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Original Research

Au NPs decorated TiO_2 nanotubes array candidate for UV photodetectors

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ABSTRACT

This work reports the Au nanoparticles (NPs) deposited on TiO_2 nanotubes (NTs) which were successfully synthesized by a simple two-step anodization method. This fabrication process is notable for a simple and inexpensive method for obtaining pure TiO_2 NTs and Au NPs deposited TiO_2 NTs. The prepared samples were characterized by field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and I-V curve. We found that the size of Au NPs can be controlled by changing the bias voltage during the deposition. The photodetectors of Au NPs/TiO_2 devices showed good wavelength selectivity with high photocurrent as compared to pure TiO_2 NTs devices. Subsequently, Au NPs deposited on TiO_2 NTs at bias voltage of 70 V was potentially used in fabrication of UV photodetector. At this applied voltage, a high density of Au NPs was uniformly deposited on TiO_2 NTs. As a result, it enables a high photocurrent and great responsivity in UV region. It is suggested that the Au NPs deposited TiO_2 NTs device shows good promise for UV photodetectors with possibility to fine-tune properties in both UV and visible regions and is worthy of further investigation.

1. Introduction

Titanium dioxide (TiO_2) is a n-type semiconductor. There has been much interest in its basic characteristics and for applications in gas sensor, dye sensitized solar cells, hydrogen generation by water photoelectrolysis, photocatalysts, and so forth [1–3]. This is due to its outstanding physical and chemical properties. Recently, special interest has been focused on TiO_2 nanostructures such as nanowires, nanorods, or nanotubes. These structures have a large surface area to volume ratio, long term stability, non-toxicity, low cost, easy preparation and broad functionality. Among these nanostructures, TiO_2 nanotubes (TiO_2 NTs) are a popular material due to its vertically oriented, highly ordered structure. In addition, it can be easily prepared by the anodization of Ti foil [3–11]. TiO_2 NTs have been extensively studied for their applications in sensors for hydrogen, oxygen, humidity, and glucose [9–11]. It is found that the TiO_2 NTs based sensors usually exhibit high performance with low detection limit, high stability, good reproducibility, and fast response. TiO_2 is a wide band gap 3.2 eV for anatase phase and 3.0 eV for rutile phase, [11]. Due to its wide band gap, it is only sensitive to the light wavelengths below 380 nm which belong to the UV region [12]. However, there are some problems for TiO_2 applications. One problem is the fast recombination of photo-induced electrons and holes, (charge carriers) in TiO_2. To solve this problem, various attempts have been studied for surface modification of TiO_2 with noble metals. These metals can greatly enhance the surface activity due to the rapid transfer of photoelectrons. Recently, gold nanoparticles (Au NPs) supported on TiO_2 have raised interest because of the reduction of electron-hole recombination in Au-TiO_2 composite. Additionally, the presence of Au NPs on the surface of TiO_2 can increase the electron-hole pair separation. Up to now, several techniques have been reported on the deposition of Au NPs on the surface of TiO_2 nanostructures such as photoreduction, ultrasonic assistance reduction, thermal evaporation, sol-gel, electrochemical methods, deposition-precipitation RF-sputtering, dip coating, spin-coating, and other methods [13–21]. Of the previously mentioned methods are expensive and complex procedures, in addition metal cluster of non-uniform size and shape are difficult to control. In this work, we report on the innovative and facile fabrication of Au NPs decorated on the surface and the walls of TiO_2 NTs by using the two-step anodization method. To our knowledge, Au NPs anodized on the surface of TiO_2 has been rarely reported. It can easily, quickly, and inexpensively obtain Au NPs on TiO_2 NTs. Furthermore, the size of Au NPs can be controlled by changing the time, concentration of precursor $HAuCl_4$ and bias voltage of deposition. Pure TiO_2 NTs and Au NPs decorated on TiO_2 NTs were successfully synthesized by two-step anodization method, and subsequently it was used in the fabrication of a highly sensitive UV

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photodetector device. We found that the UV photodetector device is highly sensitive to 365 nm UV light, and the Au NPs on TiO_2 NTs devices can enhance the responsivity as compared to pure TiO_2 NTs devices. The research of Au NPs decorated TiO_2 NTs for UV photodetector applications are seldom reported. There are several reported for applications in visible light photocatalysis, efficient visible light hydrogen generation, photoelectrochemical water splitting, surface enhanced Raman scattering, and so on [13–21] due to the localization surface plasmonic resonant effect of Au NPs.

