

Article



Preparation of ZnO/Bi₂O₃ Composites as Heterogeneous Thin Film Materials with High Photoelectric Performance on FTO Base

Yuhan Nie¹, Yadong Xie¹, Ying Zheng¹, Yao Luo¹, Jianguo Zhang², Zao Yi^{1,*}, Fusheng Zheng^{1,*}, Li Liu¹, Xifang Chen¹, Pinggen Cai³ and Pinghui Wu⁴

- ¹ Joint Laboratory for Extreme Conditions Matter Properties, Southwest University of Science and Technology, Mianyang 621010, China; nieyuhan0604@163.com (Y.N.); xieyadong2021@163.com (Y.X.); zhhezyx@163.com (Y.Z.); ly408728507@163.com (Y.L.); liuli_jlu@163.com (L.L.); chenxifang1988@yeah.net (X.C.)
- ² Department of Physics, Jinzhong University, Jinzhong 030619, China; phys.zhangjg@gmail.com
- ³ Department of Applied Physics, College of Science, Zhejiang University of Technology, Hangzhou 310023, China; caippgg@zjut.edu.cn
- ⁴ Fujian Provincial Key Laboratory for Advanced Micro-Nano Photonics Technology and Devices, Quanzhou Normal University, Quanzhou 362000, China; phwu@zju.edu.cn
- ^t Correspondence: yizaomy@swust.edu.cn (Z.Y.); zhengfusheng@swust.edu.cn (F.Z.); Tel./Fax: +86-08-1624-80872 (Z.Y. & F.Z.)

Abstract: In recent years, ZnO nanomaterials have achieved great performance in solar energy applications. How to synthesize a ZnO nanocomposite structure with high photoelectric conversion efficiency has become an urgent problem to solved. In this paper, a narrow band gap bismuth trioxide (Bi_2O_3) coated on a ZnO nanoarray by magnetron sputtering was used to prepare a composite heterojunction ZnO/Bi₂O₃. Studies have found that ZnO/Bi₂O₃ exhibits excellent photoelectric conversion performance. By preparing a composite heterostructure of ZnO/Bi₂O₃, it can effectively compensate for the insufficient absorption of ZnO in the visible light range and inhibit the recombination of carriers within the material. The influence of Bi₂O₃ thickness on the microstructure and electronic structure of the ZnO/Bi₂O₃ composite structure was explored and analyzed. The energy gap width of the composite heterostructure decreases with the increase in the Bi₂O₃ thickness on the surface of the ZnO nanorod array. At the same time, the conductive glass composite film structure is simple to prepare and is very environmentally friendly. The ZnO/Bi₂O₃ composite heterogeneous material prepared this time is suitable for solar cells, photodetectors, photocatalysis and other fields.

Keywords: heterojunction; nanoarray; photoelectric conversion; band regulation

1. Introduction

The efficient application of clean energy is the focus of current research. Among them, the application of solar energy is particularly critical [1-3]. As a clean energy, solar energy is widely used in many fields, such as photocatalysis, solar cells and so on [4-6].

Wide bandgap ZnO is a semiconductor material with a direct energy gap of 3.2 eV and is an important material in the fields of sensors, varistors, pigments, electrophoresis, and medical materials [7]. It can generate a large number of carriers under the action of light and can be applied in the field of solar energy [8]. Compared with other semiconductor materials, ZnO has the following basic advantages: (1) ZnO has high electron mobility, can quickly transfer the generated photoelectrons, and effectively form photocurrent; (2) it has a natural substrate and can be closely combined with the material deposited on it; (3) wet chemical treatment (the method of liquid phase and preparation by chemical reaction of the chemical reaction is collectively referred to the as wet chemical method, such as chemical liquid phase deposition (CBD), electrochemical deposition (electroplating),



Citation: Nie, Y.; Xie, Y.; Zheng, Y.; Luo, Y.; Zhang, J.; Yi, Z.; Zheng, F.; Liu, L.; Chen, X.; Cai, P.; et al. Preparation of ZnO/Bi₂O₃ Composites as Heterogeneous Thin Film Materials with High Photoelectric Performance on FTO Base. *Coatings* **2021**, *11*, 1140. https:// doi.org/10.3390/coatings11091140

Received: 2 August 2021 Accepted: 16 September 2021 Published: 20 September 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). solvent gel, etc.,) can be applied to various treatment methods [9]; (4) it has strong resistance to radiation damage and can maintain good performance in extreme environments. The commonly used ZnO crystal preparation methods are the sol-gel method, solution evaporation decomposition method (EDS), wet synthesis, and gas-phase reaction [10–12]. These methods are cumbersome to operate and costly. The hydrothermal method is easy to operate, low in cost, and can produce high-quality zinc oxide in large quantities. In actual application, zinc oxide nanoarrays are more widely applied because of their high electron mobility and easy preparation characteristics [13]. Because the effective surface area of the ZnO nanoarrays structure is larger than that of the ZnO thin film, the smaller size of the ZnO nanoarrays not only helps to improve photoelectric conversion efficiency but also increases its signal-to-noise ratio. This is because the nanorod structure greatly reduces the transfer of holes and electrons generated inside the crystal to the surface, and improves the photoelectric conversion efficiency of the ZnO nanorod array. Although ZnO has good photocatalytic properties, its energy gap is about 3.2 eV, and it can only absorb ultraviolet light at a wavelength of less than 380 nm. Ultraviolet light only accounts for 5% of solar energy, so its utilization efficiency of sunlight is low. The smaller the bandgap of the photovoltaic semiconductor, the larger the light absorption range, but due to the rapid recombination of surface photogenerated holes and electrons, its photoelectric conversion efficiency is also very low. Therefore, traditional single-material catalysts find it difficult to achieve high-efficiency photoelectric conversion due to their energy gap limitation. Therefore, the modification of small molecules on the surface of inorganic nanostructures is an effective strategy to improve its interface performance and material performance [14–18]. Bimaterial coupled semiconductors are an effective way to solve the above problems. The two materials can form a heterojunction (i.e., a junction composed of two different elements or materials with different components. The gap width of the materials on both sides of the junction is different, and the heterojunction material has high magnification and response speed) [19–21]. The electric field in the junction region helps charge transport, enhances the electron-hole separation in the system, reduces recombination, and increases the carrier concentration involved in the catalytic process.

