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Modulating electrical and photoelectrical properties of one-step electrospun one-dimensional SnO₂ arrays

Di Liu¹, Hao Li¹, Longfei Song¹, Xinxu Zhu¹, Yuanbin Qin², Hongliang Zu¹, Junyu He¹, Zaixing Yang³ and Fengyun Wang¹

¹ College of Physics and State Key Laboratory of Bio Fibers and Eco Textiles, Qingdao University, Qingdao 266071, People's Republic of China
² Center for Advancing Materials Performance from the Nanoscale, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

³ School of Microelectronics and Center of Nanoelectronics, Shandong University, Jinan 250100, People's Republic of China

E-mail: fywang@qdu.edu.cn

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Abstract

One-dimensional nanostructured SnO₂ has attracted intense research interest due to its advantageous properties, including a large surface-to-volume ratio, high optical transparency and typical n-type properties. However, how to fabricate high-performance and multifunctional electronic devices based on 1D nanostructured SnO₂ via low-cost and efficient preparation techniques is still a huge challenge. In this work, a low-cost, one-step electrospun technology was employed to synthesize the SnO₂ nanofiber (NF) and nanotube (NT) arrays. The electrical and photoelectrical parameters of SnO_2 NTs-based devices were effectively controlled through simple changes to the amount of Sn in the precursor solution. The optimal 0.2 SnO₂ NTs-based field effect transistors (FETs) with 0.2 g SnCl₂*4H₂O per 5 ml in the precursor solution exhibit a high saturation current (~9 \times 10⁻⁵ A) and a large on/off ratio exceeding 2.4 \times 10⁶. Additionally, 0.2 SnO₂ NTs-based FET also exhibit a narrowband deep-UV photodetectivity (240–320 nm), including an ultra-high photocurrent of 307 μ A, a high photosensitivity of 2003, responsibility of 214 A W⁻¹ and detectivity of 2.19×10^{13} Jones. Furthermore, the SnO₂ NTs-based transparent photodetectors were as well be integrated with fluorine-doped tin oxide glass and demonstrated a high optical transparency and photosensitivity (~199). All these results elucidate the significant advantages of these electrospun SnO₂ NTs for next-generation multifunctional electronics and transparent photonics.

Supplementary material for this article is available online

Keywords: SnO₂ nanotubes and nanofibers, electrospinning, field effect transistor, photodetector

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years, one-dimensional (1D) semiconductor nanostructures have been widely explored as fundamental building blocks for future multifunctional electronics and transparent optoelectronics, owing to outstanding properties such as quantum confinement effect, high aspect ratio, and channel specificity for carriers transport [1-5]. Among different 1D candidates, metal-oxides (MOXs) such as In_2O_3 [6–8], ZnO [9, 10] CuO [11] and SnO₂ have attracted extensive attention as the ideal channel materials due to its unique electronic and optoelectronic properties [12–15]. Even though the In_2O_3 -based materials attracted a great deal of attention due to its excellent electrical properties, it still may not be the best material choice for future sustainability because of the scarcity of In. A potential candidate to replace In_2O_3 , ZnO materials suffer from the poor carrier concentration and instability [9], which needs to be further studied for practical application.

As a multifunctional MOX material, 1D SnO₂ nanofibers (NFs) has been applied in many aspects, such as field effect transistors (FETs) [15-17], chem/bio-sensors [18, 19], optoelectronic devices [20–22] and super capacitors [23], owing to their chemical stability, optical transparency, and high carrier mobility (μ_{FE}). Especially for FETs and UV photodetectors, the low formation energies of oxygen vacancies and tin interstitials create shallow donor levels lying below the conduction band, which lead to the high n-type conductivity of nonstoichiometric SnO₂ [17]. Sun et al reported highly-oriented SnO2 NFs network based transistors fabricated through photolithography-free techniques. These NFs networks showed ultra-high on/off current ratio exceed 10⁸ in vacuum environment. This result demonstrates that 1D SnO₂ materials with excellent electrical performance, fault tolerance, and high transparency as a channel transport material could be a suitable candidate for low-cost, large-area electronics [16]. Unfortunately, their preparation process is expensive and difficult to control, and is not suitable for large-scale production.

