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Ultraviolet-visible Photodetectors Based on Tungsten Oxide Electrospun Nanofibers

Muhammad Shahid, Wang Yuting, Li Tianjun, Yang Jun, Zhang Mengfei, Xing Yan, Cheng Jing, Pan Wei

State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China

Abstract: We reported highly sensitive photodetectors, prepared by a thin film of electrospun polycrystalline tungsten oxide (WO_3) nanofibers. Structural properties have been investigated by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. UV-Visible absorption spectra was used to calculate the band gap of the electrospun nanofibers, showing a broad range in the UV spectrum. A high photosensitivity has been observed in the prepared photodetectors by WO_3 nanofibers. A facile assembly method has been used to make the device. The results suggest that WO_3 can be used as UV -visible photodetectors.

Key words: photodetectors, nanofibers, polycrystalline, photosensitivity

Recently, one dimensional nanomaterials have attracted great attention for their application in opto-electronics devices, such as field effect transistors, ultraviolet sensors, actuators and in MEMS and micro[1]. This field has become most promising for their practical applications. The assembly and device integration has become one of the hot topics in nanotechnology. Ultraviolet radiation (UV) applications in biotechnology, astronomy, materials science and medical sciences has attracted much attention[2]. In all these activities the monitoring of UV radiations has become much more important because the UV radiations can burn the skin resulting in a cancer, can damage the DNA structure, affect the immune system, and also it can damage eyes[3]. Therefore for safety point of view high efficiency and low energy operated photodetectors have great demand[4,5]. In all these applications, there are several semiconducting materials with a wide band gap like SnO_2, ZnO, GaN, Ga_2O_3, V_2O_4 etc. have been employed for UV detection system. Among all these important semiconductor materials WO_3 has attracted special attention due to its promising physical and chemical properties[6]. It has been used to synthesize the panel displays, smart windows, gas sensing, optical devices and also in field emission devices. Tungsten oxide with a bandgap (2.4~2.8 eV) of one dimensional nanostructures so far has been employed mainly based on its single crystalline structure[7-10]. According to the best of our knowledge there have been only few reports about the polycrystalline structures of the nanowires.

In this study we have investigated the photosensitivity in the electrospun nanofibers photodetectors, assembled with a facile device assembly method. A very low cost and facile device assembly method is employed for the preparation of the photodetectors based on WO_3 electrospun nanofibers. The photosensitivity of the prepared device was tested under UV (254 nm) and near visible (425 nm) wavelengths of light.

1 Experiment

Tungsten oxide nanofibers were prepared by a sol-gel assisted electrospinning method. First of all the precursor solution of 1 g tungsten hexachloride (WCl_6) was prepared by dissolving it in absolute ethyl alcohol and N,N-dimethyl formamide (DMF) with a volume ratio of 2:8 and stirred at room temperature for 2 h. Then 8% of the solvent PVP was added to it and again stirred at room temperature for 2 h to get homogenous sol-gel solution. All the chemicals used in this experiments were of analytical grade and were used without any further purification or impurity addition unless otherwise stated. After this the prepared solution was delivered to a syringe with a steel needle with an internal diameter of 0.9 mm. A positive voltage of 15 kV was applied to the needle, while the negative terminal of the voltage supply was connected to the aluminum foil which was used as a collector for the electrospun nanobelts. It was placed at a distance 15 cm from the syringe. The electrospun nanofibers were collected in form of a mat on the aluminum foil. After completing the electrospinning, nanofibers were collected and placed in a furnace for heat treatment at a temperature of 500 ℃ for 1 h at

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Corresponding author: Pan Wei, Ph. D., Professor, State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, P. R. China, Tel: 0086-10-62772858, E-mail: panw@mail.tsinghua.edu.cn

a heating rate of 5 ℃/min in the air.

2 Result and Discussion

2.1 Structural properties

Fig.1 shows the X-ray diffraction pattern of electrospun nanofibers after calcination at a temperature of 500 ℃ for 1 h in air.

It can be seen that all crystalline peaks in the XRD pattern shows a monoclinic phase of WO_3 according to the JCPDS Card No. 71-2141. All the peaks have been indexed in, which exactly match with the JCPDS of monoclinic tungsten oxide[11].