Bi₂O₃ is an important metal oxide semiconductor. Its valence bands relative to NHE (it is a general hydrogen electrode which is an electrode formed by the platinum electrode in a strong acid solution of 1 M. Here, the bandgap of Bi_2O_3 is under the electrode system, since subsequent tests such as photocurrent tests will be completed in the system) are 0.33 and 3.13 V, respectively, and the direct energy gap is 2.8 eV, respectively, which is suitable for light absorption in the visible light band [22]. Bessekhouad et al. [23] used Bi_2O_3 semiconductors to degrade pollutants in water under visible light. Under the conditions of ultraviolet light and visible light, nano-Bi₂O₃ particles or films can effectively decompose Rb and methyl orange pollutants in water, respectively [24]. It can be seen that it has good photoelectric conversion efficiency under visible light. As we all know, the photogenerated carriers in micron-sized semiconductor particles cannot be effectively transferred to the surface of the material, and the recombination effect is further weakened, resulting in low photoelectric conversion efficiency. If the grain radius is adjusted from micron to nanometer, the probability of recombination will be greatly reduced. Therefore, the preparation of nano-scale Bi_2O_3 is a key activity to improve photocatalytic performance. At present, it has been found that sonochemical treatment can quickly and effectively prepare various nanostructures under normal pressure and normal temperature [25-28]. Among them, the specific surface area of Bi_2O_3 nanoparticles is very high, but the practical application advantage is not obvious, because the suspended nanoparticles are easy to lose during the reaction and separation process, and may pollute the treated water again [29]. The Bi_2O_3 film has the advantage of being easy to recycle. Therefore, the Bi_2O_3 film can be modified with ZnO to form a coupled semiconductor and improve photoelectric conversion performance. As a kind of transparent electrode, FTO-based (SnO2 conductive glass doped with F on the surface, referred to as FTO, used as the substrate for this experiment) conductive glass has become the focus of researchers' attention due to its

good conductivity, transparent optical performance, and low cost [30]. A large number of studies have shown that the combination of the sol–gel method, magnetron sputtering (it has realized high speed, low temperature, and low damage. It demonstrates high-speed sputtering at low pressure by introducing a magnetic field on the target cathode surface, using the magnetic field constraints on charged particles to increase the plasma density to increase the sputtering rate), and other methods using oxides can change the Fermi energy of the material, make the structure have excellent diode characteristics, and greatly increase the positive current. Among them, magnetron sputtering has the advantages of low cost, low temperature, good bonding force, good film uniformity, and good density [31].

At present, research is being conducted on ZnO/Bi_2O_3 composite structure at home and abroad, but it is basically in the field of biomedicine and electrothermal physics [32–34]. There are few reports in the field of photoelectric conversion. Therefore, this article will explore the photoelectric conversion of a ZnO/Bi_2O_3 nanocomposite structure.

In this study, ZnO was first sputtered on FTO conductive glass substrate, and then a layer of high-quality ZnO nanorod array was grown by hydrothermal energy, and finally, a layer of Bi_2O_3 film with controllable thickness was sputtered on the array. The structure has excellent light absorption efficiency, and the ZnO nanorod array greatly increases the effective surface area of the material. By changing the thickness of Bi_2O_3 , the energy bandwidth of the composite structure can be adjusted to broaden the wavelength range of light absorption. Bi_2O_3 and ZnO, ZnO and FTO all form heterojunctions.

 $FTO/ZnO/Bi_2O_3$ has a double heterojunction structure as a whole, which increases the effective area of the built-in electric field. The carrier separation effect is enhanced, and the carrier recombination is suppressed, which is beneficial to improve the photoelectric conversion efficiency. The material also has excellent hydrophilic properties. Based on the above advantages, the material is suitable for solar energy, sensors, electroluminescence, and other fields.

2. Experimental Part

Purchased acetone (C₃H₆O) (67-64-1), absolute ethanol (99.5% purity) (64-17-5), hexamethylenetetramine (HMTA, C₆H₁₂N₄) (100-97-0), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) (10196-18-6), and sodium sulfate solution (Na₂SO₄, 0.1 mol/L) (7757-82-6) from the chemical reagent company of Chinese medicine. All drugs and reagents are purely analytical. The resistivity of the ultrapure water used in the experiment is about 18.2 mΩ·cm (Ω is resistance unit). Conductive glass (FTO), target (specification: $60 \times 5 \text{ mm}^2$, purity 99.99%) (1304-76-3), ZnO target (specification: $60 \times 5 \text{ mm}^2$, purity 99.99%) (1314-13-2) were all purchased from Beijing Zhongnuo New Material Technology Co., LTD (Beijing, China).

Required instruments are as follows: high vacuum magnetron sputtering coating system (JGP-560B, Shenyang Scientific Instrument Co., LTD., Chinese Academy of Sciences, Shenyang, China): electronic balance (CP214, Aowus Instrument (Changzhou, China) Co., LTD.); high purity water plant (Direct-Q3, Millipore, Burlington, MA, USA); Ultrasonic cleaning machine (JP-080ST, Shenzhen Jiemeng Cleaning Equipment Co., LTD., Shenzhen, China); electric constant temperature blast drying oven (DHG-9036A, Shanghai Jinghong Laboratory Equipment Co., LTD., Shanghai, China); electrochemical workstation (CHI760E, Shanghai Chenhua Instrument Co., LTD., Shanghai, China); xenon lamp source (CEL-LS500/350, Beijing Zhongjiao Jinyuan Technology Co., LTD., Beijing, China); ultravioletvisible spectrophotometer (UV-2700, Shimadzu Co., LTD., Kyoto, Japan); optical contact angle measuring instrument (SDC-35OH, Dongguan Shengding Precision Instrument Co., LTD., Dongguan, China); X-ray diffractometer (X 'Pert PRO, Panaco); scanning electron microscope (ZEISS Ultra 55, ZEISS Instruments, Oberkochen, Germany).

First, follow the order of acetone (C_3H_6O), absolute ethanol (99.5% purity), and ultrapure water to ultrasonically clean the FTO substrate for 15 min each. Then, make high-pressure nitrogen to dry the water. The ZnO magnetron sputtering power is 60 W, evacuated to 10^{-4} Pa and then argon gas is introduced, the flow rate is 40 sccm (gas flow unit), the working pressure is 1 Pa during sputtering, and the surface impurities are

removed by pre-sputtering for 10 min. In the experiment, ZnO sputtered for 2 min at 20 nm. Weigh 0.4486 g of hexamethylenetetramine (HMTA) and 0.9519 g of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), add 80 mL of ultrapure water, and put them into the inner bladder (polytef) of the pressure reactor. Sonicate for 15 min to make it evenly mixed. Put the FTO sputtered with ZnO face down into the inner container of the reactor and put the inner container into the stainless steel reactor. Put the reaction kettle into an oven, start timing when the temperature is raised to 98 °C, and heat at a constant temperature for 4 h. After taking it out, wash away the remaining solution with ultrapure water, and let it dry naturally in the air.

