Adjusting the Energy Bands of WO$_3$@ZnO Nanocomposite Heterojunction Through the Combination of WO$_3$ Thin Film to Improve Its Photoelectric Performance

YAN XU$^1$, QIN CAO$^2$, ZAO YI$^2$, PINGHUI WU$^{3,4}$, (Member, IEEE) AND SHUANGSHUANG CAI$^5$

$^1$School of Science, Huzhou University, Huzhou 313000, China
$^2$Joint Laboratory for Extreme Conditions Matter Properties, Southwest University of Science and Technology, Mianyang 621010, China
$^3$Fujian Provincial Key Laboratory for Advanced Micro-Nano Photonics Technology and Devices, Research Center for Photonic Technology, Quanzhou Normal University, Quanzhou 362000, China
$^4$Collaborative Innovation Center for Ultra-Precision Optical Engineering and Applications, Quanzhou Normal University, Quanzhou 362000, China
$^5$School of Biomedical Engineering, Wenzhou Medical University, Wenzhou 325035, China

Corresponding authors: Pinghui Wu (phwu@zju.edu.cn) and Shuangshuang Cai (css@wmu.edu.cn)

This work was supported in part by the National Natural Science Foundation of China (NNSFC), under Grant 11704223, in part by the Natural Science Foundation of Fujian Province, under Grant 2018J05008 and Grant JZ160459, in part by the Ph.D. Research Startup Foundation of Quanzhou Normal University under Grant G16057, in part by the Scientific Research Fund of Sichuan Provincial Science and Technology Department, under Grant 2020YJ0137, in part by the Non-Competitive Project of Talent Training and Subject Competition Innovation Fund of Southwest University of Science and Technology, under Grant LX2020003, and in part by the Distinguished Young Scholars Program of Fujian Province under Grant C18032.

ABSTRACT At present, nanomaterials with high-quality photoelectric properties are urgently needed to be used in the manufacture of solar cells. In this study, the hydrothermal synthesis method was first used to grow ZnO nanorod arrays, and then a layer of WO$_3$ thin film with controllable thickness was prepared on ZnO nanorod arrays by magnetron sputtering, forming a series of WO$_3$@ZnO nanocomposite heterojunction. We found that the value of the photocurrent of the prepared nanocomposite samples is nearly 30 times higher than WO$_3$ films under illumination, and it is more stable. The results show that this controllable microstructure can further modify the surface properties of ZnO nanorods, and possess the high visible absorption and photoelectric conversion efficiency. By controlling the thickness of the WO$_3$ film, the band can be regulated and ultimately optimized the photoelectrochemical properties of the composite structure.

INDEX TERMS WO$_3$@ZnO nano-heterostructures, hydrothermal method, magnetron sputtering, photoelectric, band regulation.

I. INTRODUCTION
In recent years, tungsten oxide has drawn widespread attention because of its characteristic properties, just like electrochromism, gas sensitivity, photoluminescence and superconductivity [1]–[9]. In addition, tungsten oxide semiconductor materials are non-toxic and have a narrow forbidden bandwidth (2.4 $\sim$ 2.8 eV) [10]. They can exploit a part of visible light and good stability to refrain photocorrosion [11]–[15], so they can be used as catalysts for visible light catalytic reactions to degrade organic compounds in sewage [16]. Tungsten trioxide (WO$_3$) is the most stable of tungsten oxides with a band gap of 2.8 eV and it is an important n-type semiconductor material [17]. It is widely used as an active photocatalyst of visible light [18]–[20]. However, in practical applications, the photoelectric performance of WO$_3$ needs to be improved. Recently, there have been extensive studies on the photoelectric performance of WO$_3$, which have a bearing on solar energy utilization and photocatalytic. In recent years, the appearance of nanostructured tungsten oxide materials has a great impact on the research in the above fields. At present, many forms of WO$_3$ materials have been prepared, such as nanoparticles, nanotubes, nanosheets, nanorods and nanowires, etc., [21]–[26]. There are many methods for preparing WO$_3$ thin films, including electrochemical deposition, magnetron sputtering,
sol-gel, hydrothermal synthesis, and the like [27], [28]. However, the photoelectric performance of the various shapes of pure WO3 is still limited. According to the analysis reports, compositing other materials is a valid method for electron-hole pair separation. If the semiconductor materials are combined with other semiconductors to constitute a special composite heterojunction, which can availably control the structure of energy band and adjust the photo-generated charges spread of the composite materials, increase the life of carriers and enhance the performance of materials [29]–[31].

Among low-dimensional nano-materials, titanium dioxide (TiO2) is the most studied material owing to its characteristics of high light conversion efficiency, good heat stability, high thermal conductivity, low cost and non-toxicity [32], [33]. TiO2 nanofibers, mesoporous TiO2, etc. have important applications in the field of solar cells [34]–[36]. In 2016, Aadesh Pratap Singh, Bodh Raj Mehta et al. applied hydrogenation treatment to the top TiO2 layer in the BiVO4/TiO2 heterostructure to change the band edge to improve the photoelectrochemical performance[37]. An appropriate substitute material for TiO2 is ZnO, which has a similar band structure and electron affinity to TiO2, and has a larger absorption ratio in the solar spectrum than TiO2 [38]. It has a lot of research in the photoelectrochemical water splitting experiment [39]–[41]. ZnO is a semiconductor material with a wide band gap (Eg=3.37 eV). Therefore, the ultraviolet band has high absorption [42], [43]. In addition, the combination of electron-hole pairs occurs rapidly in a very short time (10−12 s) [44]. There are many preparation methods of ZnO nanomaterial, including hydrothermal method, magnetron sputtering, chemical vapor deposition, sol-gel method and so on [45]–[52]. Therefore, the morphology of the ZnO structure can be highly adjusted by a simple method [53]. In those methods, the hydrothermal synthesis method is proverbially used in laboratories for it has mild reaction conditions, simple operation, good product crystallinity, no pollution, and the ability to prepare materials with advanced morphological characteristics [54]. Coupling ZnO with WO3 can enlarge the spectral response range, increase the utilization of visible light, change the band structure and repress the combination of electron-hole pairs, thus improving the performance of the material.