The electrospun nanofibers was observed by the JEOL scanning electron microscope (JSM-7001F) to analyze the shape and surface morphology of the nanofibers. Fig.2a and 2b show the SEM images of the electrospun nanofibers annealed at 500 ℃ for 1 h in air at different magnification. All the nanofibers have dense shape and are continuous. The average grain size of the nanofibers is about (20±5) nm, as it was estimated by the image J software for several grains and then the average was taken, which is in good agreement with the XRD data.

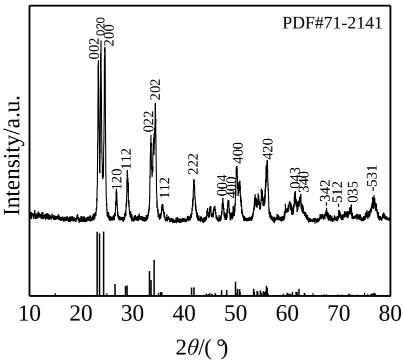

Fig.1 X-ray diffraction pattern of nanofibers after calcination at a temperature of 500 ℃ for 1 h in air

Internal structure of the nanofibers was investigated by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). For TEM analysis, first of all, a suitable amount of nanofibers was dispersed in ethanol ultrasonically. Then they were dropped on a copper electrode that was used in a JEOL transmission electron microscope (JEM-2010) to capture TEM images.

TEM image of the electrospun nanofibers is shown in Fig.2c. The average diameter of the nanofibers is about (100 ± 10) nm, which is in good agreement with the SEM data. The selected area transmission electron diffraction (SAED) pattern reveals that the nanofibers have polycrystalline structure that comprises of grains and grain boundaries. The high resolution TEM (HRTEM) image indicates that the lattice constants between two adjacent parallel planes is about 0.376 nm and 0.384 nm which can be assigned to the peak (020) and (002), respectively, according to JCPDS card No. 71-2141[11].

2.2 Opto-electronics properties of nanofibers

Fig.3a represents UV-vis diffuse reflection spectra of WO_3 nanofibers by UV/VIS/NIR spectrometer (UV-3600, Shimadzu, Tokyo, Japan) between the wavelengths from 300 nm to 700 nm. The absorbance band edge of the electrospun nanofibers is observed around 490 nm. The absorption band edges confirm that WO_3 can be used in the broad UV spectrum and also in the near visible spectrum for photodetectors. The bandgap energy of the electrospun nanofibers could be obtained from the diffuse reflection spectra using the Tauc plot.

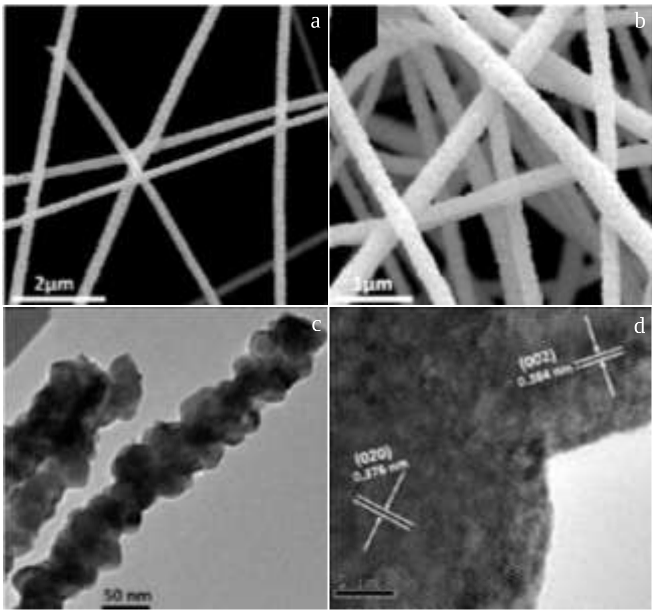

Fig.2 SEM images (a, b) of WO_3 nanofibers, TEM image of the nanofibers (c), and HRTEM image (d) of the nanofibers from a selected area