The growth of ZnO nanorods in precursor solution is driven by the following four chemical reactions. Decomposition:

$$(CH_2)_6N_4 + H_2O \rightarrow 6HCHO + 4NH_3 \tag{1}$$

Hydroxyl supply:

$$NH_3 + H_2O \rightarrow NH_{4^+} + OH^-$$
⁽²⁾

Excessive saturation:

$$2OH^- + Zn^+ \to Zn(OH)_2 \tag{3}$$

Growth of ZnO nanorods:

$$Zn(OH)_2 \to ZnO + H_2O \tag{4}$$

The Bi₂O₃ magnetron sputtering power is 60 W, evacuated to 10^{-4} Pa and then argon gas is introduced, the flow rate is 40 sccm, the working pressure is 0.8 Pa during sputtering, and the surface impurities are removed by pre-sputtering for 10 min. In the experiment, Bi₂O₃ was sputtered 10, 15, 20, 25, 30 nm.

XRD is applied to determine the crystal orientation of the sample and compare it with the standard document. Scanning electron microscopy (SEM) characterizes the morphology of the sample. The solid-ultraviolet spectrophotometer measures its UV (ultraviolet) reflectance and absorbance. The contact angle measuring instrument tests its hydrophilicity and hydrophobicity. A three-electrode system is used to test its photoelectric performance and endurance.

3. Result in Analysis

X-ray diffraction was performed on the prepared FTO/ZnO/Bi₂O₃. As shown in Figure 1, the Bi₂O₃ deposited thereon are, respectively 0, 10, 15, 20, 25, and 30 nm. The (110), (101), (200), (211), (220) peaks of FTO conductive glass (SnO₂) correspond to 2θ values of 26.48°, 33.7°, 37.77°, 51.58°, 54.52°, respectively. The 20 values of the prepared ZnO on (002), (101), (102), (103) correspond to 34.43°, 36.24°, 47.5°, 62.84°, respectively. Compared with the standard picture (JCPDS card no. 36-1451) [35–37], it is wurtzite ZnO. In Figure 1, it can be observed that several newly grown peaks with 2θ values of 31.76° , 47.5° , and 61.67° correspond exactly to the (002), (-141), (232) peaks of α -Bi₂O₃ (JCPDS no. 71–2274) [38]. It can be judged that Bi_2O_3 exists in wurtzite ZnO as α - Bi_2O_3 (monoclinic crystal form). The (002) peak of ZnO has relatively high intensity, showing anisotropic growth. As the thickness of Bi_2O_3 increases, the intensity of (002), (-141), (232) diffraction peaks corresponding to α -Bi₂O₃ in the sample will gradually increase. Among them, the (-141) peak of Bi₂O₃ over laps with the (102) peak of ZnO. It can be seen in the Figure 1 that as the thickness of Bi_2O_3 increases, the height of the overlapped peak increases continuously, which proves that the Bi_2O_3 (-141) is contained in this peak. In each set of data, the peak of ZnO did not move significantly, proving that Bi₂O₃ did not affect the lattice orientation of ZnO. It just attaches to the ZnO nanoarrays.



Figure 1. Shows the XRD pattern of ZnO nanoarrays + Bi_2O_3 . 1. Pure ZnO nanoarrays; 2. ZnO nanoarrays + Bi_2O_3 (10 nm); 3. ZnO nanoarrays + Bi_2O_3 (15 nm); 4. ZnO nanoarrays + Bi_2O_3 (20 nm); 5. ZnO nanoarrays + Bi_2O_3 (25 nm); 6. ZnO nanoarrays + Bi_2O_3 (30 nm).

Many factors limit the growth of ZnO nanoarrays. The reaction temperature and time, and the concentration of the precursor solution have an influence. According to referenced literature and experimental results, we chose 40 mol/L mixed solutions of hexamethylenetetramine (HMTA) and zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O)$ as the precursor solution, 4 h reaction time, and a reaction temperature of 98 °C was used to prepare the required ZnO nanoarrays. Figure 2A clearly shows the SEM photo of ZnO nanoarrays (FTO/ZnO). It can be observed in the figure that there are a large number of well-grown ZnO nanoarrays on the FTO substrate, every nanoarray is separated and not adhered to. In the figure, it can be seen that the zinc oxide nanoarrays grow vertically on the FTO. The SEM images of Figure 2B–E correspond to FTO/ZnO/Bi₂O₃ (10, 15, 20, 25 nm), respectively. You can see the Bi₂O₃ particles deposited on the nanoarrays. These particles adhere well to the ZnO nanoarrays, which increases the roughness of the ZnO nanoarrays. Additionally, more nanoclusters are formed between the Bi₂O₃ particles and the ZnO nanoarrays. However, it can be seen that the originally vertical ZnO nanoarrays have become somewhat curved. The SEM images of Figure 2F correspond to FTO/ZnO/Bi₂O₃ (30 nm). At this time, the ZnO nanoarrays become thicker, and the bending angle and the lodging area are further enlarged. This is because as the thickness of Bi₂O₃ increases, a large number of Bi_2O_3 particles accumulate at the bottom, which bends due to gravity. This will reduce the photoelectric performance of the structure, so the thickness of Bi_2O_3 is not as big as possible. Only with proper thickness can the maximum difference between performance increase and performance decrease be reached. Inferred from the morphology, 20, 25 nm may have the best performance.



Figure 2. SEM image of ZnO nanoarrays. (**A**) Pure ZnO nanoarrays; (**B**) ZnO nanoarrays + Bi_2O_3 (10 nm); (**C**) ZnO nanoarrays + Bi_2O_3 (15 nm); (**D**) ZnO nanoarrays + Bi_2O_3 (20 nm); (**E**) ZnO nanoarrays + Bi_2O_3 (25 nm); (**F**) ZnO nanoarrays + Bi_2O_3 (30 nm).

Figure 3 shows the hydrophilicity of the sample. According to Young's formula, the hydrophilicity of an object is judged by the static contact angle (θ) between the liquid and the solid. When $\theta > 90^\circ$, the surface of the material is hydrophobic, that is, the material is not easily wetted by liquid. When $\theta < 90^\circ$, the surface of the material is hydrophilic, that is, the material is easily wetted by liquid [39–41]. It has good hydrophilicity it can be in closer contact with pollutants in water. If it is applied in the field of photocatalysis, its photocatalytic effect will be very good. It can be seen that the contact angle of the pure ZnO nanoarray without Bi₂O₃ is 65°. The contact angles of deposited (10, 15, 20, 25, 30 nm) Bi₂O₃ are 36.48°, 24°, 14.99°, 13.41°, 22.08°, and it can be seen that the 25 nm thick Bi₂O₃ has the best hydrophilic properties. The gradual increase in hydrophilicity from 0 to 25 nm occurs because the Bi₂O₃ particles change the roughness of the contact surface with water, allowing the material to have a larger area in contact with water. Up to 30 nm, the lodging of ZnO nanoarrays increases, and the filling effect of the Bi₂O₃ particles on the gully is intensified, which reduces the contact area, so hydrophilicity decreases.



