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Enhanced field emission from titanium dioxide nanotube arrays decorated with graphene sheets and silver nanoparticles

Da Lei [a, *], Qiqige Menggen [a, **], Liya Du [a], Gus Te [b], Tao Jin [a], Yingbiao Zhi [a], Jingping Liu [a], Xiaoyu Fan [a]

[a] Ordos College of Inner Mongolia University, Inner Mongolia University, Ordos 017000, People's Republic of China
[b] School of Physics, Inner Mongolia Normal University, Hohhot 010022, People's Republic of China

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ABSTRACT

The TiO_2 nanotube arrays decorated with graphene sheets (GSs) and Ag nanoparticles were prepared on Ti foils and field emission performances were explored in detail. The conventional electrochemical anodization process was used to synthesize TiO_2 nanotube arrays on Ti foils. The GSs and Ag nanoparticles were deposited on as-prepared TiO_2 nanotube arrays by electrophoretic deposition process and chemical deposition. The field emission properties of samples were dramatically improved after depositing GSs and Ag nanoparticles on TiO_2 nanotube arrays. Compared with pristine TiO_2 nanotube arrays, the TiO_2 nanotube arrays decorated with GSs and Ag nanoparticles composite film show good field emission stability and a higher field enhancement factor of 3450. The turn-on and threshold fields can be decreased from 6.63 to 2.68 V/μm and from 15.28 to 6.13 V/μm, respectively. Quantitative discussion about the hybrid hetero-nanostructure field emission improvement is presented. The good field emission properties of the decorated TiO_2 make it a promising candidate for applying in high-performance emission device.

1. Introduction

Due to their atom-thick sharp edges, high aspect ratio, large electrical mobility, excellent electrical conductivity, and good mechanical properties, graphenes (GSs) may be considered as a potential two-dimensional field emission (FE) material [1–6]. Many of efforts have been devoted to exploiting the sharp edges of graphenes for efficient field emission. For example, Yang et al. [7] and Lin et al. [8] reported the enhanced field emissions from graphene supported by ZnO nanowires and nanorods, and that these hybrid structures exhibited the low turn-on fields (E_{to}) 5.4 and 3.7 V/μm, respectively. Wu et al. constructed the patterned zinc oxide-adhering graphene cathodes with E_{to} of 2.7 V/μm, low threshold field (E_{th}) of 5.1 V/μm and a large field enhancement factor of 5493 [9]. Chen et al. [10] fabricated Ag decorated graphene/carbon nanotube hybrids field emitter with even low E_{to} of 0.76 V/μm.

The semiconducting material TiO_2 with a wide band gap of 3.2 eV has been extensively studied especially in field emission devices construction [11,12]. One-dimensional TiO_2 nanostructures have drawn much attention [13–15] in recent years because they have low work function of 4.4 eV, small curvature radius, excellent structural controllability, and chemical and thermal stabilities. Many approaches such as hydrothermal method [16], chemical vapor deposition [17], and electrochemical anodization [18] have been used to prepare one-dimensional TiO_2 nanostructures. Among these approaches, electrochemical anodization is a simple and cost-effective method to synthesize various highly ordered TiO_2 nanotubes. However, well-aligned TiO_2 nanotubes (TNTs) have poor field emission properties such as the high turn-on fields (E_{on}), the high threshold fields (E_{th}) and the low field enhancement factor (β). To achieve a high emission performance from TiO_2 arrays, various approaches have been applied in the previous reports [19–23]. Wang et al. [19] reported that Fe doping into TiO_2 nanotube arrays could improve field mission properties. Liu et al. [20] prepared nitrogen implanted nanotube arrays and obtained a lower turn-on electric field of 11.2 V/μm. Wang and his coworkers [21] suggested that the turn-on electric fields were reduced from 21.9 to 5 V/μm with the carbon doped TiO_2. Moreover, hydrogenated TiO_2 nanotubes [22] and aggregated TiO_2 nanotubes [23] were prepared by

* Corresponding author.
** Corresponding author.
E-mail addresses: leida126@126.com (D. Lei), menggen1858@126.com (Q. Menggen).

