduction
Conductive polymers and metal oxide composites are widely used in photocatalysis, solar cells, gas sensors and optoelectronic applications.[1-3] Such inorganic-organic heterojunction structures are capable of complementing each other while overcoming their respective disadvantages, and their schottky structure or p-n structure can promote separation of carriers. [4] Among inorganic metal oxides, zinc oxide is widely used in catalysis, optics and electronics, mainly due to its wide band gap (3.3 ev), low power threshold and exciton binding energy (~60 meV). And low cost. [5] Common conductive polymers are polyaniline, polypyrrole, polythiophene, etc., and polyaniline is one of the most widely used p-type semiconductor materials, with unique electrical, optical, and good stability. [6] Therefore, polyaniline/zinc oxide composites have a good application prospect in photoelectric performance. Ameen [7] has reported that a polyaniline/zinc oxide composite prepared by a simple method has good rectifying properties and can be used for light emitting diodes. Zhang [8] successfully prepared a mixed photocatalyst of zinc oxide and monolayer molecular polyaniline, which has good catalytic performance for degrading methylene blue under ultraviolet and visible light. Mridha [9] studied the photoelectric properties and carrier transport mechanism of polyaniline/zinc oxide based on inorganic/organic heterojunction structure. Lin [10] research shows that zinc oxide and conductive polymer composite can improve carrier mobility and improve conductivity. The results show that zinc oxide and polyaniline composites have been widely used in UV photodetection. [11]
Although there are many ways to prepare such composite materials, it is important to improve the migration of photogenerated carriers and reduce recombination. [8] However, the interfacial effects based on may be lead to accelerate the recombination. So it is necessary to control the content of zinc oxide or polyaniline. In the paper, we have prepared PANI/ZnO nanocomposites by simple mechanical mixing method and tested the photoelectric response. By testing the photoelectric response of the composites with different composition ratios, the optimum content of the polyaniline in the composite has been determined. In the paper, the percolation value has been determined based on quickly testing the photocurrent. We hope this work can help us to explore more materials with higher photoelectric response.

### 2. Experiment

#### 2.1. Materials Preparation
Polyaniline and zinc oxide are commercially available and have an average particle size of 1 μm and 80 nm, respectively. The reagents used in the experiments were all analytically pure reagents and were not subjected to any chemical treatment. The two powders were mixed together with a certain amount of organic solvent. The ball was milled in a QM-3SP04 ball mill of Nanjing University Instrument Factory for 3 h (rotation speed: 250 rpm) until a uniformly mixed sample was obtained. The sample was printed on a ceramic substrate printed with gold electrodes. The device has a shape of 8 mm * 6 mm and a thickness of 10 μm. The printing machine was used by the WJ-LCD4050CHL type printing machine of Shenzhen Jinxing Company. These samples were calcined at 200 °C for 2 h to remove the organic solvent. After the appeal step, a porous film can be obtained. [12] Preparation of six different polyaniline composite materials, the product numbers are listed in Table 1:

| The Number | The content of Polyaniline (wt %) |
|------------|----------------------------------|
| ZP000      | 0%                               |
| ZP001      | 1%                               |
| ZP005      | 5%                               |
| ZP010      | 10%                              |
| ZP050      | 50%                              |
| ZP100      | 100%                             |

#### 2.2. Characterization
In the experiment, the phase of the prepared material was analyzed by X-ray diffractometer (XRD; X’pert PRO; PANalytical B.V., Almelo, the Netherlands), and the experimental conditions were: Cu Ka ray, (λ = 0.1542 nm), 2θ ranges from 10° to 90°. The morphology of the samples was characterized by a field emission scanning electron microscope (FESEM, FEI Sirion 200) produced by the Dutch company.

#### 2.3. Photoconductivity Measurement
The test chamber was made of stainless steel, the test environment temperature was 20 °C, the relative humidity was ≦20%, and the ultraviolet light LED source used as the test source. The parameters were: wavelength 365 nm, and the light density is 36 W/m².

The whole test process was detected in real time. The test process was as follows: (1) put the device into the test chamber and let dry air pass for 30 min; (2) add 1 v bias voltage after 10 s of the test; (3) 20 seconds to start adding light; 4) Stop adding light for 180 seconds; (5) Remove the bias voltage for 350 s. The test flow for all samples lasted 360 s.
the test; (3) 20 seconds to start adding light; (4) Stop adding light for 180 seconds; (5) Remove the bias voltage for 350 seconds. The test flow for all samples lasted 360 seconds. To obtain the $I–V$ characteristics, current was continuously measured as function of voltage. In the light irradiation experiments, we used UV LED array (365nm, 36W/m²) and the lamp-to-sample distance was 1cm.

3. Results and Discussion

3.1. Characterization

Figure 1 is an SEM image of different samples. It can be seen from the figure that the particle size of zinc oxide particles is 40–60 nm, and the particle size of polyaniline particles is about 500 nm. It can be seen from the SEM image that polyaniline is surrounded by zinc oxide having a small particle size and the dispersion is relatively uniform.

