

Ultraviolet photodetector based on NaTaO₃/ZnO composite with enhanced photoelectric performance*

ZHAO Yun-fei (赵云飞), ZHANG Min (张敏)**, YANG Lin-yu (杨林钰), ZHANG Jun (张军), and WANG Zhao-jun (王兆军)

School of Physics Science and Technology, Xinjiang University, Urumqi 830046, China

(Received 8 February 2020; Revised 5 April 2020)

©Tianjin University of Technology 2021

NaTaO₃/ZnO composites were synthesized via a two-step hydrothermal method. Then ultraviolet detectors based on pure NaTaO₃, ZnO and their composites with different mole ratio were fabricated. Among all the devices, the 1:1 NaTaO₃/ZnO possessed a high photo-to-dark current ratio and stable periodic photoresponse. The photoresponse is facilitated by the synergistic effect between different components and the improved ZnO morphology in the composites, the reduced dimensionality in which provides a straight electron conduction pathway. Additionally, the 1:1 NaTaO₃/ZnO detector also exhibits a low dark current less than 1 nA at 5 V bias, which benefits a lot to the low power dissipation and high sensitivity of devices. These results reveal that NaTaO₃/ZnO composites are good candidates for the fabrication of ultraviolet detectors.

Document code: A **Article ID:** 1673-1905(2021)02-0075-5

DOI <https://doi.org/10.1007/s11801-021-0018-5>

Ultraviolet (UV) photodetectors have drawn much attention owing to civil and military applications in the fields of ultraviolet communication, smart wears, meteorological monitoring, and medical fields^[1,2]. Wide band gap semiconductors, especially metal oxide semiconductors, such as TiO₂, ZnO and some perovskite materials, have wide usage in fabricating functional electron devices^[3-5]. These semiconductors are environmental friendly as well as thermally and chemically stable. As one of the perovskite semiconductor, NaTaO₃ (band gap of 4 eV) has always been studied as photocatalysts under UV irradiation, or sensors to detect humidity and light signals^[6-8]. Previously reported NaTaO₃ (NTO) based detectors still exhibit low photoelectric conversion efficiency and slow response time, which may be ascribed to its relatively low separation rate between photo-excited electron and hole pairs^[5]. The wide band gap of ZnO (band gap of 3.37 eV) decides its excellent photoelectric performance occurring in the ultraviolet region. Thus, ZnO often appears as promising substrate for photoelectric devices^[9,10]. It is known that composite materials usually not only possess the properties of raw materials, but also embrace new property. All the components complement each other in performance and produce synergistic effect^[11,12]. Thus, it is reasonably expected, the combination of ZnO and NTO may result in a synergistic effect and show the advantages of every component. Besides, doping with metal oxides can modify the electronic and morphological properties, which is also regarded as an effective way

to enhance the sensing performance^[13,14]. However, to the best of our knowledge, the UV sensitive properties of NTO/ZnO have seldom been reported.

In this work, NTO/ZnO composites were synthesized via a hydrothermal method. The photoelectric properties of pure NTO, ZnO and their composites were investigated. The current-voltage (*I-V*) characteristics under different conditions as well as the time response properties were explored. The device performance and material morphology were compared among pure and composite samples. The mechanism of photoresponse was interpreted in detail.

NTO/ZnO composites were synthesized through a facile two-step hydrothermal process. NTO materials were prepared as follows: 0.225 mol NaOH were dissolved in deionized water. Thereafter, 0.01 mol Ta₂O₅ were added under continuous magnetic stirring. The mixed solution was transferred into a Teflon-lined autoclave with a capacity of 100 mL. The autoclave was sealed and kept at 200 °C for 24 h. After cooling to room temperature naturally, the precursor was filtered and washed with absolute ethanol and deionized water for several times. Then pure NTO powders were obtained by dried in air at 60 °C. For the preparation of NTO/ZnO composites, certain amount of NTO were put into 60 mL deionized water under ultrasonic treatment. Subsequently, zinc acetate and hexamine were added into the above mixture under continuous stirring. The mole ratios of NTO and ZnO in composite samples were 2:1, 1:1, 1:2 and 1:4.