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Zhu and Huang et al. The turn-on electric field of hydrogenated TiO_2 nanotubes was reduced from 32.75 to 4.12 V/μm. The aggregated TiO_2 nanotubes present low turn-on electric field of 4.87 V/μm and high field enhancement factor of 1486.

Although the methods mentioned above are quite efficient to improve the field emission performances of TiO_2 nanotubes based emitters. The TiO_2 nanotubes and its hybrid nanostructures don't satisfy the requirements of practical applications in field emission yet. A great deal of efforts still should be done to enhance field emission performances, especially fabricating hybrid nanostructure to magnify the field enhancement factor, and to increase field emission sites and so on. In this study, the TiO_2 nanotube arrays covered with GSs and Ag nanoparticles (Ag/GSs/TiO_2 NTAs) were prepared on Ti foils by electrophoretic deposition and combined with chemical deposition process. Compared with pristine TiO_2 nanotube arrays (TiO_2 NTAs), the field emission performances of the TiO_2 NTAs were significantly improved after decorating with the GSs and Ag nanoparticles. The detail field emission performances for GSs and Ag nanoparticles deposited on TiO_2 arrays are explored and discussed.

2. Experimental

Mainly three steps including synthesizing pristine TiO_2 NTAs on Ti foils, decorating TiO_2 NTAs with GSs and Ag nanoparticles, and the annealing process for the preparation of the Ag/GSs/TiO_2 NTAs on Ti foils were involved in our experiments process. Firstly, the TiO_2 NTAs covered on Ti foils were synthesized by conventional electrochemical anodization process. To remove impurities on the surface of Ti foils, Ti foils (0.3 mm thick, 1 cm × 2 cm, 99.7%) were cleaned with acetone, ethanol and deionized water, respectively. A mixture of 40% hydrofluoric acid solution and 36% hydrochloric acid (their weight ratio is 1:8) was used to remove oxides. After making the surfaces of cleaned Ti foils smooth for 40s and then the foils were rinsed in deionized water for several times. And then one of the cleaned foil was anodized in a 0.5 wt.% HF solution with another cleaned Ti foil acting as a counter electrode at 15 V for 3 h. The anodized Ti foil was washed for several times with deionized water, dried with nitrogen and heated in atmosphere at 500 °C for 3 h. Secondly, the electrophoretic deposition (EPD) and chemical deposition methods were used to decorate the TiO_2 NTAs with GSs and Ag nanoparticles, respectively. A multi-layer GSs with a size of 20 μm, aspect ratio of 500, and 97% purity prepared by chemical vapor deposition (CVD) were used in this EDP process. The 5 mg GSs and 5 mg $Mg(NO_3)_2 \cdot 6H_2O$ were added into 200 ml of ethanol to obtain suspension and then the suspension was put into a sonic bath at room temperature for 3 h. The as-prepared pristine TiO_2 NTAs on Ti foil was used as cathode and a cleaned Ti foil was used as the anode, respectively. The cathode and anode foils were submerged into electrophoretic suspension under an applied DC voltage of 200 V for 6 min and the distance between the two electrodes was kept at 1.0 cm. After finishing EDP, the sample was slowly picked up from the solution and washed for many times with deionized water. In order to cover Ag nanoparticles on the surface of the sample, the sample was immerged into 0.5 M $AgNO_3$ solution for 10 min for electrochemical deposition. Then the sample was rinsed with distilled water for many times and dried with nitrogen. Finally, the sample was annealed in ambient N_2 at 300 °C for 2 h to induce strong adhesion with substrate.