Although various preparation methods including chemical vapor deposition (CVD), hydrothermal, template-assisted electrodeposition, and photolithography-free techniques can produce a variety of 1D SnO₂ MOXs nanomaterials [16, 17, 24-26], the production is relative low, and the fabrication of large-area electronic devices still remain an open challenge. Electrospinning is a cheap and facile method to prepare various 1D NFs in large scale, and have already been applied for transistors, sensors, solar cells and many other devices [14, 27–29]. By adjusting the composition of the precursor solution or the voltage, electrospinning can produce continuous and uniform NFs, nanotubes (NTs) or nanobelts. Li et al have produced a visible-blind UV photodetector based on polycrystalline SnO₂ NTs by electrospinning technique which exhibit better detectivity than that of single crystal nanowires photodetectors due to their Schottky barrier [30]. Although polycrystalline SnO2 NTs achieved a high light-to-dark current ratio of 850 times, the photocurrent of their devices are only 25.6 nA [30]. In this regard, it is essential to fabricate large-scale, low-cost and high performance 1D SnO2 nanomaterials electrical and photoelectrical devices.

In this work, polycrystalline SnO_2 NT and NF arrays were synthesized by a simply one-step electrospun technology. According to our experimental results, the more Sn added into the precursor solution, the easier it is to form typical solid NFs, and both the electrical and photoelectrical performances of SnO_2 NF or NT arrays can be modulated through a process of adding Sn. Among all the samples, the prepared 0.2 SnO₂ NTs-based devices display the optimal electrical properties, including an impressively low off-current $(I_{off}) \sim 3.8 \times 10^{-11}$ A, a high on-current $(I_{on}) \sim 9.1 \times 10^{-5}$ A, and large on/off current ratio $\sim 2.4 \times 10^6$. If the Sn content in the precursor solution is reduced, the saturation current will be greatly reduced, resulting in a decrease in the on/off current ratio. If the Sn content in the precursor solution is increased, the off-state of the device will show a large rise, which then results in poor device performance. The reason for the above results is attributed to the different carrier concentrations in the NTs and NFs. Meanwhile, the photoelectrical properties of SnO₂ NTs-based FET were also investigated, which further prove this inference. While applying a bias voltage of 10 V, the 0.2 SnO₂ NTs-based devices also showed a high photosensitivity (~2003), responsibility (~214 A W^{-1}) and detectivity (~2.19 \times 10¹³ Jones) when exposed to 280 nm UV light. Both higher and lower Sn amounts in the precursor solution will lead to poor photoelectrical performance in the precursor solution. When the SnO₂ NTs were prepared on fluorine-doped tin oxide glass (FTO glass) to construct transparent photodetectors, a high optical transparency of over 85% and high sensitivity (~199) was seen. The electrical and photoelectrical properties of our SnO₂ NTs devices were better than most 1D SnO₂based FETs and photodetectors, and these SnO2 NTs devices will have many prospective uses after modifications.

2. Materials and methods

2.1. Preparation of precursor solution for electrospinning

Different SnO₂ precursor solutions were prepared by dissolving different masses of stannous chloride tetrahydrate (SnCl₂·4H₂O, Aladdin) and 0.8 g of PVP (MW of 1 300 000 g mol⁻¹, Aladdin) into 5 ml of N,N-Dimethylformamide (DMF). 5 types of precursor solutions containing 0.1 g, 0.15 g, 0.2 g, 0.25 g and 0.4 g of SnCl₂·4H₂O were prepared by the above method. Then, the obtained solution was stirred at room temperature for 12 h. To ensure the formation of SnO₂ NFs, 0.11 g acetic acid (CH₃COOH, Aladdin) was added to the 0.4 g SnCl₂·4H₂O precursor solution. The final products were named as 0.1, 0.15, 0.2, 0.25 and 0.4 SnO₂, respectively, based on the mass of the SnCl₂·4H₂O added in the precursor solution.

2.2. Electrospinning Process

The p-type heavily-doped Si-substrate with a 300 nm SiO₂ dielectric layer or FTO glass were used as the collector in the electrospinning process, and both their channel widths were 100 μ m. The following electrospinning processes and parameters performed on both substrates are completely consistent.

Our basic electrospinning equipment included a needle, needle tube, propulsion pump, high voltage power supply and collection device. In this experiment, Stainless steel needles with diameter of 0.43 mm were used, and the distance between the needle and the collecting device was about 15 cm, and the positive voltage and the negative voltage applied to the collecting device was 13 kV and -3.5 kV, respectively. The propulsion speed of the propulsion pump was set at 0.48 ml h⁻¹.