Figure 3. Shows the contact angle of ZnO nanoarrays + Bi_2O_3 . (A) Pure ZnO nanoarrays; (B) ZnO nanoarrays + Bi_2O_3 (10 nm); (C) ZnO nanoarrays + Bi_2O_3 (15 nm); (D) ZnO nanoarrays + Bi_2O_3 (20 nm); (E) ZnO nanoarrays + Bi_2O_3 (25 nm); (F) ZnO nanoarrays + Bi_2O_3 (30 nm).

Figure 4 shows the reflection of the composite structure in the 200–850 nm band. It can be seen that the reflectance in the ultraviolet band of 200–400 nm is almost zero, as ZnO has a forbidden bandwidth of 3.2 eV, which has a strong absorption effect in the ultraviolet band [42,43]. By increasing the thickness of Bi_2O_3 , the reflectivity in the visible light region gradually decreases. This is closely related to the 2.8 eV energy gap of Bi_2O_3 , which matches the visible light band. When the thickness of Bi_2O_3 increases to 25 nm, the reflectivity is the lowest. At this point, the reflection at 850 nm is 21.224%. At 30 nm, the reflectivity increases again. This is likely due to the fact that as the thickness of Bi_2O_3 increases, the trenches in the formed ZnO nanoarrays are filled, the surface gradually changes from a three-dimensional structure to a flat film, and its reflectivity to light begins to increase.



Figure 4. UV-Visible reflectance spectrum of the sample.

Figure 5 shows the absorption of the composite structure in the 200–850 nm band. The absorption is consistent with the reflection pattern. In the ultraviolet band, it is mainly absorbed by the ZnO nanoarrays, and the influence of Bi_2O_3 on the absorption is not significant. When it reaches about 380 nm, the absorption value of each group is the same, the wavelength continues to increase, and the influence of Bi_2O_3 on the absorption can be clearly seen. In a certain range, the absorption value increases with the increase in Bi_2O_3 thickness and then decreases with the increase in Bi_2O_3 thickness. The decrease in the 30 nm absorption value is related to the increase in the reflectivity of the structure surface, and also to the filling of the trenches between the ZnO nanoarrays, the surface area of the structure decreases, and the absorption of light will also decrease. The efficient absorption of light is a fundamental means to improve photocatalytic performance [44–46]. Experiments show that coupled two materials with different energy gap widths are an effective means of wideband and high absorption. It can be seen from the figure that the Bi_2O_3 composite structure with a thickness of 25 nm has the highest light absorption efficiency.



Figure 5. UV-Visible absorbance spectrum of the sample.

By processing the UV absorption data by the Tacu plot method, the energy gap of the compound semiconductor can be calculated [47–49]. The formula is:

$$(\alpha h v)^{1/n} = Q(h v - Eg)$$
⁽⁵⁾

where α is the light absorption index, h represents Planck's constant, $h = 6.6260755 \times 10^{-34}$ J·s, v is the photon frequency, Q is a constant, and Eg is the energy gap of the material. The value of *n* is related to the energy band structure of the material. Direct energy gap semiconductor (such as ZnO) n = 1/2, indirect energy gap semiconductor n = 2. Ultraviolet absorption value (Abs) is proportional to α . For the sake of simplicity, the ultraviolet absorption value (Abs) is used instead of α in the calculation. The specific method is to use the value of $(\alpha hv)^{1/n}$ as the y-axis, and the hv value as the x-axis. After the curve is drawn, there is a straight line in the curve. Extend the straight line to intersect the x-axis. The x-coordinate value of the intersection is the forbidden bandwidth of the material [50–52]. When calculating the pure ZnO nanoarrays, n = 1/2. When calculating the ZnO/Bi₂O₃ composite structure, n = 2. Since electrons do not directly excite the valence band to

The calculated energy gaps of each group are listed in Table 1. The results show that the energy gap width of ZnO is 3.233 eV, which is close to that reported in the literature. As the thickness of Bi_2O_3 increases, the energy bandwidth of the composite structure decreases, and the absorption range becomes wider. When the thickness of Bi_2O_3 is 25 nm, the energy gap decreases to 2.942 eV, and when the thickness of Bi_2O_3 increases, the energy gap width increases again. These data indicate that the energy band of ZnO can be modified by changing the thickness of Bi_2O_3 . Additionally, for ZnO with a thickness of 20 nm, the best matching Bi_2O_3 thickness is 25 nm.

Bi ₂ O ₃ Content (nm)	Energy Gap (eV)
0	3.233
10	3.114
15	3.092
20	3.061
25	2.942
30	3.055

Table 1. Energy gap widths of each experimental group.

Under a bias voltage (photoelectrons move incompetently towards the electrode under the external anode bias, avoiding the simple combination of the electron–hole and thus prolonging the life of the hole) of 1.5 V, the calomel electrode is used as the reference electrode, and the Pt electrode is used as the auxiliary electrode, and the sample is clamped on the working electrode. The metal piece of the electrode touches the coated side. To make 0.1 mol/L Na₂SO₄ solution as electrolyte. The formed three-electrode system performs photocurrent tests on the sample [53–55]. The sample is 20 cm away from the light source, and the side coated with the composite film structure faces the light source. The dark–light conversion is performed every 40 s to test the net photogenerated current density and the response to light. The total test time is 400 s. We judge the photocatalytic performance of the composite structure based on the generated photocurrent density.

It can be seen in Figure 6 that the photoresponse characteristics of each control group are all excellent. The photocurrent density of the ZnO nanoarrays with the thickness of Bi_2O_3 increased within a certain range from the dark to the light response group is significantly higher than that of pure ZnO. As the thickness of Bi_2O_3 deposited on the ZnO nanoarrays gradually increases, the resulting photocurrent density also increases, and reaches the maximum photocurrent density of $0.458 \text{ mA} \cdot \text{cm}^{-2}$ at a thickness of 25 nm, which is about 5.5 times that of the pure ZnO nanoarrays (the photocurrent density of the pure ZnO nanoarray is 0.088 mA·cm⁻²). This is because the smaller energy gap of Bi_2O_3 has a good absorption effect on visible light, and the heterojunction structure formed by ZnO/Bi₂O₃ has the effect of inhibiting the recombination of photogenerated electrons and holes. The generated carriers can have a longer lifetime. That is, there is a higher concentration at the reaction interface, which greatly improves the photoelectric conversion efficiency, while the photocurrent density at 30 nm is reduced. Additionally, the photocurrent density at 25 nm is the largest. It is proved that the quantum traps in the combined system are the least, and only a small part of the generated photoelectrons are used for trap filling [56–58]. More photoelectrons form the photocurrent.