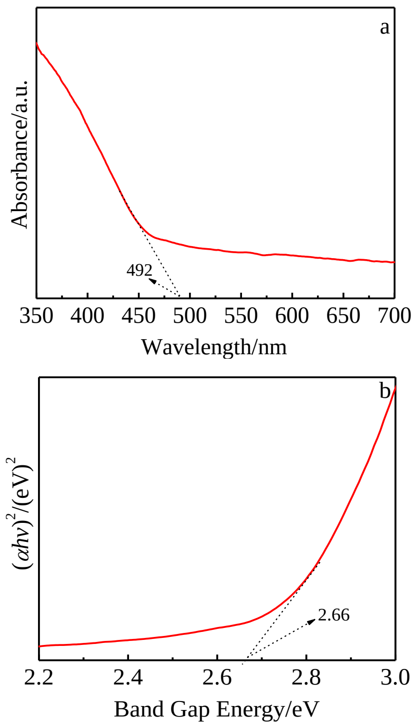

Fig.3 UV diffuse absorption spectra (a) of WO_3 nanofibers and the corresponding plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) (b)

The band gap energy of the WO_3 nanofibers was calculated based on the UV-Vis diffuse reflection spectra using the following equation:

$$(\alpha h\nu)^2=A(h\nu-E_g) \tag{1}$$

where α is the absorption coefficient, h is the Planck's constant, ν is the incident light frequency, A is a constant and E_g is the band gap[12]. The band gap energy of the WO_3 nanofibers was estimated about 2.6 eV which was found within the theoretical value (2.5~3 eV). The band gap energy has been shown in Fig.3b.

To investigate the optoelectronic properties of the WO_3 based photodetectors aligned nanofibers were collected by a modified collector[13]. Then they were transferred to an ultrasonically cleaned quartz substrate with pre-deposited platinum electrodes with a gap distance of about 100 μm. The device assembly of the WO_3 nanofibers photodetectors have been shown in Fig.4a. About 2000 aligned nanofibers were collected on a quartz substrate to make the photodetector device. After collecting aligned nanofibers the device was annealed at 500 ℃ for 2 h in air. The electrical properties were measured by a semiconductor characterizing instrument Keithely SCS 4200. To explore the optoelectronic properties of the assembled photodetector we measured the current and voltage (*I-V*) curves under dark and light of wavelengths of 254 nm and 425 nm as shown in the Fig.4b and 4d. The *I-V* curves, both in dark and light, exhibit straight lines which shows a good ohmic contact between the nanofiber arrays and the Pt deposited electrodes. A very low dark current about 0.11 nA and photo current 43 nA is observed in the electrospun based photodetector which shows a photosensitivity of about 3.9×10^2 under UV light illumination at