In order to make the electrospun composite fibers come into close contact with the substrate and allow the solvent to evaporate better, after electrospinning, silicon wafers were placed on the 150 °C hot stage for 10 min. They were then treated with UV light for 40 min. (1 kW, 290–320 nm) The UV light treatment promotes the chemical deactivation of NFs, thus obtaining stable NF arrays and an interface that is electronically clean [6]. In order to decompose the polymer completely and form fully crystallized SnO₂ NTs or NFs, the as-spun PVP/Sn NFs array needed to be annealed at 600 °C with a rate of temperature increase of 2 °C min⁻¹ and then held for two hours.

2.3. Characterization and measurements

The images of parallel arrays of composite fibres were taken through an optical microscope (LEICA ICC50W). In order to study the morphology and cross section of SnO₂ NTs and NFs on the silicon wafers, scanning electron microscopy (SEM, TESCAN MIRA3) was applied. XRD (Rigaku D/max-rB) was used to analyze the composition and crystal structure of SnO₂ NTs and NFs. Transmission electron microscope, selected area electron diffraction, and high-resolution transmission electron microscope (TEM, SAED, and HRTEM, JEOL JEM 2100 F) was used to analyze the crystal and internal structure of SnO₂ NTs and NFs. The absorption spectra of SnO₂ NTs were conducted using a Shimadzu ultraviolet-visible spectrophotometer (UV-3600).

The Al electrodes were evaporated thermally through a shadow mask with the finished transistor channel dimension of 1000 μ m in width and 100 μ m in length. Transistors performance were tested with probe table and I–V tester (KEYSIGHT B2912A). Photocurrent measurements were carried out by a semiconductor characterization system (Keithley 4200-SCS) integrated with a monochromatic system (Omin-13005) and light source (LSH-500). The I–V curves were measured with sweep voltage from –10 V to 10 V or –2.5 V to 2 V in the dark with a step of 0.01 V and under illumination of a 280 nm light.

3. Results and discussions

Figures 1(a) and (b) show the SEM images of $0.2 \text{ SnO}_2 \text{ NT}$ and $0.4 \text{ SnO}_2 \text{ NF}$ parallel arrays after annealing, and the corresponding insets show the typically enlarged SEM images of single NT and NF, respectively. The quasi-aligned NT and NF arrays have similar trends and densities, which is also proved by the optical images of as-spun PVP/Sn NT and NF arrays before annealing (figure S1) (available online at stacks.iop.org/NANO/31/335202/mmedia). It can be seen that the diameter of the NT and NF are 81.6 nm and 83.4 nm, respectively. In order to determine the morphology of the cross-section of SnO₂ NTs and NFs, thick NTs and NFs layer were peeled from the substrate with the same preparation process minus the long electrospinning time of 600 s, and the relative SEM images are shown in figures 1(c) and (d), respectively. It is clear to see that 1D 0.2 SnO₂ nanomaterials (figure 1(c)) show a prominent hollow structure, while 1D 0.4 SnO₂ nanomaterials (figure 1(d)) have a solid structure which is further proven by the high magnification SEM image (figure S2).

The formation process and mechanism of hollow SnO2 NTs is disclosed in figure 2. According to the previous reports, electrospun 1D SnO₂ NFs easily form a hollow structure [31, 32]. Figures 2(a) and (b) illustrate the process of electrospinning and UV treatment, respectively, and figures 2(c) and (d) show the formation process of SnO₂ NTs. The formation of NTs depends on the inward and outward diffusion rates caused by the Kirkendall effect during the subsequent calcination process [19]. The outward diffusion rate (defined as J_A) of Sn is greater than that of the inward diffusion rate (defined as J_B) of the organics in the initial fibres due to the fact that Sn was more highly solubility in DMF than in PVP (figure 2(c)). Thus the hollow structured NTs were formed after calcination (figure 2(d) [19, 31, 33]. A small amount of CH₃COOH can improve the solubility of SnCl₂·4H₂O when added to the precursor solution, and will increase the concentration of SnCl₂·4H₂O in the precursor solution which leads to solid SnO₂ NFs.