* This work has been supported by the Natural Science Foundation of the Xinjiang Uygur Autonomous Region (No.2016D01C049).

** E-mail: minzhang0816@163.com

The mixed solution was then sealed in a Teflon stainless autoclave of 100 mL capacity and maintained at 120 °C for 12 h. After cooled down to room temperature, the remain products were washed several times with absolute ethanol and deionized water, and dried in air at 60 °C. Similar with the above experimental process, pure ZnO sample was synthesized by mixing 1.212×10^{-4} mol zinc acetate and 0.17 g hexamine into 60 mL deionized water. The following reaction conditions and washing ways are the same as the preparation of composites.

The phase structure was carried out by X-ray diffraction measurement (XRD, Bruker D8 Advance). Field-emission scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (Bruker Nano GmbH Berlin, Germany) were used to investigate the morphology and the different elements type of the samples. Further analysis of sample morphology was accomplished by a JEM-2100 transmission electron microscope (TEM). The absorption and transmittance spectra were measured on a PerkinElmer UV/Visible spectrometer (Lambda 650S). The Raman spectra was tested through an iHR550 spectrometer. For the detector fabrication, pure and composite samples were mixed with deionized water and ground in a mortar to form a paste. The paste was then coated on a ceramic substrate by a thin brush to form the sensing film. On the ceramic substrate, Ag-Pd interdigitated electrodes were previously printed with both finger-width and finger spacing of about 200 μm . The devices were dried naturally in air. The photoelectric response and I - V characteristics in dark and under illumination were recorded by a Controlled Intensity Modulated Photocurrent Spectrometer 70 (CIMPS-2, ZAHNER) system under 365 nm ultraviolet light. The measurement was conducted in a conventional two electrode configuration. The optical power density of UV light was measured by a UV power meter (CEAULIGHT CEL-NP 2000).

Fig.1 illustrates the XRD patterns of the as-prepared pure NTO, ZnO and 1:1 NTO/ZnO composite. It is shown that the diffraction peaks in pure samples can be indexed to be cubic system NTO (JCPDS card No.25-0863), and hexagonal wurtzite structured ZnO (JCPDS card No.36-1451). No other impurity peaks were found, indicating that the samples were formed in a high purity phase. As for the 1:1 NTO/ZnO composite, there appears main diffraction peaks from both ZnO and NTO phases. The strong and clear peaks indicate the good crystallinity and stable structure of the composite sample. These XRD analyses reveal that the NTO/ZnO composite was successfully synthesized and consists both of NTO and ZnO components.

Energy dispersive spectroscopy analysis of the 1:1 NTO/ZnO composite was performed as shown in Fig.2. The emissions from Na, Ta, Zn and O were clearly observed. According to the EDS measurement, the atom ratios of Na:Ta:Zn are 1.17:1.00:1.13, which is approximately consistent with the mole ratio of raw materials,

suggesting the composite was close to the target. The inset shows the final device structure.

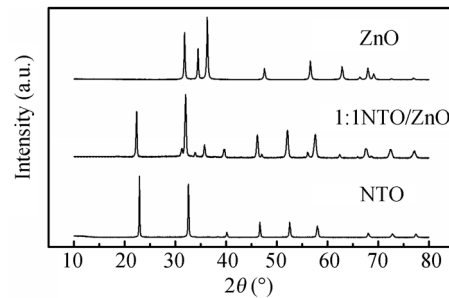


Fig.1 The XRD patterns of pure NTO, ZnO and their 1:1 NTO/ZnO composite

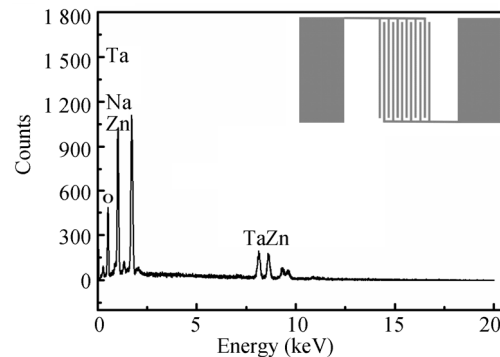


Fig.2 The EDS spectrum of 1:1 NTO/ZnO composite, where inset shows the final device structure

Fig.3 displays the SEM images of pure NTO, ZnO and their composites with different component proportions. The pure NTO sample presents cubic shape with diameters around 100—250 nm. The morphology of pure ZnO is irregular sheet and seems like unshaped for lacking of template.