In this experiment, loading an appropriate amount of WO3 can maximize the photo-current. We have found the best amount of WO3 that displays the maximum photoelectrochemical performance of ZnO nanorods. For this purpose, WO3@ZnO core-shell nanocomposites were synthesized by magnetron sputtering and hydrothermal method. Compared with a single WO3 nanomaterial, the WO3@ZnO nanocomposites structure simply prepared by magnetron sputtering and hydrothermal method can availably suppress the recombination of electron-hole pairs. The specifics of the crystal structure, apparent morphology and optical properties of WO3 and WO3@ZnO composite oxide materials were studied systematically. Moreover, the energy band gap has been calculated to comprehend the optical absorption mechanism of ZnO nanorods with optimum WO3 loading.

**II. EXPERIMENT**

**A. REAGENTS AND MATERIALS**

Absolute ethanol (purity 99.5%), hexamethylenetetramine (HMTA), acetone (C2H4O), zinc nitrate hexahydrate (Zn(NO3)2·6H2O), and sodium sulphate solution (Na2SO4, 0.1 mol/L) were purchased from Sinopharm Chemical Reagent Company. All drugs and reagents are analytical pure. The ultrapure water used in the experiment was obtained from a Mill-Q (electric resistivity 18.2 MΩ·cm) water purification system. Conductive glass (FTO), WO3 target (specification: 60°3 mm, purity: 99.99%), and ZnO target (specification: 60°5 mm, purity: 99.99%) were purchased from Beijing Zhongnuo New Material Technology Co., Ltd.

**B. PREPARATION OF ZnO NANORODS**

First, we clean and dry the required amount of Conductive Glass FTO, then attach the FTO to the substrate tray with high temperature tape and place it in the vacuum chamber. When the vacuum is less than 4 × 10−4 Pa, set the argon flow to 40 sccm, the air pressure to 1 Pa, and the radio-frequency (RF) sputtering power to 60 W, then pre-deposition for 10 minutes to remove the surface impurities and improve sample purity. FTO was aimed to the center of the target to ensure the uniformity of the film and each sputtered for 2 min. In this study, the sputtering velocity is 10 nm per minute, so the seed layer is about 20 nm thick. After the sputtering is completed, the samples and target were cooled for 60 min and then taken out. Before hydrothermal growth of ZnO nanorods, hexamethylenetetramine (HMTA) and zinc nitrate hexahydrate (Zn(NO3)2·6H2O) were mixed with a ratio of 1:1 and then deionized water was added to prepare precursor solution having a concentration of 40 mol/L. The hydrothermal synthesis process will be performed at 95 °C for 4 hours. Then taking out the sample, rinse the surface attachment with ultra-pure water and dried at room temperature naturally.

**C. PREPARATION OF WO3@ZnO NANOCOMPOSITE HETEROJUNCTION**

The WO3@ZnO thin film was further synthesized on the above samples through magnetron sputtering. The ambient air pressure is 1 Pa and the RF sputtering power is 65 W. In this study, the sputtering velocity of this particle is 2.82 nm per minute. The composite samples with different WO3 thickness (about: 20 nm, 40 nm, 60 nm, 80 nm, 100 nm) were prepared separately by controlling the length of the sputtering time. After all samples were sputtered, they were cooled in vacuum for 60 min and then removed. Finally, the samples were put into the sintering furnace at room temperature (25 °C) and heated to 450 °C at the rate of 7 °C per minute and then maintained for 3 hours to complete the annealing experiment. For better comparison of composite samples,
the samples containing only pure ZnO nanorods were also annealed.

**D. CHARACTERIZATION**

The scanning electron microscopy and X-ray diffractometry were used to investigate the structure, elemental composition and structure of the prepared thin film composite samples. The ultraviolet reflection spectra were established by a solid-ultraviolet-visible spectrophotometer. The contact angle tester was used to test the hydrophilic and hydrophobic properties (DSA30, Krüss, Hambourg, Germany). The samples were passed through a three-electrode chemical workstation to measure the photoelectric properties of the samples, such as photocurrent and impedance.

**III. RESULTS AND DISCUSSIONS**

**A. MORPHOLOGY AND STRUCTURE OF WO$_3$@ZnO NANOCOMPOSITE HETEROJUNCTION**

Figure 1(A) exhibits the SEM photograph of ZnO nanorods (FTO+ZnO nanorods). The morphology of ZnO nanorods is decided by the growth conditions, for instance the density of precursor solution, reaction temperature and time. According to a series of previous reports, we selected the conditions of 40 mol/L, 95°C reaction temperature and 3 h reaction time to generate ZnO nanorods. We can see that ZnO nanorods with uniform size grow over a large area on the surface of FTO and there is no connection between the nanorods. A cross-sectional SEM picture of ZnO nanorods array can be observed in Figure 1(B), which shows the nanorod arrays arranged vertically on the FTO. We can plainly see from Figure 1(C) that after sputtering WO$_3$ on the surface of the nanorods, many WO$_3$ nanoparticles are well adhered to the ZnO nanorods, resulting in increased the surface roughness.

