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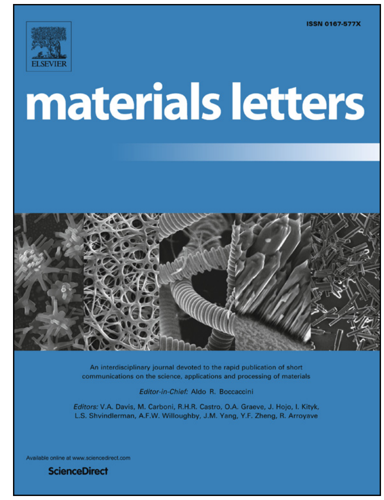

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Minimal layer graphene/TiO_2 nanotube membranes used for enhancement of UV photodetectors

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Abstract. Vertically aligned titanium dioxide (TiO_2) nanotubes (NTs) and graphene/TiO_2 NTs were fabricated on transparent substrate by anodization of Ti foil. TiO_2 NTs in anatase phase with and without graphene films coated on their surface were confirmed by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and Raman spectra. Enhancement of photocurrent and good responsivity of the graphene/TiO_2 NT devices were observed as compared with pure-TiO_2 NT devices. At the interface, the electrons will transfer from TiO_2 to graphene due to the difference in energy levels of the two materials. The heterojunction was formed there, and the photo-excited electron-hole pairs could hinder the charge recombination. The graphene/TiO_2 NT devices have high potential for ultraviolet (UV) photodetectors with the possibility to fine-tune properties, and it is worth of further investigation.

1. Introduction

Recently, special interest has been focused on titanium dioxide (TiO_2) nanostructures such as nanowires, nanorods, and nanotubes. These structures have a large surface area to volume ratio, long term stability, non-toxicity, low cost, and broad functionality which generating great interest in potential applications. Among these nanostructures, TiO_2 nanotubes (NTs) are a prominent material due to their vertically oriented and highly ordered structure. TiO_2 NT arrays have been extensively studied for their applications in sensors for hydrogen, oxygen, humidity, and glucose [1-5]. It found that TiO_2 NT-based sensors usually exhibit high performance with low detection limit, high stability, good reproducibility, and fast response. One of the important applications for TiO_2 NTs is for efficient ultraviolet (UV) photo-detection which is crucial for space communication, ozone layer monitoring, flame sensing, and so on. TiO_2 is a wide band gap 3.2 eV for anatase phase and 3.0 eV for rutile phase [6]. Due to its wide band gap, it is only sensitive to the light with wavelengths below 380 nm which belong to the UV region [7]. This supports that TiO_2 nanostructures are suitable for UV detection against a background with infrared and visible light. Due to the large surface to volume ratio and exceptional properties of TiO_2 nanostructures, many researchers are interested in UV photodetectors based on TiO_2 nanostructures [1]. Further, it has also been suggested that the heterojunction based on TiO_2 NTs can improve the performance of photodetectors as compared to pure TiO_2 NTs [8-11].

Graphene has increasingly attracted an attention for different applications in recent years due to its high surface area, transparency, high carrier mobility, mechanical flexibility, good interfacial contact with adsorbents and so forth [12-16]. Therefore, graphene is widely used in optoelectronic and photonic devices where graphene based devices proved effective in such areas as photoelectric, photo thermoelectric, etc. In terms of electromechanical properties, graphene makes a great contribution to the enhancement of the performance of the devices. Therefore, it is a preferable material for improvement of the heterojunction-based photodetectors in a broad-wavelength range. At the interface of the heterojunction-based devices, graphene/TiO_2 devices, electrons transfer from TiO_2 to graphene because of the difference in energy levels of the two materials. Consequently, the heterojunction is formed at the interface, and it hinders the charge recombination of the photo-excited electron-hole pairs. The results lead many researchers to further investigation of graphene-TiO_2 nanostructure-based UV photodetectors.

Generally, there are three methods used to fabricate TiO_2 NTs; template synthesis [16], hydrothermal methods [17-18], and electrochemical synthesis (anodization of Ti foil). Of all the methods, electrochemical anodization is the most popular method for synthesis of TiO_2 nanostructures due to uniformity in diameter, high quality, and superior alignment of the tubes. Free standing TiO_2 NTs were easily obtained by this method. The free standing TiO_2 nanotubes would be flexible allowing for a variety of applications and it can be attached onto foreign substrates [19].

In this work, we report the fabrication of a high density of TiO_2 NTs that were fabricated by anodization of Ti foils. Subsequently, TiO_2 membranes were transferred onto ITO substrates. This method allows film production on other substrates. The UV photodetectors based on TiO_2 NTs on transparent substrate coated with a few layers of graphene film will be reported in this paper. However, to our best knowledge, there are few reports about the graphene/TiO_2 NTs on transparent glass substrate. We found that the UV photodetector devices are highly sensitive to 365 nm UV light and also the graphene/TiO_2 NT devices can enhance the responsivity and photocurrent gain as compared to pristine-TiO_2 NTs devices.

2. Experimental details

TiO_2 NTs were grown on a Ti foil by anodization. The anodization process was divided into three parts. The 1st anodizing, a cleaned Ti foil was anodized in a mixture of 0.3 wt. % NH_4F, 97.7 wt. % ethylene glycol and 2 wt. %