Electrochemical Impedance Spectroscopy (EIS) is used to measure the ratio of the AC potential to the current signal (the impedance of the system) changes with the frequency α of the sine wave by applying a small amplitude alternating sine potential wave with different frequencies to the electrochemical system, or the change of the phase angle φ of the impedance with α . An external voltage signal can produce a current signal, which is somewhat similar to a normal circuit. Levie et al. [59] made an equivalent circuit to the impedance diagram that appeared to analyze the working state of the material. This



Figure 6. J-V image of a sample measured by an electrochemical workstation using a xenon lamp to simulate sunlight exposure.

The impedance diagram of each group can be seen in Figure 7, which can be seen in two parts. Part I is that the impedance diagram at high frequency, which resembles an exponential function. According to Levie's theory, the working state of the material at this stage can be equivalent to a collection circuit composed of many tiny resistors and capacitors. As the frequency decreases, the effect of capacitor C increases. As the frequency increases, the effect of the resistance R increases. When the frequency is low, it can be equivalent to the resistance R and the capacitor C in series, and when the frequency is high, it mainly shows the characteristics of the resistance R.



Figure 7. In a 0.1 mol/L Na₂SO₄ (PH (Hydrogen ion concentration index) = 7) solution, keeping the bias voltage at 1.5 V, using a standard calomel electrode as the reference electrode to test the J-T image of the sample.

Part II demonstrates that when the low-frequency part changes from a semicircle to close to zero, the curve becomes warped upwards at a certain angle. According to the equivalent circuit model shown in Figure 8, this section can be equivalent to the circuit shown in the figure. When the frequency is relatively high, $Z\omega$ approaches zero. At this time, the impedance diagram is semicircular, and the material is mainly based on charge transfer at this time. When the frequency approaches zero, it is mainly material transfer. The reason why the impedance curve tilts upward at a certain angle is most likely due to the rough surface of the electrode, which makes a part of the diffusion process equivalent to spherical diffusion. The height of the apex of the impedance curve of the 25 nm thick Bi_2O_3 is the smallest, indicating that it has the least hindrance to the photocurrent.



Figure 8. Part II equivalent circuit diagram.

The working principle of ZnO/Bi₂O₃ can refer to the scheme proposed by Medina et al. [60]. As shown in Figure 9, the photogenerated electrons on ZnO move in the direction of Bi_2O_3 , and the holes on Bi_2O_3 move in the direction of ZnO. This process not only accelerates the generation of carriers but also promotes the migration of carriers in Bi_2O_3 to ZnO. However, also, we also introduced the FTO substrate. According to the report of Saha et al. [61], the combination of FTO and oxide also forms a heterojunction, which greatly improves the response to light. Therefore, compared with ZnO/Bi₂O₃ composite materials, FTO/ZnO/Bi₂O₃ has better photoelectric conversion performance and is more convenient to recycle.



Figure 9. ZnO/Bi₂O₃ composite band diagram.

4. Conclusions

In summary, the ZnO/Bi₂O₃ composite heterostructure was successfully prepared on the FTO base using magnetron sputtering and hydrothermal growth methods, and characterized. The XRD analysis showed that the (-141) crystal orientation of Bi₂O₃ and the (101) crystal orientation of ZnO exist in the heterostructure. In the SEM image, it can be seen that the ZnO nanoarrays grow well, have the same direction, and that the Bi_2O_3 adheres well. Ultraviolet absorption is several times higher than that of the pure ZnO structure, and the photocurrent performance is improved several times. This is mainly due to the formation of heterostructures between ZnO nanoarrays and ZnO and Bi_2O_3 . The ZnO nanoarrays can effectively improve the system signal-to-noise ratio. It also promotes the movement or transfer of electrons and holes generated inside the crystal to the surface. The electric field in the heterojunction region facilitates charge transport, improves electronhole separation in the system, reduces recombination, and increases the concentration of photogenerated carriers. Bi_2O_3 is used as a light absorber and ZnO photogenerated electron transmitter, which helps to improve photoelectric conversion efficiency. Through this research, it is found that the materials prepared this time have great research and application prospects in the field of solar cells. However, the current problem is mainly that the stability of thin film materials needs to be improved, which is also a problem that we need to continue to study and solve.

Author Contributions: Y.N.: Conceptualization, Formal analysis, Investigation, Data curation, Writing—original draft, Writing—review and editing. Y.X.: Conceptualization, Formal analysis, Investigation, Data curation, Funding acquisition. Y.Z.: Conceptualization, Formal analysis, Investigation, Data curation, Writing—original draft, Writing—review and editing. Y.L.: Conceptualization, Formal analysis, Revision. J.Z.: Conceptualization, Formal analysis, Revision. J.Z.: Conceptualization, Formal analysis, Revision. F.Z.: Formal analysis, Funding acquisition. L.L.: Conceptualization, Formal analysis, Revision. X.C.: Conceptualization, Formal analysis, Revision. P.C.: Conceptualization, Formal analysis, Revision. P.W.: Conceptualization, Formal analysis, Revision. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are grateful to the support by National Natural Science Foundation of China (No. 51606158, 11604311, 12074151); The funded by the Scientific Research Fund of SiChuan Provincial Science and Technology Department (2020YJ0137; 2020YFG0467; 2021JDRC0019); the College Students' innovation and entrepreneurship training program (S202110619073; S202110619069); ecision Funding by Southwest University of Science and Technology (JZ20-027, JZ20-025); the Undergraduate Innovation Fund Project of SWUST (CX 21-099, LX2020010).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Publicly available datasets were analyzed in this study. This data can be found here: [https://www.lumerical.com/], accessed on 15 September 2021.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Tang, N.M.; Li, Y.J.; Chen, F.T.; Han, Z.Y. In situ fabrication of a direct Z-scheme photocatalyst by immobilizing CdS quantum dots in the channels of graphene-hybridized and supported mesoporous titanium nanocrystals for high photocatalytic performance under visible light. RSC Adv. 2018, 8, 42233–42245. [CrossRef]
- Cheng, T.T.; Gao, W.H.; Gao, H.J.; Wang, S.F.; Yi, Z.; Wang, X.X.; Yang, H. Piezocatalytic degradation of methylene blue, tetrabromobisphenol A and tetracycline hydrochloride using Bi₄Ti₃O₁₂ with different morphologies. *Mater. Res. Bull.* 2021, 141, 111350. [CrossRef]
- Su, J.; Yang, H.; Xu, Y.; Tang, Y.J.; Yi, Z.; Zheng, F.S.; Zhao, F.; Liu, L.; Wu, P.H.; Li, H.L. Based on ultrathin PEDOT: PSS/c-Ge solar cells design and their photoelectric performance. *Coatings* 2021, 11, 748. [CrossRef]
- 4. Zhou, F.Q.; Qin, F.; Yi, Z.; Yao, W.T.; Liu, Z.M.; Wu, X.W.; Wu, P.H. Ultra-wideband and wide-angle perfect solar energy absorber based on Ti nanorings surface plasmon resonance. *Phys. Chem. Chem. Phys.* **2021**, *31*. [CrossRef]
- 5. Lin, X.; Li, Y.J.; Chen, F.T.; Xu, P.; Li, M. Facile synthesis of mesoporous titanium dioxide doped by Ag-coated graphene with enhanced visible-light photocatalytic performance for methylene blue degradation. *RSC Adv.* **2017**, *7*, 25314–25324. [CrossRef]
- Li, J.; Chen, X.; Yi, Z.; Yang, H.; Tang, Y.; Yi, Y.; Yao, W.; Wang, J.; Yi, Y. Broadband solar energy absorber based on monolayer molybdenum disulfide using tungsten elliptical arrays. *Mater. Today Energy* 2020, 16, 100390. [CrossRef]
- 7. Zhang, F.; Wang, B.; Shen, Y.Q. Blue luminescent ZnO nanoclusters stabilized by esterifiable polyamidoamine dendrimers and their UV-shielding applications. *Asian J. Chem.* **2014**, *26*, 3467–3470. [CrossRef]
- 8. Wu, H.; Jile, H.; Chen, Z.Q.; Xu, D.Y.; Yi, Z.; Chen, X.F.; Chen, J.; Yao, W.T.; Wu, P.H.; Yi, Y.G. Fabrication of ZnO@MoS₂ nanocomposite heterojunction arrays and their photoelectric properties. *Micromachines* **2020**, *11*, 189. [CrossRef]