The SEM images in Figure 2 are FTO+ZnO+WO$_3$ (60 nm, 80 nm, 100 nm) corresponding to (A-C), respectively. As the thickness of WO$_3$ increased, the surface of the nanorods was covered gradually and many nanoclusters formed by the aggregation of WO$_3$ particles. As the WO$_3$ particles gradually filled the nanorods, the diameter of the nanorods first increased, and then decreased with the further increase in the content of WO$_3$. Moreover, the inset in Figure 2 indicates that the cross-linking between the nanorods becomes serious. Overall, the ZnO nanorods loaded with 60 nm WO$_3$ have the best growth morphology, and it can be seen from Figure 2(A) that the surface of the nanorods is tightly coated.

**FIGURE 1.** SEM images of ZnO nanorods: (A) pure ZnO nanorods, (B) cross-sectional SEM image of pure ZnO nanorods, (C) ZnO nanorods + WO$_3$ (20 nm).

**XRD patterns of synthesized WO$_3$@ZnO nanocomposite**

are represented in Figure 3. Sample 1# shows that the crystal structure of ZnO nanorods corresponds to that of wurtzite ZnO and there is no impurity peak (These peaks can be well indexed to the standard diffraction pattern of wurtzite ZnO structure (PDF # 01-089-1397)). The results reflect that the nanorods prepared by the hydrothermal method have good crystallinity and purity. The diffraction peaks of ZnO correspond to (100), (002), (101), (102), (110), (103) and (004) crystal orientation, respectively [55]–[57]. Among them, the diffraction peaks of WO$_3$ correspond to the crystal orientations of (100), (110), (102) and (120) at 18.88°, 24.47°, 30.48° and 38.37°, respectively [58], [59]. By comparison, it was found that the value of the (100) crystal orientation peak was the highest, meaning that the growth of WO$_3$ along the (100) crystal plane was dominant. As shown in the figure, compared with the peaks of Sample 1#, the peaks belonging to ZnO in all composites haven’t moved, which means that the transition metal oxide WO$_3$ will not replace the lattice of ZnO, and the thickness of WO$_3$ has a trivial impact on the crystallization phases of ZnO nanorods formed previously. At the same time, it was found that the characteristic peaks of WO$_3$ weren’t obvious when WO$_3$ was initially sputtered, which may be due to the high dispersion of WO$_3$ or the low concentration of WO$_3$, which was lower than the XRD detection limit. With the increase of sputtering thickness, the characteristic diffraction peak of WO$_3$ increases gradually. However, when the sputtering thickness is increased to a
certain amount, the diffraction peak in (120) crystal direction reaches the maximum and then begins to decrease.

**B. HYDROPHILICITY ANALYSIS**

Figure 4 shows the hydrophilicity of the samples. We know from Young’s formula that when the static contact angle between liquid and solid material surface is less than 90° ($\theta < 90^\circ$), the sample’s surface is hydrophilic, which means that the liquid is easier to wet the material; if the angle is greater than 90° ($\theta > 90^\circ$), the surface of the material is hydrophobic, that is, the liquid is not easy to wet the material and is easy to move on the surface [60]–[62]. Figure 4 shows that modifying the surface of ZnO nanorods with WO$_3$ can appropriately change the hydrophobicity of the material. We found that when there are only pure ZnO nanorods on the FTO, there are a large number of uniformly distributed voids between the ZnO nanorods, which increases the surface liquid/gas contact area fraction. Therefore, the hydrophobicity of the ZnO nanorod films which is modified by WO$_3$ increased (the contact angle increased gradually), as shown in Figure 4A, B, C. However, we found that when the sputtering amount of WO$_3$ is relatively large, the modified nanorods will become larger accordingly and the flatness of the material will increase, so the contact angle is smaller and its hydrophobicity will be reduced to varying degrees.

**C. UV-VIS OPTICAL PROPERTIES**

Figure 5 A and B show the UV-visible reflectance spectra of the samples, and Figure 5C is the UV-visible absorption spectrum. From Figure 5A, it can be seen that the light reflectivity increases rapidly in the near ultraviolet region, and there is a trailing edge of the reflection spectrum, which is a characteristic of direct band gap semiconductors. Since ZnO nanorods have a high absorption of light in the UV band, it can be seen from Figure 5B that the optical reflectivity is almost 0 in the band of 200 nm-380 nm. At the initial of sputtering WO$_3$ on the surface of ZnO nanorods, the optical reflectivity of the samples increased and the absorptivity decreased, but later, with the increase of sputtering thickness of WO$_3$, the optical absorptivity increased gradually. When the thickness of WO$_3$ reached 60 nm, the light absorption of the sample was maximum, and then decreased gradually, even lower than the pure ZnO nanorods. We analyzed that this was because when we sputtered WO$_3$ on the ZnO nanorods surface at the beginning, the roughness of the nanorods was increased as mentioned before, so some reflective surfaces.
Y. Xu et al.: Adjusting the Energy Bands of WO$_3$@ZnO Nanocomposite Heterojunction Through the Combination of WO$_3$ Thin Film

FIGURE 5. UV-visible reflectance spectra of the samples: (A) and (B). UV-visible absorption spectra of the samples: (C).

with different crystal directions were added on the surface of nanorods to promote the increase of light reflection. The surface of nanorods began to become dense and compact with the increase of WO$_3$ particles, the absorption increased, so the light reflectance began to decrease. However, when the amount of WO$_3$ was too much, the nanorods were covered in a large area and connected to each other, resulting in the reduction of the light absorption, so the light reflectance increased finally. Comparing Figure 5, it can be obtained that the light reflection of pure WO$_3$ film fluctuates in different degrees in the band of 500-800 nm, while the composite samples modified with WO$_3$ do not. Furthermore, the spectra of the composite samples loaded with WO$_3$ have a red shift. This is the result of the band-gap narrowing, and the composite of ZnO with WO$_3$ will produce defect levels in the band gap [63]. When the Zn$^{2+}$ ions in the nanocomposites are replaced by W$^{6+}$ ions, the defect energy level corresponding to the oxygen vacancy has come into being, which serves as the color center of visible light absorption. As a result, the reflectance of the composites in the visible band is much lower than that of pure WO$_3$.