2. Experimental

TiO_2 NTs with ultrahigh aspect ratio were grown on a Ti foil by electrochemical anodization method. Ti foils (0.25 mm in thickness, 99.7% in purity, Sigma Aldrich) was cut into a 1.0 × 1.5 cm piece. Then, it was cleaned by acetone, ethanol and deionized water, respectively, each step for 5 min in ultrasonic bath and dried with the flowing nitrogen gas. The anodization of Ti foil was performed at room temperature in a two -electrode electrochemical cell in which the graphite sheets and Ti foils were used as the cathode and anode, respectively. The anodization process was divided into two steps. First step for anodizing; the cleaned Ti foil was anodized in mixture of 0.3 wt% NH_4F, 87.7 wt% ethylene glycol and 12 wt% deionized water, for 2 h under a constant voltage of 50 V. After anodizing the sample was cleaned with DI water, acetone, and ethanol, respectively, for 10 min in each process, and then the resulting oxide layers were annealed at temperature of 450 °C for 2 h. In this work, the structure and thickness of TiO_2 NTs was controlled by the anodization process. Second step, $HAuCl_4{\cdot}3H_2O$ (Sigma Aldrich) solution in DI water was used as the Au NPs precursor. The annealed TiO_2 were again anodized [graphite sheets (anode) and TiO_2 nanotubes (cathode)], in an aqueous solution of $HAuCl_4{\cdot}3H_2O$ (0.1 mM in DI water) at different voltages (3–140 V) for

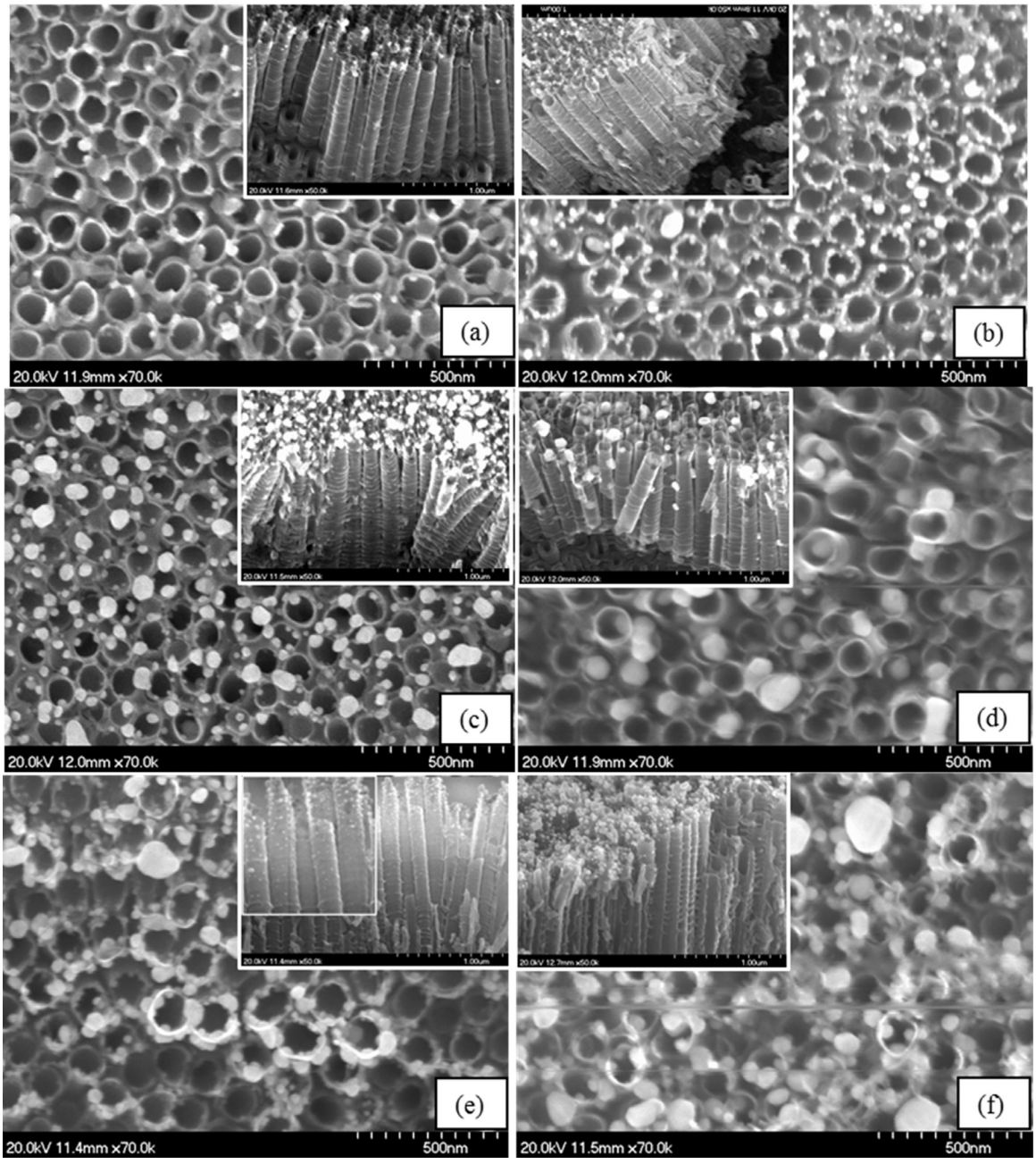

Fig. 1. FE-SEM images of the Au NPs decorated TiO_2 NTs at different applied bias voltages, top views and cross section (inset) at 3 V as shown in Fig. 1(a), at 5 V (b), 10 V (c), 40 V (d), 70 V (e), and 140 V (f), respectively.