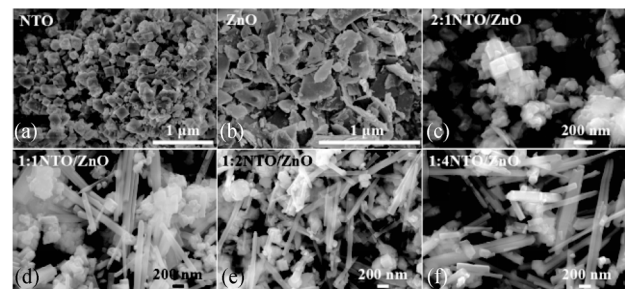


Fig.3 The SEM images of (a) pure NTO, (b) pure ZnO, (c) 2:1 NTO/ZnO, (d) 1:1 NTO/ZnO, (e) 1:2 NTO/ZnO, (f) 1:4 NTO/ZnO under different resolutions

Under a high magnification, the images of NTO/ZnO composites exhibit a pluralistic appearance, reflecting the existence of both components. For all the composite samples, NTO part still maintains the original cube shape, while ZnO component has changed the morphology from irregular sheet to one-dimensional nanorod. With the increase of ZnO content, more and more nanorods appear in the composite. By contrast, the amount of NTO cubes

reduces evidently. An obvious morphology improvement was observed in the composites when compared with that of pure ZnO. It is speculated that in the synthesis of composite samples, the NTO cubes restrict the free growth of ZnO. With the help of hexamine, the raw material zinc acetate was formed into ZnO with a one-dimensional structure. From the 1:1 and 1:2 NTO/ZnO images, different components blend together closely, heterostructures may formed at the contact interface. However, for the 2:1 and 1:4 NTO/ZnO composites, cubes and nanorods are in the majority, respectively, which may affect the sensing characteristics of these samples and bring them nearer to pure NTO or ZnO. The composites with different proportion may be expected to show a good photoelectric performance due to their special morphology.

Fig.4 displays the TEM images of pure NTO, ZnO and all the composite samples. The morphology of pure NTO and ZnO were consistent with that in the SEM analysis. The images of NTO/ZnO samples still exhibit a pluralistic appearance, cubes and nanorods coexist in these composites. Furthermore, with the decrease of NTO component in the composites, a growing number of nanorods appear.

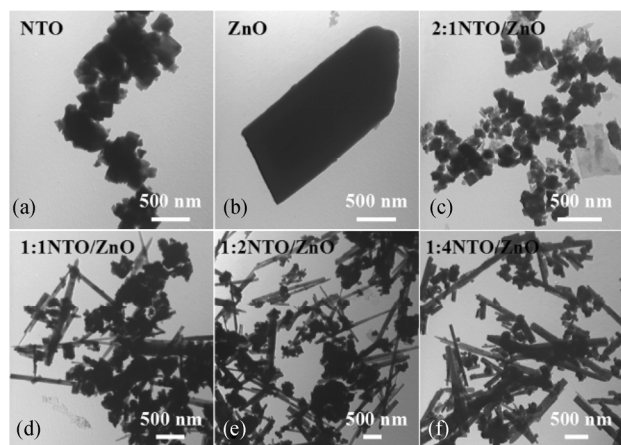


Fig.4 The TEM images of (a) pure NTO, (b) pure ZnO, (c) 2:1 NTO/ZnO, (d) 1:1 NTO/ZnO, (e) 1:2 NTO/ZnO, (f) 1:4 NTO/ZnO