From the UV-visible reflectance spectra, the energy band gap for all the composite samples can be calculated as the following equation:

$$E_g = \frac{hc}{\lambda} = \frac{1240.7}{\lambda} \text{ (1)}$$

where $h$ is Planck constant ($6.62607015 \times 10^{-34}$ J·s or $4.1356676969 \times 10^{-15}$ eV·s), $c$ is the velocity of light ($3 \times 10^8$ m·s$^{-1}$), $\lambda$ is the wavelength (nm) of absorption onset and $E_g$ is the energy band gap (eV) [64], [65]. The results are shown in Table 1. We can see that the band gap of ZnO nanorod is 3.317 eV, which is close to the reported value. The band gap of the composite samples decreased with the raise of WO$_3$ load, and the absorption edge moves to longer wavelengths until the WO$_3$ load is 60 nm and it is reduced to 2.55 eV. Then the absorption edge moves towards the short wavelength direction. The above results indicate that the composition of WO$_3$ particle layers with different thicknesses changes the band gap of WO$_3$@ZnO nanostructures, thus adjusting their ability to absorb visible light. Therefore, an optimal content is needed to decrease the composite effect of ZnO nanorods.

TABLE 1. Calculated energy band gap of pure ZnO nanorod and synthesized composite samples.

| WO$_3$ content (nm) | Absorption onset (nm) | eV |
|---------------------|-----------------------|----|
| 0                   | 374                   | 3.317 |
| 20                  | 376                   | 3.300 |
| 40                  | 420                   | 2.954 |
| 60                  | 486                   | 2.552 |
| 80                  | 395                   | 3.141 |
| 100                 | 365                   | 3.399 |

D. THE PHOTOCURRENT PERFORMANCE OF COMPOSITES

Figure 6 shows the photocurrent response with five light/dark cycles of intermittent illumination at a fixed bias voltage of 0.3 V (vs. Ag/AgCl). It can be found that the value of photocurrent rapidly decreases to about 0 mA/cm$^2$ when the illumination is stopped, and the photocurrent whipped up when the illumination is turned on again. In Figure 6A, the photocurrent of each sample decays severely under illumination; in Figure 6B, only a slight photocurrent attenuation is found for each sample. The reason for the attenuation is that the energy brought by the sudden illumination makes the electron-hole pairs generate rapidly and produces a large photocurrent excitement, and then gradually begin to stabilize over time. It signifies that the composite film reveals better stability and repeatability compared with the pure WO$_3$, and the photocurrent is increased nearly 30 times. Furthermore, we also observed that the photocurrent value first increased...
Y. Xu et al.: Adjusting the Energy Bands of WO$_3$@ZnO Nanocomposite Heterojunction Through the Combination of WO$_3$ Thin Film

Adjusting the Energy Bands of WO$_3$@ZnO Nanocomposite Heterojunction Through the Combination of WO$_3$ Thin Film

Y. Xu et al.

FIGURE 6. The photocurrent-time plots of the sample was prepared in a 0.1 M Na$_2$SO$_4$ (pH=7) electrolyte under the action of a constant potential of 0.3 V (vs. Ag/AgCl) with chopping light.

and then decreased with the increase of WO$_3$ which sputtered on ZnO nanorods surface. When the thickness of the sputtered WO$_3$ is 60 nm, the photocurrent value reaches the maximum of 0.412 mA/cm$^2$. And after a continuous light/dark alternation, the optical current is stable at about 0.397 mA/cm$^2$.

Later, with the increase of the thickness of WO$_3$ sputtering on the surface of ZnO nanorods, the value of light current began to decrease. When WO$_3$ is sputtered to a thickness of about 100 nm, the photocurrent value was very close to that of the sample loaded with 20nm WO$_3$, and dropped to about 0.353 mA/cm$^2$. In Figure 6B, when the sample of only ZnO nanorods on FTO receives light, the electrons absorb energy to jump to the conduction band. Since this sample is a single material, the electrons that arrive at the conduction band will immediately release energy return to the valence band to stabilize, so the combination velocity is very high [66], [67]. At the beginning of sputtering WO$_3$, the WO$_3$ material itself can also absorb energy to enhance the light conversion rate, and the heterojunction formed between ZnO and WO$_3$ can effectively inhibit the recombination of electron-hole pair, enhance its mobility to increase the photocurrent [68]. With the increase of the thickness of sputtered WO$_3$, the increase in the amount of surface WO$_3$ results in an increase of surface resistance, which lessens the photocurrent ultimately.

When two semiconductors contact to form an interface structure, due to the different band gaps width of the two materials, band steps will be formed at the bottom of the conduction band and the top of the valence band of the two materials. The alignment of the energy bands on both sides of the interface depends on the charge transfer of the materials on both sides. Figure 7 shows a schematic diagram of the photocurrent generated by the ZnO@WO$_3$ nano heterojunction under light. The heterojunction was used as a photoanode, and the photoelectric response was tested by an electrochemical workstation at a bias voltage of 0.3V. When light strikes both materials, the electrons in the valence band use photon energy to jump into the conduction band and leave holes. At this time, when a bias voltage is applied, the electrons flow into the WO$_3$ conduction band and flow out through the external Pt electrode. The holes migrate from WO$_3$ valence band to the ZnO valence band and then are transported together with the holes in the ZnO valence band through the FTO conductive glass to the external circuit. Finally, the external circuit collects and utilizes the carriers flowing out from the two electrodes.