![Figure 1](image)

**Figure 1.** The SEM images of the different samples
(a) PANI (b) ZP050 (c) ZP010 (d) ZP005 (e) ZP001 (f) ZnO

The crystal phases of the different samples were analyzed by X-ray diffraction XRD, and the results are shown in Fig. 2. It can be obtained by analysis that the polyaniline exhibits an amorphous state, and the diffraction peaks of the hexagonal wurtzite structure ZnO appear in other samples, which is consistent with the standard XRD card of ZnO (JCPDS 80-0074). The three diffraction peaks 20 in the figure are: 31.9°, 34.5°, and 36.4°, respectively corresponding to the (100), (002), and (101) crystal planes of zinc oxide. The intensity of the diffraction peak in the composite increases as the zinc oxide content increases. After XRD analysis of the sample, the crystal structure of zinc oxide was not changed in the composite after doping with polyaniline.

![Figure 2](image)

**Figure 2.** The XRD patterns of the different samples
3.2. Photoconductivity Response of the PANI/ZnO Nanocomposites

Figure 3 is the response of different samples to ultraviolet light at room temperature. It can be seen from the figure that polyaniline has almost no response to ultraviolet light. To better discuss the photoelectric response, the response values are defined as follows:

\[ R = \frac{(I_{\text{max}} - I_0)}{I_0} \]  

(1)

- \( I_0 \): the initial current before the light
- \( I_{\text{max}} \): the maximum current after the light

**Figure 3.** Photoconductivity responses of the PANI/ZnO nanocomposites

Figure 4 is the magnitude of response of different samples to ultraviolet light at room temperature. It can be seen that PANI is not responsive to ultraviolet light at room temperature, while zinc oxide and PANI/ZnO composites are responsive to ultraviolet light at room temperature. When the mass content of PANI was 0%, 1%, 5%, 10% and 50%, the response values of PANI/ZnO composites were 36, 43, 1938, 724, 259 and 1.03, respectively. It can be seen that with the mass of PANI increasing, the response performance has gradually increased. However, continuously increasing the content of PANI, it will result in the decreased response. When the mass content of PANI is 5%, the response reaches the maximum. Therefore, the optimum mass percentage of PANI in the composite is 5%.

**Figure 4.** The response of the different samples

Figure 5 illustrates the \( I-V \) characteristics of the ZP010 nanocomposites in the dark and UV irradiation conditions at room temperature, respectively. The linear curve in the Figure 5 (a) can indicate that the ohmic contact is formed between the ZnO and PANI (ZP010). The non-linear curves in Figure 5 (b) exhibit almost symmetric characteristic with an extended plateau suggestive of tunneling conduction.
through the PANI/ZnO nanocomposites. This result confirms that a p-n junction was successfully formed.

![Figure 5. I-V characteristics of ZP010](image)

(a) in the dark (b) in the UV light

3.3. Mechanism Analysis

The UV source (365 nm) used in the experiment can excite the electronic transitions in ZnO and PANI to the conduction band (CB) and the lowest occupied orbit (LUMO), while the valence band of ZnO (VB) and PANI are the highest. A positively charged hole appears in the occupied orbit (HOMO). Because of the relative positional relationship between the two, electrons will transition from the lowest occupied orbital of PANI to the conduction band of ZnO, and the hole will jump from the valence band of ZnO to the highest occupied orbit of PANI. [13] PANI as a p-type hole transport material [14] accelerates the transport of holes from the valence band of ZnO. In addition, oxygen molecules adsorbed on the surface of ZnO are very important for photoelectric reaction. Oxygen molecules trap electrons on the ZnO conduction band to form oxygen anions. [15] During the light phase, oxygen anions will react with photogenerated holes. The adsorbed oxygen is released while reducing the barrier of the material. The reduction of the interface barrier facilitates the migration separation of carriers. (Response mechanism diagram is shown in Figure 6.)

![Figure 6. The Band Diagram and Mechanism](image)

When the mass content of PANI is less than 5%, it leads to increase the p-n heterojunction with the increasing the content of PANI. And it is contributed to separate the carriers. When the mass content of PANI is 5%, the response reaches the maximum response, and if the content of PANI continues to
increase, the response of the composites to the UV light is reduced. With increasing the content of PANI, it will increase the specific surface area and interface density. And that it is lead to increase the recombination probability of photogenerated electron-holes. Therefore, the excessively high amount of PANI doping will be detrimental to the response of UV light.

4. Conclusion
This paper introduces a simple method for preparing PANI-doped ZnO composites, and tests the response of PANI-doped ZnO composites with different doping ratios to ultraviolet light at room temperature. When the mass percentage of PANI is 5%, the response of the composites to UV light reaches the maximum. Based on the results, it can be attributed to two factors. One: the interface between p-type PANI and n-type ZnO forms a p-n heterojunction, which contributes to the separation of photogenerated hole-electron pairs. Secondly, the dispersed PANI can inhibit the formation of the interfacial recombination center and accelerate the transport of holes from the ZnO valence band, so that the photocurrent of the composite material is significantly improved. Combining experimental results with mechanism studies, we hope to help develop more p-n heterojunction composites that have higher response to UV light at room temperature.

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