Fig.5 shows the UV-visible absorption spectra and transmittance spectra of the pure NTO, ZnO and their composites. The absorption edges of 1:1, 1:2-composites are close to that of ZnO, showing an obvious shift towards long wavelength as compared to that of NTO. In addition, the absorption of 2:1-composite is located between the two pure samples. The strong absorption peak of NTO/ZnO composites indicates an excellent UV photoelectric properties. The enhanced absorption towards UV light of the composites maybe derived from the formation of one dimensional nanorod structure of ZnO after NTO induced, which would promote the efficient transmission of photo-generated carriers. The energy band gap can be calculated according to the absorption

edges of different samples^[15]. For the pure NTO and ZnO samples, the absorption edges were approximately consistent with their band gap energy. It's also shown clearly all of the samples have little absorption in the visible region. The transmittance spectra shown in Fig.5(b) were in good agreement with the absorption spectra. It can be seen that the transmittance becomes strong with the increase of wavelength, and low transmittance appears in short wavelength range below 400 nm.

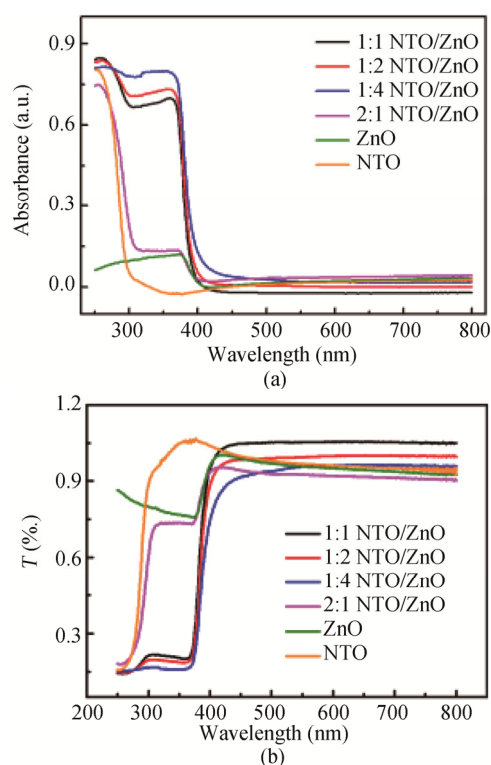


Fig.5 (a) The UV-visible absorption spectra and (b) transmittance spectra of pure NTO, ZnO and their composites

Fig.6 displays the Raman spectra of pure NTO, ZnO and their composites under the excitation wavelength of 532 nm. The obvious Raman peak of ZnO appears at 442 cm^{-1} , while that of NTO locates at 629 cm^{-1} . Moreover, it is found that with the increase of ZnO component, its corresponding Raman peak intensity in composites was enhanced.

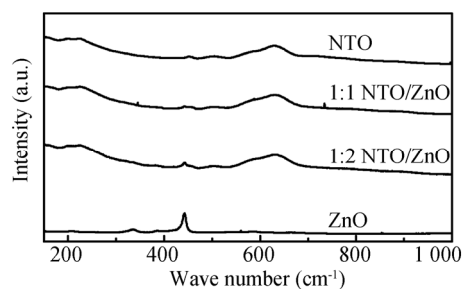


Fig.6 The Raman spectra of pure NTO, ZnO and their composites

Fig.7 shows the periodic photocurrent response of the 1:1, 1:2, 1:4, 2:1 NTO/ZnO and pure ZnO based detectors under 365 nm UV illumination. The time interval between light on and off are 20 s and the applied bias is set as 1 V. When the devices are illuminated, the photocurrent increases quickly, and drops sharply with the light removing. The peak photoresponse during different testing cycle changes little and behaves almost the same, indicating the high stability of the devices. In addition, the 1:1 and 1:2 NTO/ZnO detectors exhibit a higher photocurrent and faster response as compared with that of pure ZnO. The pure NTO based detector was also fabricated and its photoelectric performance was measured, which shows little response towards ultraviolet. The 1:1 and 1:2 NTO/ZnO detectors show a higher sensitivity (more than two orders of magnitude) than that of other composites. The enhanced photoelectric performance may be ascribed to the formation of NTO/ZnO heterostructure as well as the improved appearance of ZnO component. The cubes and nanorods are completely mixed in these composite samples, instead of showing an irregular morphology as pure ZnO does. The formation of one dimensional nanorod structure would promote the straight conduction of photo-generated carriers^[16]. Hence, the improved morphology together with the introduced heterostructures contributed much to this dramatic photoresponse improvement. The 1:1 and 1:2 NTO/ZnO samples exhibit the advantages of both components and consequently, a synergistic effect between them makes these composites more sensitive to UV light than the other ones.