FIGURE 7. Energy band schematic diagram of ZnO@WO$_3$ heterojunction under an external bias voltage.

FIGURE 8. Nyquist diagram of the samples under visible light illumination: (1#) pure ZnO nanorods, (2#) ZnO nanorods + WO$_3$ (20 nm), (3#) ZnO nanorods + WO$_3$ (40 nm), (4#) ZnO nanorods + WO$_3$ (60 nm), (5#) ZnO nanorods + WO$_3$ (80 nm), (6#) ZnO nanorods + WO$_3$ (100 nm).

Combined with the alternating current (AC) impedance test results show in Figure 7, the photoelectric performance of the sample can be further analyzed. It can be seen from Figure 7 that there is only one semicircle in the spectrum of all samples, so it can be judged that they all have only one time constant. The equivalent circuit diagram is shown in Figure 8. It is observed that the impedance value is very high when there are only ZnO nanorods, but it is greatly reduced when WO$_3$ is sputtered on the surface of ZnO nanorods to form a heterojunction. As the thickness of WO$_3$ increases to
about 60-80 nm, the impedance value decreases. However, the impedance of the samples began to increase after 80 nm. This is because when a small amount of WO$_3$ is sputtered on the surface of nanorods, the formation of heterojunction contributes to the improvement of photoelectric performance (as described above). But with the increase of WO$_3$, it will cover the nanorods and form heterojunctions in a large area. Moreover, the nanorods will be corroded gradually, so the impedance increase. Therefore, we can sputter WO$_3$ with a thickness of about 60nm on the ZnO nanorods surface to obtain the best photoelectric performance.

IV. CONCLUSION
In summary, a series of WO$_3$@ZnO core-shell nanorods array composites with different amounts of WO$_3$ were successfully synthesized on FTO conductive glass by combining magnetron sputtering and hydrothermal. The SEM and XRD have been tested the morphology and structure. The study found that WO$_3$@ZnO composite has higher photosensitivity compared with pure WO$_3$ thin films, which can maintain good reversibility and stability under dark/visible light cycle switching. And when a small amount of WO$_3$ particles are modified on the surface of ZnO nanorods, the photocurrent can be effectively enhanced. WO$_3$ can change the overall band structures through abating the effective band-gap to extend the light absorption edge of ZnO from the ultraviolet to the visible light region. Therefore, this material can greatly increase the photoelectric conversion efficiency in the application of solar cells and improve the utilization rate of sunlight.

AUTHOR CONTRIBUTIONS
Y.X., Q.C., and Z.Y., conceived the idea of experiment; Y.X., Q.C., and Z.Y., performed the experiments; Y.X., Q.C., Z.Y., P.W., and P.J. discussed the results; Y.X., Q.C., wrote the manuscript; All authors read and approved the final manuscript.

FUNDING
This research received no external funding.

ACKNOWLEDGMENT
(Yan Xu and Qin Cao contributed equally to this work.)

CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

REFERENCES
[1] J. Wang, E. Khoo, P. S. Lee, and J. Ma, “Controlled synthesis of WO$_3$ nanorods and their electrochromic properties in H$_2$SO$_4$ electrolyte,” J. Phys. Chem. C, vol. 113, no. 22, pp. 9655–9658, Jun. 2009.
[2] J. Zhang, X. L. Wang, X. H. Xia, C. D. Gu, and J. P. Tu, “Electrochromic behavior of WO$_3$ nanotree films prepared by hydrothermal oxidation,” Sol. Energy Mater. Sol. Cells, vol. 95, no. 8, pp. 2107–2112, Aug. 2011.
[3] J. Li, X. Chen, Z. Yi, H. Yang, Y. Tang, Y. Yi, W. Yao, J. Wang, and Y. Yi, “Broadband solar energy absorber based on monolayer molybdenum disulfide using tungsten elliptical arrays,” Mater. Today Energy, vol. 16, Jun. 2020, Art. no. 100390.
[4] P. Yu, H. Yang, X. Chen, Z. Yi, W. Yao, J. Chen, Y. Yi, and P. Wu, “Ultra-wideband solar absorber based on refractory titanium metal,” Renew. Energy, vol. 158, pp. 227–235, Oct. 2020.
[5] F. Zhao, X. Chen, Z. Yi, F. Qin, Y. Tang, W. Yao, Z. Zhou, and Y. Yi, “Study on the solar energy absorption of hybrid solar cells with trapezoidal-pyramidal structure based PEDOT:PSS/c–ge,” Sol. Energy, vol. 204, pp. 635–643, Jul. 2020.
[6] H. Najafi-Ashtiani, A. Bahari, and S. Ghaseemi, “A dual electrochromic film based on nanocomposite of copolymer and WO$_3$ nanoparticles: Enhanced electrochromic coloration efficiency and switching response,” J. Electroanal. Chem., vol. 774, pp. 14–21, Aug. 2016.
[7] H. Najafi-Ashtiani and A. Bahari, “Optical, structural and electrochromic behavior studies on nanocomposite thin film of aniline, o-toluidine and WO3,” Opt. Mater., vol. 58, pp. 210–218, Aug. 2016.
[8] S. Hoseinzadeh, R. Ghasemi, A. Bahari, and A. H. Ramezani, “Effect of post-annealing on the electrochromic properties of layer-by-layer arrangement FTO-WO$_3$–Ag/Ag-WO$_3$,” J. Electron. Mater., vol. 47, no. 7, pp. 3552–3559, Jul. 2018.
[9] S. K. Deb, “Opportunities and challenges in science and technology of WO3 for electrochromic and related applications,” Sol. Energy Mater. Sol. Cells, vol. 92, no. 2, pp. 245–258, Feb. 2008.
[10] P. Chu, J. Chen, Z. Xiong, and Z. Yi, “Controllable frequency conversion in the coupled time-modulated cavities with phase delay,” Opt. Commun., vol. 476, Dec. 2020, Art. no. 126338.
[11] P. Rao, L. Cai, C. Liu, I. Cho, C. Lee, J. Weisse, P. Yang, and X. Zheng, “Nanowire photoanode for photovoltaic solar water oxidation,” Nano Lett., vol. 14, no. 2, pp. 1099–1105, 2014.
[12] J. Zheng, G. Song, C. Kim, and Y. Kang, “Fabrication of (001)-oriented monoclinic WO$_3$ films on FTO substrates,” Nanoscale, vol. 5, no. 12, pp. 5279–5382, 2013.
[13] L. Yin, D. Chen, M. Hu, H. Shi, D. Yang, B. Fan, G. Shao, R. Zhang, and G. Shao, “Microwave-assisted growth of In$_2$O$_3$ nanoparticles on WO$_3$ nanoplates to improve H$_2$S-sensing performance,” J. Mater. Chem. A, vol. 2, no. 44, pp. 18867–18874, 2014.
[14] C. Cen, Y. Zhang, X. Chen, H. Yang, Z. Yi, W. Yao, Y. Tang, Y. Yi, J. Wang, and P. Wu, “A dual-band metamaterial absorber for graphene surface plasmon resonance at terahertz frequency,” Phys. E, Low-Dimensional Syst. Nanostruct., vol. 117, Mar. 2020, Art. no. 113840.
[15] D. Chen, L. Yin, L. Ge, B. Fan, R. Zhang, J. Sun, and G. Shao, “Low-temperature and highly selective NO-sensing performance of WO$_3$ nanoplates decorated with silver nanoparticles,” Sens. Actuators B, Chem., vol. 185, pp. 445–455, Aug. 2013.
[16] X. Luo, F. Deng, L. Min, S. Luo, B. Guo, G. Zeng, and C. Au, “Facile one-step synthesis of inorganic-framework molecularly imprinted TiO$_2$WO$_3$ nanocomposite and its molecular recogntive photocatalytic degradation of target contaminant,” Environ. Sci. Technol., vol. 47, no. 13, pp. 7404–7412, Jul. 2013.
[17] G. Waldner, A. Brüger, N. S. Gaikwad, and M. Neumann-Spallart, “WO$_3$ thin films for photoelectrochemical purification of water,” Chemosphere, vol. 67, no. 4, pp. 779–784, Mar. 2007.
[18] Y. Zhang, P. Wu, Z. Zhou, X. Chen, Z. Yi, J. Zhu, T. Zhang, and H. Jile, “Study on temperature adjustable terahertz metamaterial absorber based on vanadium dioxide,” IEEE Access, vol. 8, pp. 85154–85161, 2020.
[19] G. R. Bambwenda and H. Arakawa, “The visible light induced photocatalytic activity of tungsten trioxide powders,” Appl. Catalysis A, Gen., vol. 210, nos. 1–2, pp. 181–191, Mar. 2001.
[20] L. Li, W. Yang, T. Shuai, and X. Wang, “Ultrasensitive sizing sensor for a single nanoparticle in a hybrid nonlinear microavity,” IEEE Photon. J., vol. 12, no. 3, Apr. 2020, Art. no. 4500708.
[21] S.-M. Lam, J.-C. Sin, A. Z. Abdullah, and A. R. Mohamed, “ZnO nanorods surface-decorated with WO$_3$ nanoparticles for photocatalytic degradation of endocrine disruptors under a compact fluorescent lamp,” Ceram. Int., vol. 39, no. 3, pp. 2343–2352, Apr. 2013.
[22] Z. Yi, Y. Zeng, H. Wu, X. Chen, Y. Fan, H. Yang, Y. Tang, Y. Yi, J. Wang, and P. Wu, “Synthesis, surface properties, crystal structure and dye-sensitized solar cell performance of TiO$_2$ nanotube arrays anodized under different parameters,” *Phys. Chem. B*, vol. 15, Dec. 2019, Art. no. 102609.

[23] H. Najafi-Ashtiani, A. Bahari, S. GholiPour, and S. Hoseinzadeh, “Structural, optical and electrical properties of WO$_3$–Ag nanocomposites for the electro-optical devices,” *Appl. Phys. A: Solids Surf.*, vol. 124, no. 1, pp. 1–9, Jan. 2018.

[24] Z. Cheng and Y. Cheng, “A multi-functional polarization converter based on chiral metamaterial for terahertz waves,” *Opt. Commun.*, vol. 435, pp. 178–182, Mar. 2019.

[25] X. Zeng, Z. Wang, G. Wang, T. R. Gengenbach, D. T. McCarthy, A. Deletic, J. Yu, and X. Zhang, “Highly dispersed TiO$_2$ nanocrystals and WO3 nanorods on reduced graphene oxide: Z-scheme photocatalyst system for accelerated photocatalytic water disinfection,” *Appl. Catal. B: Environ.*, vol. 218, pp. 163–173, Dec. 2017.

[26] S. Adhikari, D. Sarkar, and G. Madras, “Highly efficient WO$_3$–ZnO mixed oxides for photocatalysis,” *RSC Adv.*, vol. 5, no. 16, p. 11895, 2015.