X-ray diffusion (XRD) patterns of SnO₂ NTs and NFs with different amount of SnO_2 are shown in figure 3(a). Both SnO_2 NTs and NFs have similar XRD spectra of 26.61°, 33.89°, 37.95° , 38.97° , 51.78° , 54.76° , 57.82° , 61.87° , 64.72° , 65.94° , 71.28° and 78.71° , corresponding well to the tetragonal SnO₂ phases (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (202) and (321) lattice planes, respectively (JCPDS#41-1445). This indicates that the amount of SnCl₂·4H₂O in the precursor solution almost had no affection on the crystalline structure of the SnO₂. There are no impurities or secondary terms produced, inferring the pure phase of the SnO₂ NTs and NFs. As shown in figure S3, TEM and SAED were applied to further illustrate the morphology and microstructure of individual NT and NF. Figure S3(a) and (d) show low-magnified TEM images of a typical single SnO₂ NT and NF, respectively. Both NTs and NFs consist of a large number of small nanoparticles with an average diameter of 15 nm, indicating the multi-crystalline phase of SnO₂. As shown in figure S3b and S3e provided by the selected area as designated in figures S3a and S3d, the 0.33 and 0.32 nm spacing of the lattice fringes matches well with the (110) and (001) planes of tetragonal SnO₂, respectively. The corresponding SAED plots in figure S3 c and 3 f show typical SnO₂ diffusion fraction rings, respectively. The four brightest rings are designated as (110), (101), (211) and (301) planes of tetragonal SnO2 which agreed well with the XRD measurements, and the discontinuous diffraction rings indicate the multi-crystalline phase of SnO₂, which agreed well with the XRD measurements. The results of SEM, XRD and TEM verify each other, which proves that our SnO₂ NTs and NFs reached high quality and purity, and that there was no difference except for hollow or solid. The absorption spectra (figure 3(b)) of the SnO₂ NTs were recorded by a UV–Vis spectrometer. The 0.2 SnO₂ NTs have a high absorption of deep UV light with a below-light wavelength of 325 nm, demonstrating its potential as a high performance deep-UV photodetector.



Figure 1. SEM images of (a) SnO_2 nanotube arrays, (b) SnO_2 nanofiber arrays, (c) nanotubes cross-section and (d) nanofibers cross-section. (Bottom inset corresponding to the amplified single nanotube and nanofiber in figures 1(a) and (b)).



Figure 2. Schematic diagram of the electrospun process and the nanotubes formation processes.

The band gap of $0.2 \text{ SnO}_2 \text{ NTs}$ is 3.63 eV obtained by the maximum curvature of the $(Ah\nu)^{1/2}$ - $(h\nu)$ curves (figure 3(b) inset), which is similar to the previous report (3.6 eV) [20, 34].

As shown in figure 4(a), the SnO₂ NTs and NFs-based FETs were fabricated with a typical back-gate construction with the same channel length and width between sources and drains, using a p-type heavy-doped Si as a gate, and a thermally grown 300 nm thick SiO₂ as the dielectric layer. At the same time, the density of SnO₂ NT or NF arrays was controlled to be 0.5 NFs μ m⁻¹ with an electrospun time of ~25 s. Both too low and too high density NFs lead to poor device performance

[6, 35]. Figure 4(b) demonstrates the transfer curves of FETs based on SnO₂ NTs or NFs with different amounts of Sn, and all the curves show n-type conduction behaviours. The transfer curve of 0.4 SnO₂ NFs (black line) shows a large I_{off} of 3.27×10^{-4} A and saturation current of 6.48×10^{-4} A, which lead to the extremely low on/off current ratio of ~2. When the amount of SnCl₂ · 4H₂O in the precursor solution was reduced to 0.1, 0.15, 0.2 and 0.25 g, the I_{off} of these FETs was significantly reduced to 1.19×10^{-11} A, 1.97×10^{-11} A, 4.64×10^{-11} A and 2.58×10^{-8} A, respectively, while the corresponding I_{on} was just reduced by 2–80



Figure 3. (a) XRD of SnO₂ nanotubes and nanofibers with different Sn contents. (b) Absorption spectra of 0.2 SnO₂ and middle inset corresponding $(Ahv)^{1/2}$ -(hv) curves.

times. The 0.2 SnO₂ NTs-based FETs achieve the best performance (red line), corresponding the I_{off} , I_{on} and I_{on}/I_{off} are 3.8×10^{-11} A, 9.1×10^{-5} A, and 2.4×10^{6} , respectively. Therefore, the I_{on}/I_{off} ratio of the SnO₂ NTs-based FETs with low SnCl₂·4H₂O concentration was increased by ~10⁶. The 0.2 SnO₂ NTs-based FETs performed the best (red line), and its typical output curves are shown in figure 4(c), which exhibit n-type conduction, saturation current behaviours, and a clear linear-saturation region with an ohmic-like contact property. In addition, the other output curves of 0.1, 0.15, 0.25 NTs and 0.4 NFs are given in figure S4. All these illustrate that the devices with 0.2 g SnCl₂·4H₂O in the precursor solution exhibit a promising potential for high-performance electronic devices.