Fig.7 also gives the response speed for all the detectors. The rise time and fall time of the 1:1 and 1:2 NTO/ZnO devices are less than 10 s. The present NTO/ZnO photodetectors show not only a remarkable photocurrent to dark current ratio, but also a fast response speed, revealing the superiority of these composites in photodetecting application.

Considering the good overall performance and periodic stability of the 1:1 NTO/ZnO detector, the *I-V* characteristics of this device in dark and under illumination was measured as shown in Fig.8(a). Both of the curves present nonlinear behavior due to the rectifying effect. Whether a forward bias or reverse bias applied, the currents are rising with the voltage increasing. At 5 V bias, the dark current of the device is less than 1 nA. Under the illumination of 365 nm UV light with the power density of 56.5 mW/cm², the photocurrent of the detector reaches 0.23 μA. The NTO/ZnO device shows a low dark current as well as a high photocurrent. The photo-to-dark current ratio reaches more than 2 orders of magnitude.

As is reported by some research, the photoresponse of detector mainly depends on the lifetime and quantity of photo-generated carriers^[17]. The mechanism of enhanced response in composite samples can be better understood through the band structure diagrams in Fig.8(b). The

conduction band of NTO is positive than that of ZnO^[18]. Then the electrons in conduction band would transfer from NTO to ZnO side easily. When the NTO/ZnO composites are irradiated by UV light, photo-generated electrons are separated rapidly and injected from the conduction band of NTO into that of ZnO, leading to a high density of electrons in ZnO. It is reasonably speculated the heterostructure formed at the NTO/ZnO interface can reduce the recombination probability between photo-generated carriers and prolong their lifetime. As a result, a remarkable photocurrent improvement is obtained.

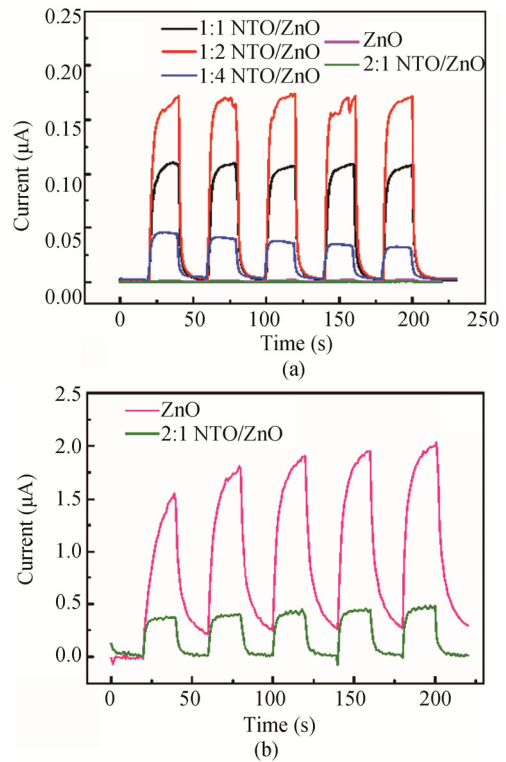


Fig.7 The response and recovery behaviors of pure ZnO and 1:1, 1:2, 1:4, 2:1 NTO/ZnO based detectors under 365 nm ultraviolet at 1 V bias

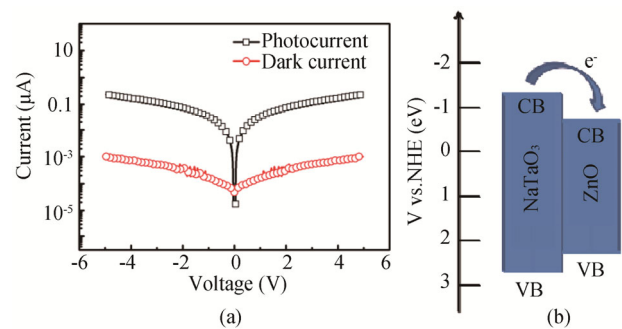


Fig.8 (a) The *I-V* characteristics of 1:1 NTO/ZnO based detector under 365 nm UV and in dark; (b) The band structure diagrams of NTO and ZnO