The field emission scanning electron microscope (FESEM, SU8010) was used to character the morphologies of the pristine TiO_2 NTAs and the GSs/Ag/TiO_2 NTAs. The possible phase and crystal structure of the TiO_2 NTAs decorated with GSs and Ag nanoparticles on Ti foil were analyzed by X-ray diffraction (XRD). The Raman spectra of the samples were determined by a laser Raman spectrophotometer with an excitation wavelength of 537 nm. For field emission test, the Ag/GSs/TiO_2 NTAs on Ti foil were used as the cathodes and the silver plates act as the anodes. The mechanical and turbo molecular pumps (F-400/3600 type) were used for vacuum pumping, and field emission characteristics of the cathodes were measured in a vacuum chamber with a Keithley 2410 power supply in diode configuration maintained at a pressure of 10^{-4} Pa and room temperature.

3. Results and discussion

The top-view FESEM images of the pristine TiO_2 NTAs are presented in Fig. 1. The cross-sectional view is shown in the inset of Fig. 1. From Fig. 1, it exhibits that the height, thickness and the average outside diameter of TiO_2 nanotube are about 300 nm, 4 nm and 100 nm, respectively. The TiO_2 nanotubes are vertically aligned deposited on Ti substrates. The TiO_2NTAs possess a lower density about of $1 \times 10^{10}/cm^2$ compared with the previous reporters [19–23]. The top edges of TiO_2 nanotubes is not planar (always have some bulges), which is in favour of the field emission from TiO_2 NTAs.

The FESEM images of surface morphology for Ag/GSs/TiO_2 NTAs are shown in Fig. 2 and the inset is the enlarged image. From images, it can be seen that GSs sheets cover on the top of TiO_2 nanotube and densely distribute and almost vertical stand on the TiO_2 arrays surface. After deposition, the TiO_2 NTAs are almost fully and uniformly covered with GSs and Ag nanoparticles to form a hybrid nanostructure of TiO_2 NTAs.

The high resolution FESEM images of Ag/GSs/TiO_2 NTAs on Ti substrate are shown in Fig. 3. Fig. 3 (a) showed the surface morphology of whole hybrid nanostructure of Ag/GSs/TiO_2 NTAs. Fig. 3 (b) and (c) showed the even high resolution FESEM images of the exposed TiO_2 nanotubes and GSs in this hybrid nanostructure, respectively. It can be seen that the GSs surfaces and exposed TiO_2 nanotubes top are uniformly covered by Ag nanoparticles with a size range of 4–15 nm. Moreover, some Ag nanoparticles are also deposited at the boundary regions of GSs edges and the exposed TiO_2 nanotubes. The thickness of TiO_2 nanotubes top wall decorated with Ag nanoparticles is about 10–20 nm and the average inner diameter of TiO_2 nanotube top is about 80 nm.

It is well known that the surface morphology is an important factor for electron field emission properties. The field enhancement factor is related to the geometry structure and the surface

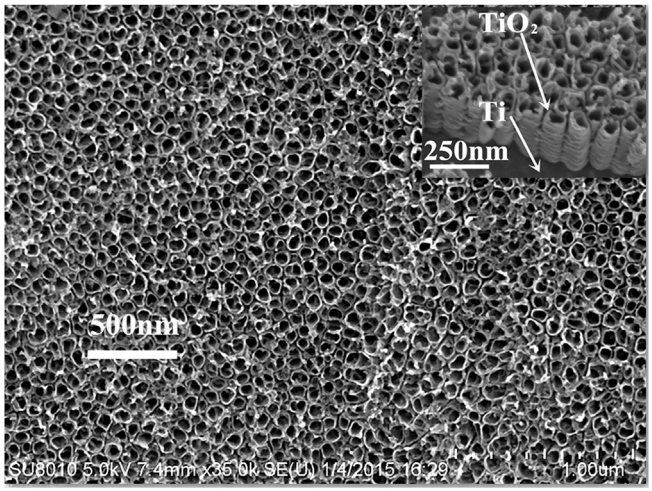

Fig. 1. The FESEM image of the pristine TiO_2 NTAs.