According to previous reports, the semiconducting nature of a number of metal oxides is strongly determined by oxygen vacancies [17]. As showed in figure S5, the excessive carrier concentration originated from the oxygen vacancies in the SnO₂ NFs is the direct reason for high saturation current. Specifically, the adsorption of chemical species such as oxygen molecules and OH- radicals cause changes in surface states that influence the width of the conducting channel. Oxygen ions such as O_2^- are form by adsorbing oxygen molecules, that extract electrons from SnO₂ resulting in a depletion of the charge carriers in the NTs and NFs. In addition, surface adsorbed H₂O and OH⁻ groups tend to accumulate electrons to form a positive space charge, which further widens the depletion layer [17]. Both the inner and outer surfaces of the NTs adsorb O₂ to form wider depletion layers, which greatly reduces its carrier concentration. Compared to SnO₂ solid NFs, the wider electronic depletion layers present in the NTs over NFs may lead to lower carrier concentration [36, 37]. To further understand the relationships between the device performance and the Sn amount, a statistical analysis of 20 devices for every Sn amount was performed. The mobility was calculated according to the following formula.

$$U_{DS} = \left(\frac{WC_i \,\mu_{FE}}{2L}\right) / \left(V_G - V_{th}\right)^2$$

Ci is the area capacitance of dielectric layer, W is channel width, L is channel length, V_G is gate voltage, V_{th} is threshold voltage, and I_{DS} is source drain current. As shown in figures 4(d) and (e), I_{on}/I_{off} and μ_{FE} took the average value and variance to make an error graph. The average I_{on}/I_{off} values could then be estimated as 2.96×10^5 , 1.01×10^6 , 1.33×10^6 , 3.7×10^3 and 1.9 for 0.1, 0.15, 0.2, 0.25 and 0.4 1D SnO₂based photodetectors respectively, with corresponding μ_{FE} are 0.04, 0.15, 0.28, 0.985 and 0.75 cm² V⁻¹ s⁻¹. The highest Ion/Ioff of 0.2 g SnO2 NTs and the optimal carrier mobility of 0.25 g SnO₂ NTs can fully be obtained, and what's more, it gives relatively small errors in all data. Through analysis of these comparative experiments (figures 4(d) and (e)), it can be concluded that when the amount of Sn was increased in the precursor solution, the mobility improved, however, its Ion/Ioff was severely decreased. These results fully demonstrate that the morphology of 1D SnO2 nanomaterials can effectively control the electrical performance of the devices, and the device performance can be easily modulated by adjusting the amount of Sn in the precursor solution. In order to further investigate the reliability of our 0.2 SnO₂-based photodetector, long-term stability of the device was tested and shown in figure 4(f). The devices were storied in the ambient conditions (temperature of ~20 °C and relative humidity of ~ 40%) for 120 days, and the transfer curse 0.2 g SnO₂ NTs device (figure 4(f)) shows negligible change, indicating that NTs devices have good stability.

Figure 5 reflects all the photoelectric performance of SnO_2 NTs and NFs based on FET structure comprehensively. Figure 5(a) illustrates the I–V curves of 0.15, 0.2, 0.25 and 0.4 of SnO_2 photodetectors measured in dark and under the light of wavelength 280 nm. The photosensitivity (S) is defined as the radio between photocurrent (I_p) and dark current (I_d) and can be calculated by the equation:

$$S = \frac{I_P}{I_d}$$

Similarly, the 0.2 SnO₂ NTs-based photodetector exhibit the highest S over 2000, and the corresponding dark current and photocurrent are 0.153 and 307 μ A with an intensity of



Figure 4. (a) FET structure of SnO_2 nanotubes array. (b) The output curve of the SnO_2 nanotubes FET. (c) Transfer curves of SnO_2 FETs with different Sn amount. (d) Average on/off current ratio of SnO_2 FETs of different Sn contents. (e) Average mobility of SnO_2 FETs with different Sn contents. (f) The stability of $0.2 SnO_2$ nanotubes FET after 120 days.