[27] J. Xie, Z. Zhou, Y. Lian, Y. Hao, X. Liu, M. Li, and Y. Wei, “Simple preparation of WO$_3$–ZnO composites with UV–Vis photocatalytic activity and energy storage ability,” *Ceram. Int.*, vol. 40, no. 8, pp. 12519–12524, Sep. 2014.

[28] C. Liang, Z. Yi, X. Chen, Y. Tang, Y. Yi, Z. Zhou, X. Wu, Z. Huang, Y. Yi, and G. Zhang, “Dual-band infrared perfect absorber based on a Ag–Dielectric–Ag multilayer films with nanoring grooves arrays,” *Plasmonics*, vol. 15, no. 1, pp. 93–100, Feb. 2020.

[29] H. Wu, H. Jile, Z. Chen, D. Xu, Z. Yi, X. Chen, J. Chen, W. Yao, P. Wu, and Y. Yi, “Fabrication of ZnOMoS$_2$ nanocomposite heterojunction arrays and their photoelectric properties,” *Microchim. Acta*, vol. 11, no. 2, p. 189, Feb. 2020.

[30] Y. Wang, F. Jiang, J. Chen, X. Sun, T. Xian, and H. Yang, “In situ construction of CNT/Cu hybrids and their application in photodegradation for removing organic dyes,” *Nanomaterials*, vol. 10, no. 1, p. 178, Jan. 2020.

[31] S. Guan, H. Yang, X. Sun, and T. Xian, “Preparation and promising application of novel LaFeO$_3$/BiOBr heterojunction photocatalysts for photocatalytic and photo-fenton removal of dyes,” *Opt. Mater.*, vol. 100, Feb. 2020, Art. no. 109644.

[32] H. Li, G. Wang, J. Niu, E. Wang, G. Niu, and C. Xie, “Preparation of TiO$_2$ nanotube arrays with efficient photocatalytic performance and super-hydrophilic properties utilizing anodized voltage method,” *Results Phys.*, vol. 14, Sep. 2019, Art. no. 102499.

[33] M. Batmunkh, M. R. Tanshen, M. J. Nine, M. Myckhlai, H. Choi, H. Chung, and H. Jeong, “Thermal conductivity of TiO$_2$ nanoparticles based aqueous nanofluids with an addition of a modified silver particle,” *Ind. Eng. Chem. Res.*, vol. 53, no. 20, pp. 8445–8451, May 2014.

[34] M. Batmunkh, T. Macdonald, C. Shearer, M. Bat-Erdene, Y. Wang, M. Biggs, I. Parkin, T. Nann, and J. Shapter, “Carbon nanotubes in TiO$_2$–Ag nanofluids with an addition of a modified silver particle,” *Ceram. Int.*, vol. 40, no. 8, pp. 12519–12524, 2014.

[35] G. Gao, L. Yu, A. Vinu, J. Shapter, M. Batmunkh, C. Shearer, T. Yin, P. Huang, and D. Cui, “Synthesis of ultra-long hierarchical ZnO whiskers in a hydrothermal system for dye-sensitised solar cells,” *Results Phys.*, vol. 10, no. 1, p. 95, Jan. 2020.

[36] S. A. Mozaffari, R. Rahmanian, M. Abedi, and H. S. Amoli, “Urea impedimetric biosensor based on reactive RF magnetron sputtered zinc oxide nanoporous transducer,” *Electrochimica Acta*, vol. 146, pp. 538–547, Nov. 2014.

[37] M. T. Z. Miyint and J. Dutta, “Fabrication of zinc oxide nanorods modified activated carbon cloth electrode for desalination of brackish water using capacitive deionization approach,” *Desalination*, vol. 305, pp. 24–30, Nov. 2012.

[38] R. Shi, P. Yang, X. Dong, Q. Ma, and A. Zhang, “Growth of flower-like ZnO on ZnO nanorod arrays created on zinc substrate through low-temperature hydrothermal synthesis,” *Appl. Surf. Sci.*, vol. 264, pp. 162–170, Jan. 2013.

[39] G. Gao, L. Yu, A. Vinu, J. Shapter, M. Batmunkh, C. Shearer, T. Yin, P. Huang, and D. Cui, “Synthesis of ultra-long hierarchical ZnO whiskers in a hydrothermal system for dye-sensitised solar cells,” *RSC Adv.*, vol. 6, no. 11, pp. 109143–109146, 2016.

[40] Y. Liu, H. He, J. Li, W. Li, Y. Yang, Y. Li, and Q. Chen, “ZnO nanoparticle-functionalized WO$_3$ plates with enhanced photoelectrochemical properties,” *RSC Adv.*, vol. 5, no. 58, p. 46928, 2015.

[41] Y. Cheng, J. Fan, H. Luo, and F. Chen, “Dual-band and high-efficiency circular polarization converter based on anisotropic metamaterial,” *IEEE Access*, vol. 8, pp. 7615–7621, 2020.

[42] P. Wu, Z. Chen, H. Jile, C. Zhang, D. Xu, and L. Lv, “An infrared perfect absorber based on metal-dielectric-metal multi-layer films with nanocircle holes arrays,” *Results Phys.*, vol. 16, Mar. 2020, Art. no. 102952.

[43] Y. Wang, H. Yang, X. Sun, H. Zhang, and T. Xian, “Preparation and photocatalytic application of ternary n-BaTiO$_3$/Ag/p-AgBr heterstructured photocatalysts for dye degradation,” *Mater. Res. Bull.*, vol. 124, Apr. 2020, Art. no. 110754.