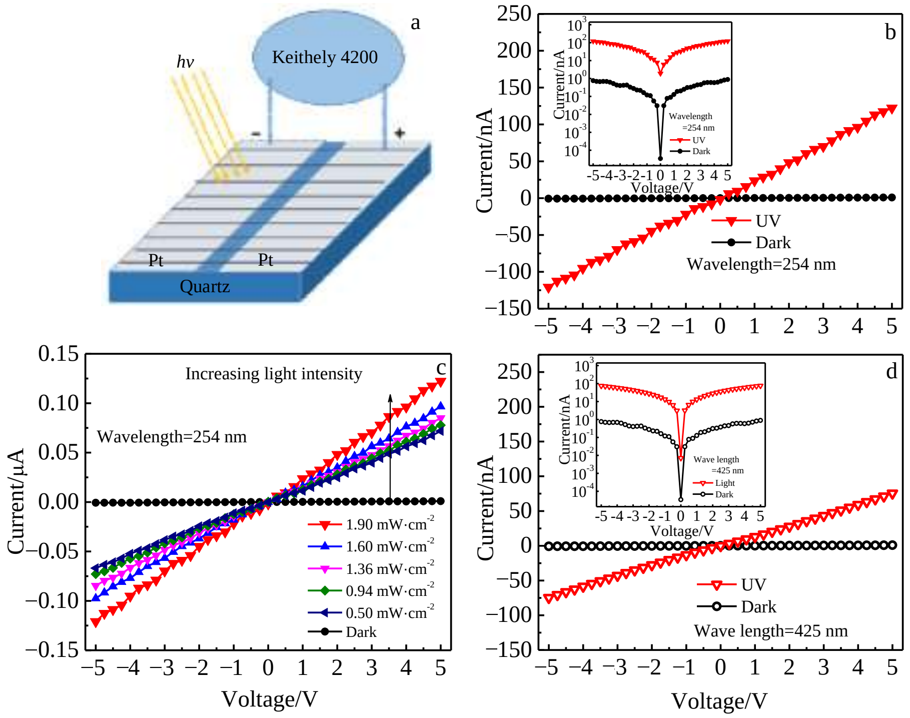

Fig.4 Schematic illustration of the device (a); *I-V* curves of WO_3 photodetector under dark and light illumination of wavelength 254 nm (b); *I-V* curves of WO_3 nanofibers under different power light intensity (c); *I-V* curves of WO_3 under dark and light illumination of wavelength 425 nm (d)

254 nm, under a power intensity of 1.90 mW/cm^2. The inset in Fig.4b shows the logarithmic scale of *I-V* curve in dark and under light illumination. Fig.4c shows the comparison of *I-V* curves under different power light illumination. As it can also be seen that the photocurrent increases with the increase of the light intensity. Thus, it is exactly according to the expectations that higher light intensities induce higher photocurrent. The photoresponse of the device was also measured under a light of wavelength 425 nm. The photocurrent under wavelength of 425 nm is than that under the light intensity of 254 nm[14]. The photosensitivity of the photodetector under this light is observed around 102.

The mechanism of high photosensitivity can be described as follows: when the nanofibers are exposed to air the oxygen molecules are adsorbed on the surface and they will capture electrons from the nanowires and will become negatively charge. This can be expressed by the following relation[15]:

$$[O_2 + e^- \rightarrow O_2] \qquad (2)$$

When the nanofibers device is exposed to light then the holes inside the nanowire will move towards the surface of the nanowire with the as-assistance of surface electric field leaving behind the unpaired electrons. These electrons will contribute to the electrical conductivity of the nanofibers. The holes will discharge the negatively charged oxygen molecules. This can also be shown by the equation as:

$$[h^+ + O_2 \rightarrow O_2] \qquad (3)$$

Because these neutralized oxygen molecules are photodesorbed from the surface, therefore the presence of the hole trap states prolongs the photocurrent time. The polycrystalline structure and high surface to volume ratio of the nanofibers also contribute to the high photosensitivity of the nanofibers for their use in photodetectors.

3 Conclusions

1) Photodetector device based on WO_3 nanofibers can be assembled by a facile assembly method.

2) The prepared electrospun nanofibers are monoclinic, single phase and have polycrystalline structure. Their calculated band gap is in good agreement with the theoretical value. These assembled photodetectors show a high sensitivity in UV and the near visible region. These photodetectors also show a good variation in the photocurrent due to change in power intensity of the light source.

3) This preparation and assembly method can be employed to prepare transparent flexible photosensors and wearable electronics.

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基于氧化钨纳米纤维的紫外探测器

Muhammad Shahid，王雨婷，李天君，杨　军，张梦霏，邢　岩，成　婧，潘　伟

(清华大学，新型陶瓷与精细工艺国家重点实验室，北京 100084)

摘　要：通过在薄膜上收集多晶氧化钨(WO_3)纳米线得到了高灵敏度的光电探测材料，并用 X 射线衍射，扫描电子显微镜和透射电子显微镜分别表征了材料的结构性能。紫外可见吸收光谱计算的结果显示纳米纤维在紫外区域有很强的吸收。在 WO_3 纳米纤维中，观察到了高光敏特性。一种简易的组装方法被用于制备 WO_3 纳米线器件。研究结果显示 WO_3 可以被用于紫外光探测器。

关键词：光探测器；纳米纤维；多晶；光敏性

作者简介：Muhammad Shahid，男，1975 年生，博士生，清华大学材料科学与工程学院新型陶瓷与精细工艺国家重点实验室，北京 100084，E-mail: shahidm10@mail.tsinghua.edu.cn