1.43 mW cm⁻² at a bias voltage of 10 V, respectively. Meanwhile, the S of 0.4 SnO₂ solid NFs-based photodetector is only 10 due to its high dark current. For metal oxide semiconductor materials, O2 are easily adsorbed on the surface, which can captured free electrons from the conduction band of the oxide forming O_2^- , thereby forming a depletion region with low conductivity on the surface [17]. When nanotubes and nanofibers are exposed to light, photo-generated holes move to the surface and recombine the O_2^- , and oxygen desorbs from the surface. As a result, the width of the depletion layer becomes narrow, and it is the carrier concentration increases, and eventually the photocurrent increases. Compared with nanofibers, nanotubes have a higher specific surface area, a thicker depletion layer can be formed on the inner and outer surfaces. Therefore, dark current will be lower than that of nanofibers. When the adsorbed O_2^- are desorbed by reaction with photogenerated holes, the width of the depletion layer will decrease [36]. The change in conductivity caused by the thickness of the depletion layer will additionally increase the photosensitivity. The statistical S of our 20 devices were collected and presented in figure 5(b), shows the consistency of the electrospun SnO₂ nano-structure for light detection ability. All the 0.2 SnO₂ NTs-based photodetectors have S in the narrow range of 1797–2217, which means that SnO₂ NTs have a similar diameter and density on the silicon substrate produced by the electrospinning. Figure 5(c) shows the I-V curves of 0.2 SnO₂ NTs devices under different wavelengths of light 240, 260, 280, 300, 320 nm and dark to systematically explore the spectral photo response 0.2 SnO₂ NTs devices, respectively,. Additionally, the responsivity (R_{λ}) and detectivity (D^*) of the 0.2 SnO₂-based device were calculated as follows.

$$R_{\lambda} = \frac{I_P - I_d}{PS}$$
$$D^* = \frac{R_{\lambda} S^{1/2}}{(2eI_d)^{1/2}}$$

Where P is the incident light intensity, S is the effective area of light irradiation (S = 10^{-3} cm²), and e is the value of electronic charge. Figure 5(d) plots both R_{λ} and D^{*} depend on various wavelength from 200 to 400 nm with 10 nm interval according to the experimental data and the previous formula of R_{λ} and D^{*}. The SnO₂ NTs-based photodetectors show high R_{λ} and D^* in UVB detection, and the peak value of R_{λ} and D^* are 214 A W^{-1} and 2.19 \times 10^{13} Jones under 280 nm light irradiation, respectively. It is worth noting that the R_{λ} of a photodetector at 280 nm is 80, and 535 times higher than that of R_{λ} at 240 nm and 320 nm, respectively, indicating that our devices have superior light selectivity. Figure 5(e) shows the photocurrent of the photodetectors measured under the wavelength of light 280 nm with varying power intensity from 0.03 to 1.43 mW cm⁻². As shown in figure 5(f), the power law can be used to fit the curves where Ip $\propto P^{\theta}$, in which θ represents the exponent. The best-fit line is at $\theta = 0.73$, and it is an exponent $(0.70 < \theta < 1)$ related to the trapping and recombination processes of the charge carriers in photodetector. In addition, Figure S6 presents the time dependent photo response of the photodetector measured by periodically turning on and off 280 nm light. The all above results indicate that SnO₂ NTs have the potential to be used as a deep-UV photodetector with excellent photoelectric performance.



Figure 5. SnO₂-based photodetectors: (a) I–V curves of photodetectors with different Sn amount in dark and under illumination of 280 nm light; (b) the photosensitivity comparison of photodetectors with different Sn amount at the bias of 10 V; (c) I–V curves of the photodetectors under different wavelengths of light, (d) responsivity, and detectivity. (e) I–V curves of photodetectors with variations in light power intensity under 280 nm wavelength of light. (f) Photocurrent versus light intensity and its power law fitting of the photodetectors.