- 9. Cheng, T.T.; Gao, H.J.; Li, R.S.; Wang, S.F.; Yi, Z.; Yang, H. Flexoelectricity-induced enhancement in carrier separation and photocatalytic activity of a photocatalyst. *Appl. Surf. Sci.* **2021**, *566*, 150669. [CrossRef]
- 10. Huan, H.; Jile, H.; Tang, Y.J.; Li, X.; Yi, Z.; Gao, X.; Chen, X.F.; Chen, J.; Wu, P.H. Fabrication of ZnO@Ag@Ag₃PO₄ ternary heterojunction: Superhydrophilic properties, antireflection and photocatalytic properties. *Micromachines* **2020**, *11*, 309. [CrossRef]
- 11. Zeng, Y.; Chen, X.F.; Yi, Z.; Yi, Y.G.; Xu, X.B. Fabrication of p-n heterostructure ZnO/Si moth-eye structures: Antireflection, enhanced charge separation and photocatalytic properties. *Appl. Surf. Sci.* **2018**, *441*, 40–48. [CrossRef]
- 12. Wang, Y.; Li, R.; Sun, X.; Xian, T.; Yi, Z.; Yang, H. Photocatalytic application of Ag-decorated CuS/BaTiO₃ composite photocatalysts for degrading RhB. J. Electron. Mater. **2021**, 50, 2674–2686. [CrossRef]
- 13. Wang, J.J.; Ling, T.; Qiao, S.Z.; Du, X.W. Double open-circuit voltage of three-dimensional ZnO/CdTe solar cells by a balancing depletion layer. *ACS Appl. Mater. Interfaces* 2014, *6*, 14718–14723. [CrossRef]
- 14. Cheng, T.T.; Gao, H.J.; Sun, X.F.; Xian, T.; Wang, S.F.; Yi, Z.; Liu, G.R.; Wang, X.X.; Yang, H. An excellent Z-scheme Ag₂MoO₄/Bi₄Ti₃O₁₂ heterojunction photocatalyst: Construction strategy and application in environmental purification. *Adv. Powder Technol.* **2021**, *32*, 951–962. [CrossRef]
- 15. Cai, L.; Zhang, Z.H.; Xiao, H.M.; Chen, S.; Fu, J.L. An eco-friendly imprinted polymer based on graphene quantum dots for fluorescent detection of p-nitroaniline. *RSC Adv.* **2019**, *9*, 41383–41391. [CrossRef]
- Li, J.H.; Jiang, J.B.; Xu, Z.F.; Liu, M.Q.; Tang, S.P.; Yang, C.M.; Qian, D. Facile synthesis of Ag@Cu₂O heterogeneous nanocrystals decorated N-doped reduced graphene oxide with enhanced electrocatalytic activity for ultrasensitive detection of H₂O₂. Sens. Actuators B Chem. 2018, 260, 529–540. [CrossRef]
- 17. Chen, P.; Liu, F.; Ding, H.; Chen, S.; Chen, L.; Li, Y.J. Porous double-shell CdS@C₃N₄ octahedron derived by in situ supramolecular self-assembly for enhanced photocatalytic activity. *Appl. Catal. B Environ.* **2019**, 252, 33–40. [CrossRef]
- Liu, H.; Wang, Q.; Zhang, F. Preparation of Fe₃O₄@SiO₂@P(AANa-co-AM) composites and their adsorption for Pb (II). ACS Omega 2020, 5, 8816–8824. [CrossRef] [PubMed]
- 19. Cai, R.; Rao, W.; Zhang, Z.H.; Long, F.; Yin, Y.L. An imprinted electrochemical sensor for bisphenol A determination based on electrodeposition of a graphene and Ag nanoparticle modified carbon electrode. *Anal. Methods* **2014**, *6*, 1590–1597. [CrossRef]
- 20. He, Z.; Xue, W.; Cui, W.; Li, C.; Li, Z.; Pu, L.; Feng, J.; Xiao, X.; Wang, X.; Li, G. Tunable fano resonance and enhanced sensing in a simple Au/TiO₂ hybrid metasurface. *Nanomaterials* **2020**, *10*, 687. [CrossRef]
- Li, J.; Wang, S.; Sun, G.; Gao, H.; Yu, X.; Tang, S.; Zhao, X.; Yi, Z.; Wang, Y.; Wei, Y. Facile preparation of MgAl₂O₄/CeO₂/Mn₃O₄ heterojunction photocatalyst and enhanced photocatalytic activity. *Mater. Today Chem.* 2021, 19, 100390. [CrossRef]