[44] P. Wu, C. Zhang, Y. Tang, B. Liu, and L. Lv, “A perfect absorber based on similar Fabry–Perot four-band in the visible range,” *Nanomaterials*, vol. 10, no. 3, p. 488, Mar. 2020.

[45] J. Fu, Q. Xu, J. Low, C. Jiang, and J. Yu, “Ultra-thin 2D/2D WO$_3$/ZnO mixed nanosheets with enhanced light harvesting and carriers kinetics for highly efficient and stable photoelectrochemical water splitting,” *Appl. Catal. B: Environ.*, vol. 267, Jun. 2020, Art. no. 118599.
[60] Y. Huang, P. Wang, Z. Wang, Y. Rao, J.-J. Cao, S. Pu, W. Ho, and S. C. Lee, “Protonated g-C3N4/Ti3+ self-doped TiO2 composite films: Room-temperature preparation, hydrophilicity, and application for photocatalytic NO removal,” *Appl. Catal. B: Environ.*, vol. 240, pp. 122–131, Jan. 2019.

[61] Y. Yan, H. Yang, Z. Yi, T. Xian, R. Li, and X. Wang, “Construction of Ag3SCaTiO3 heterojunction photocatalysts for enhanced photocatalytic degradation of dyes,” *Desalination Water Treat.*, vol. 170, pp. 349–360, Dec. 2019.

[62] S. Wang, H. Gao, C. Chen, Q. Li, C. Li, Y. Wei, and L. Fang, “Effect of phase transition on optical and photoluminescence properties of nano-MgWO4 phosphor prepared by a gamma-ray irradiation assisted polyacrylamide gel method,” *J. Mater. Sci. Mater. Electron.*, vol. 30, no. 16, pp. 15744–15753, Aug. 2019.

[63] Y. Cheng, J. Fan, H. Luo, F. Chen, N. Feng, X. Mao, and R. Gong, “Dual-band and high-efficiency circular polarization conversion via asymmetric transmission with anisotropic metamaterial in the terahertz region,” *Opt. Mater. Express*, vol. 9, no. 3, pp. 1365–1376, 2019.

[64] Y. Yan, H. Yang, Z. Yi, R. Li, and T. Xian, “Design of ternary CaTiO3/g-C3N4/AgBr Z-scheme heterostructured photocatalysts and their application for dye photodegradation,” *Solid State Sci.*, vol. 100, Feb. 2020, Art. no. 106102.

[65] S. Wang, H. Gao, G. Sun, Y. Li, Y. Wang, H. Liu, C. Chen, and L. Yang, “Structure characterization, optical and photoluminescence properties of scheelite-type CaWO4 nanophosphors: Effects of calcination temperature and carbon skeleton,” *Opt. Mater.*, vol. 99, Jan. 2020, Art. no. 109532.

[66] S. Wang, C. Chen, Y. Li, Q. Zhang, Y. Li, and H. Gao, “Synergistic effects of optical and photoluminescence properties, charge transfer, and photocatalytic activity in MgAl2O4:Ce and mn-codoped MgAl2O4:Ce phosphors,” *J. Electron. Mater.*, vol. 48, no. 10, pp. 6675–6685, Oct. 2019.

[67] Y. Yan, H. Yang, Z. Yi, X. Wang, R. Li, and T. Xian, “Evolution of bi nanowires from BiOBr nanoplates through a NaBH4 reduction method with enhanced photodegradation performance,” *Environ. Eng. Sci.*, vol. 37, no. 1, pp. 64–77, Jan. 2020.

[68] Q. Zhang, J. Liao, M. Liao, J. Dai, H. Ge, T. Duan, and W. Yao, “One-dimensional Fe7S8C nanorods as anode materials for high-rate and long-life lithium-ion batteries,” *Appl. Surf. Sci.*, vol. 473, pp. 799–806, Apr. 2019.

**YAN XU** received the M.S. degree in particle physics and nuclear physics from the University of Science and Technology of China, China, in 2005. He is currently an Experimentalist with Huzhou University. His current research interests include areas of optical materials, optical design, and laser physics.

**QIN CAO** is currently pursuing the bachelor’s degree in optoelectronic information science and engineering with Southwest University of Science and Technology, Mianyang, China. Her research interests include nanocomposite heterojunction and materials with excellent photocatalytic properties.

**ZAO YI** received the M.Sc. and Ph.D. degrees in condensed matter physics from Central South University, Changsha, Hunan, in 2010 and 2014, respectively. Since 2014, he has been with the Southwest University of Science and Technology, where he is currently a Professor of Applied Physics. His areas of research interest are plasmonics, nanophotonics, metamaterials, and their applications. He was a recipient of the Doctoral Academic Newcomer awards of Ministry of Education in 2012.

**PINGHUI WU** (Member, IEEE) received the Ph.D. degree in optical engineering from Zhejiang University, China, in 2016. Since August 2016, he has been with an Associate Professor with the Fujian Key Laboratory for Advanced Micro-Nano Photonics Technology and Devices, Research Center for Photonic Technology, Quanzhou Normal University. His current research interests include areas of nanophotonics, optical field manipulation, and laser physics.

**SHUANGSHUANG CAI** was born in Zhejiang, China, in 1981. She received the B.S. degree from the Department of Physics, Zhejiang Normal University, Jinhua, China, in 2003, and the Ph.D. degree from the Department of Physics, Zhejiang University, Hangzhou, China, in 2008. She is currently an Associate Professor with the School of Biomedical Engineering, Wenzhou Medical University, Wenzhou, China. Her current research interests include nanophotonics, mid-IR laser, and its biomedical applications.

---

Y. Xu et al.: Adjusting the Energy Bands of WO3@ZnO Nanocomposite Heterojunction Through the Combination of WO3 Thin Film