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Self-powered UV photodetector based on heterostructured TiO_2 nanowire arrays and polyaniline nanoflower arrays

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ABSTRACT

A novel self-powered ultraviolet (UV) photodetector with low cost and large area was successfully constructed which was composed of heterostructured arrays of TiO_2 nanowires (NWs)/polyaniline nanoflowers (PANI NFs)/TiO_2 NWs. The heterostructured arrays of TiO_2 NWs/PANI NFs/TiO_2 NWs were prepared by combining the hydrothermal and in-situ multiple wet chemical deposition methods. The control methods for the morphology and thickness of PANI on TiO_2 NW array were systematically investigated, and their application in UV photodetector was discussed. The results showed that PANI NFs on TiO_2 NW array could be obtained by multiple deposition method, and the thickness of PANI NF layer can be adjusted. Furthermore, compared with bare TiO_2 NW array, the sensitivity and photocurrent of the UV photodetectors based on TiO_2 NWs/PANI NFs/TiO_2 NWs heterostructured arrays were both improved greatly at 0 V bias due to the two heterojunctions of n-type TiO_2 NWs and p-type PANI NFs, and the intensity of photocurrent could be improved with the thickness of PANI layer increasing.

1. Introduction

As important members of the optoelectronic device family, ultraviolet (UV) photodetectors have attracted considerable attention recently due to their applications in scientific, military, and commercial applications, for example, UV astronomy, missile early warning, UV imaging, flame detection, environmental and biological research, etc [1–4]. Generally, most of the traditional photodetectors need an external power sources, such as batteries and other energy storage/supply systems, which not only largely increase the system size but also greatly limit their mobility and independence for applications [5–10]. For a large-area nanosystem that contain huge numbers of small UV photodetectors, energy supply will be one of the main challenges. In fact, the purpose of using external power sources is to provide potential difference as driving force to restrain the recombination of the photogenerated electron–hole pairs and generate photocurrent. In terms of the charge separation features of the interface, the self-powered photodetectors have basically three structure types: p–n junction type [11–14], Schottky junction type [5,15,16] and photoelectrochemical type [17,18]. Self-powered photodetectors based on p–n junctions have particularly received a great deal of attention due to their ability to control the directional movement of the photogenerated electrons and causes the generation of photocurrent. So far, great effort has been made to improve the performance of the self-powered p–n junction type photodetectors. For example, Yang et al. [11] fabricated a UV photodetector composed of ZnO NWs/polyaniline nanofibers p–n and PANI nanofibers/$ZnGa_2O_4$ film type-II heterojunctions. Though the UV photodetectors could generate opposite photocurrent when illuminated at different wavelengths, the highest photocurrent value was only in the region of 10^{-7} A at 0 V bias. Our group [12] also reported a self-powered UV photodetector driven only by opposite ZnO/PANI heterojunctions, and showed good sensitivity to UV light at a bias of 0 V. However, it can not work well in acid environment and the PANI layer can not be prepared by in-situ deposition method, because the ZnO layer can be dissolved in acid solution. Thus, it can be seen that fabrication of high performance and self-powered UV photodetectors still remains a challenge.

In recent years, UV photodetectors based on semiconductor nanomaterials, such as TiO_2 [17–19], ZnO [20–23], SnO_2 [7,24], ZnS [6,25], BiOBr [26], GaN [8,27] and Ga_2O_3 [28], etc, as building blocks have been investigated. In particular, nanostructural TiO_2 has been intensively studied as functional parts in UV photodetectors because of its low cost, abundance, non-toxicity, structural stability and good optoelectronic properties [29–31].

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Hussain et al. reported a solar-blind flexible ultraviolet photodetector using nanocomposite film of plasma polymerized aniline-titanium dioxide [29]. Furthermore, one-dimensional single-crystalline TiO_2 has been intensively investigated due to the greatly enhanced electrochemical properties and large specific surface area. Cao et al. reported a UV sensor based on TiO_2 nanorod arrays [19]. Han et al. reported a self-powered, visual and self-recovered UV photodetector by combining Pt-modified TiO_2 nanotubes and Prussian blue (PB)-modified ITO, in which the existence of UV could be judged easily by naked eye with the aid of PB for electrochromic display [17]. Yang et al. reported an UV photoresponse based on TiO_2-PANI core–shell nanofibers, and its photocurrent was about 1.9 μA at 0.01 V bias in an environment without O_2 [32]. However, self-powered UV photodetectors with a high tolerance of acid conditions based on TiO_2 NWs and PANI NFs heterostructured arrays have not been reported. Particularly, low cost and convenient preparation of large-area TiO_2 NWs and PANI NFs heterostructured arrays have not been reported.

Herein, we report a low cost and simple method to fabricate acid tolerant and self-powered UV photodetectors based on heterostructured arrays of TiO_2 NWs/PANI NFs/TiO_2 NWs made by the combination of the hydrothermal and in-situ multiple wet chemical deposition methods. They can work without any bias voltage due to the build-in electric field formed by two heterojunctions. Scheme 1 shows a schematic illustration of the fabrication of TiO_2 NWs/PANI NFs/TiO_2 NWs heterostructured arrays. Firstly, highly oriented n type TiO_2 NW array was grown on fluorine doped tin oxide (FTO) glass substrate by the hydrothermal method. Then, p-type PANI was deposited on as-grown TiO_2 NW array by in-situ wet chemical deposition method at about 0–5 °C. In order to control the thickness and morphology of PANI layer, the reaction solution was changed to fresh solution per hour for depositing multiple times. After that, another as-grown TiO_2 NW array was covered on TiO_2 NWs/PANI NFs heterostructured arrays face to face to obtain the heterostructured arrays of TiO_2 NWs/PANI NFs/TiO_2 NWs.