The construction of large-area transparent optoelectronic device is one of the important directions for future multifunctional electronic devices. The 0.2 SnO₂ NTs were also used in a transparent photodetector on FTO glass. Figure 6(a) illustrates the I-V curves of 0.2 SnO2 transparent photodetectors measured in dark and light of wavelength 280 nm. Since the FTO glass cannot withstand a temperature of 600 °C, the NTs were annealed at 570 °C. The lower annealing temperature resulted in insufficient crystallization, which reduced the photoelectric performance. Figure 6(b) reflects the transparency of the annealed device, and the inside image shows the actual device. The transmittance of the devices in the visible light region exceed 85%, and the words Qingdao University can be clearly seen through the glass (Figure 6(b) insert). As summarized in table 1, the performance of SnO₂ NTs is superior to other SnO₂ nanostructure and 1D MOXs materials. The high performance of the SnO₂ nanotubes devices in this work can be mainly attributed to the unique hollow nanotube structure. Table 1 shows that our SnO₂ nanotubes do not have the advantage in the photocurrent, however, the nanotube structure with a wider depletion layer width of can provide a lower dark current. In addition, the carriers in quasi-aligned nanotubes travel much shorter channels than those in disordered nanofibers network, which lead to higher photocurrent [38, 39]. Performance comparisons based on the table indicate that the SnO₂ NTs have higher ultra-high photocurrent and responsibility over the others. It should be noted that, if the SnO₂ NTs are used with a high-temperature-resistant conductive glass, the photoelectric performance of SnO_2 is expected to be further improved to be similar to that on silicon. These results predict the great ccompetence in next-generation optoelectronics market.



Figure 6. (a) The I–V curve of 0.2 SnO_2 nanotubes photodetector using FTO glass as substrate. (b) The optical transmittance curve of the FTO glass after being covered by 0.2 SnO_2 nanotubes.

Table 1. Photoelectrical performances comparison of different SnO₂-based photodetectors.

Photodetectors	Dark current	Photocurrent	Photosensitivity	Responsivity	Ref.
SnO ₂ nanotubes	0.153 µA (10 V)	307 µA (10 V)	2000 (280 nm)	214 A W^{-1}	This work
SnO ₂ nanonets	65.5 µA (5 V)	232.3 µA (5 V)	3.54 (320 nm)	_	[20]
ZnO NFs/PbS heterostructure	1 pA (10 V)	< 1 nA (10 V)	<1000 (350 nm)	0.0051 A W^{-1}	[40]
SNO ₂ /SNS ₂ heterojunction	6.9–2.8 μA (1.5 V)	11.6–14.7 µA (1.5 V)	≈4.14 (365 nm)	2.9 mA W^{-1}	[41]
TiO_2/SnO_2 heterojunction	_	-	4550 (365 nm)	0.6 A W^{-1}	[42]
SnO ₂ nanowires	1.05 µA (20 V)	105 µA (20 V)	100 (335 nm)	_	[21]
SnO ₂ -NiO NFs-array cross bar	10^{-12} A	10^{-10} A	140 (300 nm)	8.67 A W^{-1}	[43]

4. Conclusions

In summary, low-cost and high-performance FETs and photodetectors based on SnO₂ NTs were integrated by a facile electrospinning technique. The electrical and photoelectrical performance of SnO₂ NTs-based devices can be efficiently manipulated by varying the amount of Sn in the precursor solution. It was found that the FETs based on 0.2 SnO₂ NTs exhibited the best electrical and photoelectrical performance, including a low $I_{off} \sim 3.8 \times 10^{-11}$ A, an I_{on}/I_{off} of $\sim 2.4 \times 10^6$, a μ_{FE} of 0.38 cm² V⁻¹ S⁻¹, a high photosensitivity of ~2003, a responsibility of ~214 A W⁻¹ and a detectivity of ~2.19 \times 10¹³ Jones. After storage for 120 days at ambient conditions, the device showed no obvious degradation proving the excellent stability of SnO₂ NTs. To further explore the application of SnO₂ NTs in transparent optoelectronic devices, a transparent UV photodetector was constructed with SnO₂ NTs on FTO glass, which shows high optical transparency and sensitivity (~199). The SnO₂ NTs have a good development prospect for applications in transistors and photodetectors with low power consumption, high response, and convenient largescale integration.

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Author contributions

LD, LH, SLF, ZXX, QYB, and HJY conducted the extensive experiments and analyzed the data. LD, LH and WFY supervised the project and wrote the manuscript. LD, ZHL, YZX and WFY helped to review and discuss the manuscript. All authors read and approved the final manuscript.

Disclosure

The authors report no conflicts of interest in this work.

ORCID iDs

Zaixing Yang b https://orcid.org/0000-0002-9040-8805 Fengyun Wang b https://orcid.org/0000-0002-5558-423X

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