- Gurunathan, K. Photocatalytic hydrogen production using transition metal ions-doped γ-Bi₂O₃ semiconductor particles. *Int. J. Hydrogen Energy* 2004, 29, 933–940. [CrossRef]
- Bessekhouad, Y.; Robert, D.; Weber, J.V. Photocatalytic activity of Cu₂O/TiO₂, Bi₂O₃/TiO₂ and ZnMn₂O₄/TiO₂ heterojunctions. *Catal. Today* 2005, 101, 315–321. [CrossRef]
- Sakar, M.; Balakumar, S.; Saravanan, P.; Bharathkumar, S. Particulates vs. fibers: Dimension featured magnetic and visible light driven photocatalytic properties of Sc modified multiferroic bismuth ferrite nanostructures. *Nanoscale* 2016, *8*, 1147–1160. [CrossRef]
- Cheng, T.; Sun, X.; Xian, T.; Yi, Z.; Li, R.; Wang, X.; Yang, H. Tert-butylamine/oleic acid-assisted morphology tailoring of hierarchical Bi₄Ti₃O₁₂ architectures and their application for photodegradation of simulated dye wastewater. *Opt. Mater.* 2021, 112, 110781. [CrossRef]
- 26. Li, Z.Y.; Yi, Z.; Liu, T.T.; Liu, L.; Chen, X.F.; Zheng, F.S.; Zhang, J.G.; Li, H.L.; Wu, P.H.; Yan, P.G. Three-band perfect absorber with high refractive index sensing based on active tunable Dirac semimetal. *Phys. Chem. Chem. Phys.* **2021**, 23, 17374–17381. [CrossRef]
- 27. Jiang, L.Y.; Yi, Y.T.; Yi, Z.; Yang, H.; Li, Z.Y.; Su, J.; Zhou, Z.G.; Chen, X.F.; Yi, Y.G. A four-band perfect absorber based on high quality factor and high figure of merit of monolayer molybdenum disulfide. *Acta Phys. Sin.* **2021**, *70*, 128101. [CrossRef]
- 28. Lv, P.P.; Xie, D.D.; Zhang, Z.H. Magnetic carbon dots based molecularly imprinted polymers for fluorescent detection of bovine hemoglobin. *Talanta* **2018**, *188*, 145–151. [CrossRef]
- 29. Rammah, Y.S.; Mahmoud, K.A.; Kavaz, E.; Kumar, A.; El-Agawany, F.I. The role of PbO/Bi₂O₃ insertion on the shielding characteristics of novel borate glasses. *Ceram. Int.* 2020, *46*, 23357–23368. [CrossRef]
- 30. Al-Hadeethi, Y.; Sayyed, M.I. A comprehensive study on the effect of TeO₂ on the radiation shielding properties of TeO₂–B₂O₃– Bi₂O₃–LiF–SrCl₂ glass system using Phy-X/PSD software. *Ceram. Int.* **2020**, *46*, 6136–6140. [CrossRef]
- 31. Pugazhenthiran, N.; Sathishkumar, P.; Murugesan, S.; Anandan, S. Effective degradation of acid orange 10 by catalytic ozonation in the presence of Au-Bi₂O₃ nanoparticles. *Chem. Eng. J.* **2011**, *168*, 1227–1233. [CrossRef]
- 32. Ansari, S.; Ansari, M.S.; Satsangee, S.P.; Jain, R. Bi₂O₃/ZnO nanocomposite: Synthesis, characterizations and its application in electrochemical detection of Balofloxacin as an anti-biotic drug. *J. Pharm. Anal.* **2020**, *3*, 13.
- Takayuki, K.; Taisuke, I.; Tina, T.; Tsuyoshi, H.; Vesselin, D. Correlation between thermal expansion coefficient and interionic interaction parameter in ZnO-Bi₂O₃-B₂O₃ glasses. *J. Ceram. Soc. Jpn.* 2018, 126, 8–15.
- 34. Chen, X.; Zhou, Y.; Han, H.; Wang, X.; Zhou, L.; Yi, Z.; Fu, Z.; Wu, X.; Li, G.; Zeng, L. Optical and magnetic properties of small-size core–shell Fe₃O₄@C nanoparticles. *Mater. Today Chem.* **2021**, *22*, 100556. [CrossRef]
- 35. Long, F.; Zhang, Z.H.; Wang, J.; Yan, L.; Zhou, B.W. Cobalt-nickel bimetallic nanoparticles decorated graphene sensitized imprinted electrochemical sensor for determination of octylphenol. *Electrochim. Acta* **2015**, *168*, 337–345. [CrossRef]