2. Experimental

2.1. Materials

Aniline(C_6H_7N, 99+%), ammonium peroxyd sulfate (APS, 98%) and poly(styrene sulfonic acid) sodium salt(PSS, M.W. 70000) were purchased from Alfa Aesar. Titanium butoxide($[CH_3(CH_2)_3O]_4Ti$, 98%) was purchased from Tianjin Fuchen Chemical Reagents Factory. Hydrochloric acid (analytical grade) was purchased from Guangzhou Chemical Reagent No. 2 Factory. Absolute ethanol (analytical grade) was purchased from Tianjin Yongda Chemical Reagent Co. Ltd. FTO substrates were purchased from Nippon Sheet Glass Co. Ltd.

2.2. Preparation of TiO_2 NW array

TiO_2 NW array was prepared by growing on FTO substrate with a hydrothermal method [33]. Deionized water (25 mL) was mixed with hydrochloric acid (25 mL, 36.5–38 wt%) and stirred for 3 min before titanium butoxide (0.70 mL) was added. After stirring for another 5 min, a piece of FTO substrate (ultrasonically cleaned for 30 min in acetone, ethanol and deionized water, respectively), was placed at an angle against the wall of the Teflon-liner stainless steel autoclave with the conducting side facing down. The autoclave was sealed and put in an oven at a temperature of 150 °C for 20 h. Then the autoclave was taken out from the oven and cooled to room temperature. After that, the sample was rinsed with deionized water.

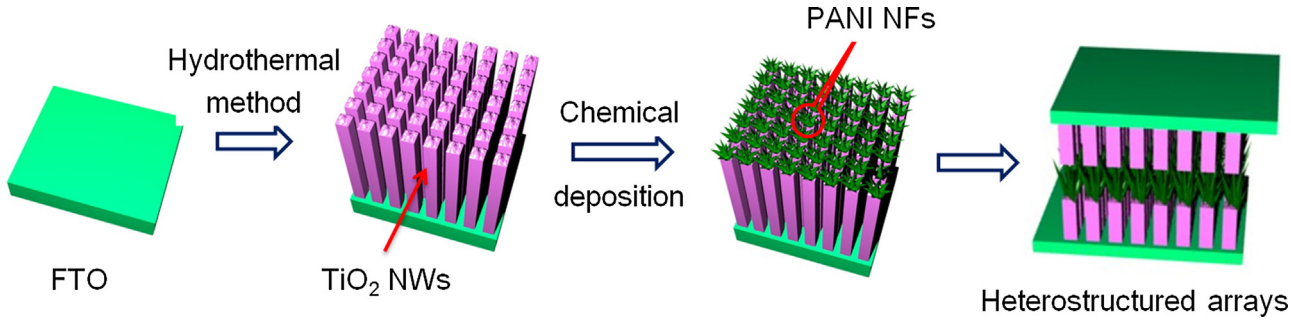
2.3. Preparation of TiO_2 NWs/PANI NFs heterostructured arrays

The TiO_2 NWs/PANI NFs heterostructured arrays were prepared by in-situ wet chemical deposition method. Typically, 0.16 mL aniline was dissolved in 20 ml 1 mol/L HCl solution under stirring, and then 0.5 mL 0.1 mol/L ammonium persulfate (APS) solution was dissolved in the mixture of aniline and HCl solution under stirring. The as-grown TiO_2 NW array was put in the bottom of the mixture with face up immediately. Finally, the reaction mixture was placed into a freezer to keep the reaction temperature at about 0–5 °C. After reacting for desired times, the sample was taken out and rinsed with deionized water, and dried in air. The TiO_2 NWs/PANI NFs heterostructured arrays were finally obtained.

In order to control the thickness and morphology of PANI, different reaction times and methods were studied. On the one hand, with the same reaction solution and temperature, the reaction was carried out for 1 h, 6 h and 24 h, respectively. On the other hand, PANI was deposited on TiO_2 NW array with above method for 1 h, and then the reaction solution was changed to fresh one depositing for another 1 h. The procedures were repeated different times, and the thickness and morphology of PANI on TiO_2 NW array were observed.

2.4. Fabrication of the self-powered UV photodetectors

The TiO_2 NW array and TiO_2 NWs/PANI NFs heterostructured arrays on FTO substrate were functionalized by immersing in 50 mg ml^{-1} PSS solution for 12 h, washed with distilled water and dried at room temperature. After that, the functional TiO_2 NW array and TiO_2 NWs/PANI NFs heterostructured arrays on FTO substrate were put together face to face and clipped tightly, and the multilayered device of FTO/TiO_2 NWs array/PANI NFs array/TiO_2 NWs array/FTO was obtained. The corresponding UV photodetector device is shown in Scheme 1. A CHI660D electrochemical workstation was used to examine the *I–V* curves and *I–t* curves of



Scheme 1. Schematic illustration of the fabrication of TiO_2 NWs/PANI NFs/TiO_2 NWs heterostructured arrays.