In conclusion, the NTO/ZnO composites have been fabricated via a simple hydrothermal method. Then UV

detectors based on these composites were fabricated by coating the samples on ceramic substrates with Ag-Pd interdigitated electrodes. Compared with pure samples and other composites, the 1:1 NTO/ZnO sample possesses better photoelectric properties. The 1:1 NTO/ZnO detector shows high performance including a large photo-to-dark current ratio of more than two orders of magnitude, and a low dark current less than 1 nA. The periodic photocurrent response characteristics show an excellent stability and repeatability of device. The enhanced photoresponse in NTO/ZnO composite devices maybe due to the synergistic effect between the two components and the improved morphology of ZnO component, which provide a larger specific surface area.

References

- [1] M. Zhang, K. Tuokedaerhan, H. Zhang and L. Li, *Optoelectronics Letters* **15**, 0081 (2019).
- [2] W. Wang, Y. Zheng, X. Li, Y. Li, L. Huang and G. Li, *Journal of Materials Chemistry C* **6**, 3417 (2018).
- [3] B. Yin, Y. Zhang, K. Li, J. Zhou, C. Liu, M. Zhang and S. Ruan, *Nanotechnology* **30**, 465501 (2019).
- [4] G. Li, L. Meng, X. Zhu, W. Gao, Y. Qin and L. Chen, *Nanoscale* **10**, 2242 (2018).
- [5] M. Zhang, G. Liu, J. Zhou, X. Ma, Z. Li, W. Chen and S. Ruan, *IEEE Electron Device Letters* **34**, 1539 (2013).
- [6] I. Ivanova, T. Kandiel, Y.-J. Cho, W. Choi and D. Bahnemann, *ACS Catalysis* **8**, 2313 (2018).
- [7] Y. Zhang, Y. Chen, Y. Zhang, X. Cheng, C. Feng, L. Chen, J. Zhou and S. Ruan, *Sensors and Actuators B* **174**, 485 (2012).
- [8] B. Guo, G. Wu, H. Chen and M. Wang, *Organic Electronics* **29**, 13 (2016).
- [9] Y. Zeng, X. Pan, B. Lu and Z. Ye, *RSC Advances* **6**, 31316 (2016).
- [10] C. Zhang, H. Xu, W. Liu, L. Yang, J. Zhang, L. Zhang, J. Wang, J. Ma and Y. Liu, *Optics Express* **23**, 15565 (2015).
- [11] J. Medina, N. Portillo-Vélez, M. Bizarro, A. Gordillo and S. Rodil, *Dyes and Pigments* **153**, 106 (2018).
- [12] L. Zheng, C. Chen, Y. Zheng, Y. Zhan, Y. Cao, X. Lin, Q. Zheng, K. Wei and J. Zhu, *Applied Catalysis B: Environmental* **148-149**, 44 (2014).
- [13] S. Yan, S. Ma, X. Xu, Y. Lu, H. Bian, X. Liang, W. Jin and H. Yang, *Materials Letters* **165**, 9 (2016).
- [14] D. Zhang, X. Gu, F. Jing, F. Gao, J. Zhou and S. Ruan, *Journal of Alloys and Compounds* **618**, 551 (2015).
- [15] H. Zhang, C. Feng, C. Liu, T. Xie, J. Zhou and S. Ruan, *IEEE Electron Device Letters* **32**, 934 (2011).
- [16] H. Zhang, S. Ruan, H. Li, M. Zhang, K. Lv, C. Feng and W. Chen, *IEEE Electron Device Letters* **33**, 83 (2012).
- [17] X. Kong, C. Liu, W. Dong, X. Zhang, C. Tao, L. Shen, J. Zhou, Y. Fei and S. Ruan, *Applied Physics Letters* **94**, 123502 (2009).
- [18] G. Xing, C. Tang, B. Zhang, L. Zhao, Y. Su and X. Wang, *Journal of Alloys and Compound* **647**, 287 (2015).