- 36. Li, Z.; Yi, Y.; Xu, D.; Yang, H.; Yi, Z.; Chen, X.; Yi, Y.; Zhang, J.; Wu, P. A multi-band and polarization-independent perfect absorber based on Dirac semimetals circles and semi-ellipses array. *Chin. Phys. B* **2021**. [CrossRef]
- Zhang, Z.H.; Cai, R.; Long, F.; Wang, J. Development and application of tetrabromobisphenol A imprinted electrochemical sensor based on graphene/carbon nanotubes three-dimensional nanocomposites modified carbon electrode. *Talanta* 2015, 134, 435–442. [CrossRef] [PubMed]
- 38. Gao, H.; Wang, Y.; Gao, Q.; Pan, X.; Wang, S.; Yang, H.; Chen, C.; Wang, Y.; Fang, L.; Yi, Z. Phase evolution and photoluminescence behavior of MMoO₄ (M = Mg, Ca, Sr) phosphors. *Optik* **2021**, 241, 167040. [CrossRef]
- Chen, Z.; Chen, H.; Yin, J.; Zhang, R.; Jile, H.; Xu, D.; Yi, Z.; Zhou, Z.; Cai, S.; Yan, P. Multi-band, Tunable, High figure of merit, high sensitivity single-layer patterned graphene—Perfect absorber based on surface plasmon resonance. *Diam. Relat. Mater.* 2021, 116, 108393. [CrossRef]
- Xiong, S.; Yin, Z.; Zhou, Y.; Peng, X.; Yan, W.; Liu, Z.; Zhang, X. The dual-frequency (20/40 kHz) ultrasound assisted photocatalysis with the active carbon fiber-loaded Fe³⁺-TiO₂ as photocatalyst for degradation of organic dye. *Bull. Korean Chem. Soc.* 2013, 34, 3039–3045. [CrossRef]
- Chen, H.J.; Zhang, Z.H.; Cai, R.; Kong, X.Q.; Chen, X.; Liu, Y.N.; Yao, S.Z. Molecularly imprinted electrochemical sensor based on a reduced graphene modified carbon electrode for tetrabromobisphenol A detection. *Analyst* 2013, 138, 2769–2776. [CrossRef] [PubMed]
- 42. Han, Z.Y.; Li, Y.J.; Lin, X.; Wang, Z.Y.; Li, Z.Q.; Wang, H. Preparation and photoelectrocatalytic performance of Fe₂O₃/ZnO composite electrode loading on conductive glass. *Chem. Res. Chin. U* **2018**, *39*, 771–778.
- 43. Chen, Z.; Chen, H.; Jile, H.; Xu, D.; Yi, Z.; Lei, Y.; Chen, X.; Zhou, Z.; Cai, S.; Li, G. Multi-band multi-tunable perfect plasmon absorber based on L-shaped and double-elliptical graphene stacks. *Diam. Relat. Mater.* **2021**, *115*, 108374. [CrossRef]
- 44. Yi, Z.; Li, J.K.; Lin, J.C.; Qin, F.; Chen, X.F.; Yao, W.T.; Liu, Z.M.; Cheng, S.B.; Wu, P.H.; Li, H.L. Broadband polarization-insensitive and wide-angle solar energy absorber based on tungsten ring-disc array. *Nanoscale* **2020**, *12*, 23077–23083. [CrossRef] [PubMed]
- 45. Zhao, F.; Yi, Y.T.; Lin, J.C.; Yi, Z.; Qin, F.; Zheng, Y.; Liu, L.; Zheng, F.S.; Li, H.L.; Wu, P.H. The better photoelectric performance of thin-film TiO₂/c-Si heterojunctionsolar cells based on surface plasmon resonance. *Results Phys.* **2021**, *28*, 104628. [CrossRef]
- 46. Jiang, L.; Yuan, C.; Li, Z.; Su, J.; Yi, Z.; Yao, W.; Wu, P.; Liu, Z.; Cheng, S.; Pan, M. Multi-band and high-sensitivity perfect absorber based on monolayer grapheme metamaterial. *Diam. Relat. Mater.* **2021**, *111*, 108227. [CrossRef]
- 47. Chen, X.; Wu, W.; Zhang, W.; Wang, Z.; Fu, Z.; Zhou, L.; Yi, Z.; Li, G.; Zeng, L. Blue and green double band luminescent carbon quantum dots: Synthesis, origin of photoluminescence, and application in white light-emitting devices. *Appl. Phys. Lett.* **2021**, *118*, 153102. [CrossRef]
- 48. Wu, P.H.; Zhang, C.F.; Tang, Y.J.; Liu, B.; Lv, L. A perfect absorber based on similar fabry-perot four-band in the visible range. *Nanomaterials* **2020**, *10*, 488. [CrossRef]
- 49. Wang, Y.; Yi, Y.; Xu, D.; Yi, Z.; Li, Z.; Chen, X.; Jile, H.; Zhang, J.; Zeng, L.; Li, G. Terahertz tunable three band narrowband perfect absorber based on Dirac semimetal. *Phys. E Low Dimens. Syst. Nanostruct.* **2021**, *131*, 114750. [CrossRef]
- Liu, Y.H.; Bo, M.L.; Yang, X.X.; Zhang, P.P.; Sun, C.Q.; Huang, Y.L. Size modulation electronic and optical properties of phosphorene nanoribbons: DFT-BOLS approximation. *Phys. Chem. Chem. Phys.* 2017, 19, 5304–5309. [CrossRef]
- 51. Cheng, Z.H.; Liao, J.; He, B.Z.; Zhang, F.; Zhang, F.A.; Huang, X.H.; Zhou, L. One-step fabrication of graphene oxide enhanced magnetic composite gel for highly efficient dye adsorption and catalysis. ACS Sustain. Chem. Eng. 2015, 3, 1677–1685. [CrossRef]
- 52. Zhang, Y.; Yi, Z.; Wang, X.; Chu, P.; Yao, W.; Zhou, Z.; Cheng, S.; Liu, Z.; Wu, P.; Pan, M.; et al. Dual band visible metamaterial absorbers based on four identical ring patches. *Phys. E Low Dimens. Syst. Nanostruct.* **2021**, *127*, 114526. [CrossRef]
- 53. Long, F.; Zhang, Z.H.; Wang, J.; Yan, L.; Lu, P.P.; Yang, Z.X. Magnetic graphene modified imprinted electrochemical sensor for detection of 4-Octylphenol. *Chin. J. Anal. Chem.* **2016**, *44*, 908–914. [CrossRef]
- 54. Li, J.H.; Jiang, J.B.; Zhao, D.; Xu, Z.F.; Liu, M.Q.; Liu, X.; Tong, H.X.; Qian, D. Novel hierarchical sea urchin-like Prussian blue@palladium core-shell heterostructures supported on nitrogen-doped reduced graphene oxide: Facile synthesis and excellent guanine sensing performance. *Electrochim. Acta* 2020, *330*, 135196. [CrossRef]
- 55. Yang, X.; Zhang, F.; Hu, Y.J.; Chen, D.Z.; He, Z.Q.; Xiong, L.Z. Gold nanoparticals doping graphene sheets nanocomposites sensitized screen-printed carbon electrode as a disposable platform for voltammetric determination of guaiacol in bamboo juice. *Int. J. Electrochem. Sci.* **2014**, *9*, 5061–5072.
- 56. Li, Y.; Li, M.; Xu, P.; Tang, S.; Liu, C. Efficient photocatalytic degradation of acid orange 7 over N-doped ordered mesoporous titania on carbon fibers under visible-light irradiation based on three synergistic effects. *Appl. Catal. A Gen.* **2016**, 524, 163–172. [CrossRef]
- 57. Deng, Y.; Cao, G.T.; Yang, H.; Zhou, X.Q.; Wu, Y.W. Dynamic control of double plasmon-induced transparencies in aperturecoupled waveguide-cavity system. *Plasmonics* **2018**, *13*, 345–352. [CrossRef]
- 58. Zhao, F.; Chen, X.F.; Yi, Z.; Qin, F.; Tang, Y.J.; Yao, W.T.; Zhou, Z.G.; Yi, Y.G. Study on the solar energy absorption of hybrid solar cells with trapezoid-pyramidal structure based PEDOT: PSS/c-Ge. *Sol. Energy* **2020**, *204*, 635–643. [CrossRef]
- 59. Levie, R.D. The influence of surface roughness of solid electrodes on electrochemical measurements. *Electrochim. Acta* **1965**, *2*, 113–130. [CrossRef]
- 60. Medina, J.C.; Portillo-Velez, N.S.; Bizarro, M. Synergistic effect of supported ZnO/Bi₂O₃ heterojunctions for photocatalysis under visible light. *Dyes Pigments* **2018**, *153*, 106–116. [CrossRef]
- 61. Saha, B.; Sarkara, K.; Bera, A. Schottky diode behaviour with excellent photoresponse in NiO/FTO heterostructure. *Appl. Surf. Sci.* **2017**, *418*, 328–334. [CrossRef]