



Low temperature synthesis of reduced titanium oxide nanotube arrays: Crystal structure transformation and enhanced field emission



Wei-Dong Zhu, Cheng-Wei Wang^{*}, Jian-Biao Chen, Xu-qiang Zhang

Key Laboratory of Atomic and Molecular Physics & Functional Materials of Gansu Province, College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou 730070, China

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ABSTRACT

There are considerable interests in the synthesis of nanostructured reduced titanium oxides because of their attractive properties. In this study, a facile and low-temperature reduction strategy using NaBH_4 to yield reduced titanium oxide nanotube arrays is proposed, which significantly lowers the requirements of instruments and costing compared to the conventional strategies. Moreover, this reduction strategy results in the homogeneous crystal structure transformation of parent tetragonal anatase TiO_2 nanotube arrays (TNAs) to orthorhombic $\text{Ti}_{2.5}\text{O}_3$ nanotube arrays with retained morphology, which show sharply improved conductivity and decreased work function. Notably, compared to the pristine TNAs precursor, the obtained $\text{Ti}_{2.5}\text{O}_3$ nanotube arrays show greatly enhanced field emission (FE) properties including substantially decreased turn-on field from $15.76 \text{ V}/\mu\text{m}$ to $1.51 \text{ V}/\mu\text{m}$, a high current density of $5.00 \text{ mA}/\text{cm}^2$ at an applied field of $4.03 \text{ V}/\mu\text{m}$, and an excellent FE stability.

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1. Introduction

One-dimensional (1D) nanomaterials with excellent physical and chemical properties are useful in numerous applications, especially hailed as charming candidates for field emitter due to their sharp tips and high aspect ratio [1–4]. As one of the most important 1D nanomaterials, carbon nanotubes (CNTs) have been the subject of studies for field emission (FE) for many years, and diverse laboratory works and prototype devices have been reported [4–6]. However, besides low turn-on field and high emission current, which have been achieved in CNTs, outstanding FE stability is equally vital in the operation of field emitters. Nevertheless, CNTs as field emitters are easily subjected to rapid degradation of FE current by oxidation and heating effects in the interface of CNTs film/conductive substrate [7], which have hindered their practical applications in FE [8]. Thus, a wide variety of 1D metal oxide nanomaterials, including ZnO [9], SnO_2 [10], Fe_2O_3 [11], and TiO_2 [12–14] with various morphologies such as nanotube, nanorod and nanowire, have been explored to expand the pool of candidates for field emitters due to their superior antioxidation ability which can operate under unfavorable environment with relatively high oxygen partial pressure in their

applications. Among various 1D metal oxide nanomaterials, TiO_2 nanotube arrays (TNAs) fabricated by anodization have attracted considerable attention due to their unique properties of inherent electrical contact with Ti substrate, a lower work function (4.5 eV) and controllable nanomorphology. However, TNAs as emitter cannot satisfy all requirements for practical applications until now. There are still some common obstacles to overcome, for instance, the values of turn-on field are somewhat inconsistent and the emission current density is relatively low resulting from their low conductivity and high electron affinity.

Many efforts have been focused on enhancing the FE performances of TNAs by element doping such as C [12], Fe [15], N [16], since doping creates additional energy levels within the band gap, which can decrease the work function and improve the conductivity of TNAs. However, the solubility of doped ions in TNAs is usually extremely low and doping may cause undesired structures, as well as characterization alteration, so the turn-on field and emission current density of TNAs still remain insufficient compared to CNTs. Recently, reduced titanium oxides have attracted increasing interest in photovoltaics, photocatalysts and fuel cells owing to their additional properties compared with TiO_2 , including narrow band gap and high electrical conductivity which is comparable to that of graphite [17]. Moreover, both theoretical and experimental results indicate that metal oxides in their more-reduced forms tend to have lower work functions than their oxidized forms [18]. So, it is expected that reduction treatment of TNAs can also substantially increase their conductivity and

^{*} Corresponding author. Tel.: +86 18509311337; fax: +86 09317971503.

E-mail addresses: cwwang@nwnu.edu.cn, chengwwang@aliyun.com (C.-W. Wang).

decrease their work function; thus enhance the FE performances of TNAs. Yet the corresponding research, to our knowledge, has not been reported elsewhere.

To obtain reduced TNAs, various methods including thermal reduction [19,20], photochemical reduction with UV laser irradiation [21], and laser ablation [22,23] have been reported. However, these methods in turn cause damage of nanotubes or compositional inhomogeneity [19,23], making them difficult to obtain high-quality nanostructures. Recently, nanosized reduced TiO_2 were successfully synthesized using a strong reducing agent CaH_2 at a low temperature of 350°C with the same morphology as that of the parent TiO_2 [24]. This reduction method is excellent for creating novel nanomaterials and can be used to reduce TNAs in principle; however, exorbitant chemical, time-consuming process, and the necessity of vacuum heating are inevitable [25]. Therefore, an alternative method needs to be developed to synthesize reduced TNAs field emitter.

Considering these factors mentioned above, in this study, a facile and low-temperature way to synthesize reduced TNAs using NaBH_4 is reported and the FE properties of the reduced TNAs are investigated. This reduction strategy, significantly reducing the requirements of instruments and costing compared to the conventional strategies, renders the homogeneous crystal structure transformation of parent tetragonal anatase TiO_2 to orthorhombic $\text{Ti}_{2.5}\text{O}_3$ nanotube arrays with retained morphology. More importantly, the obtained $\text{Ti}_{2.5}\text{O}_3$ nanotube arrays possess sharply improved conductivity and decreased work function, thus improved FE performances. Additionally, the FE stability of the prepared $\text{Ti}_{2.5}\text{O}_3$ nanotube arrays is investigated in detail and a possible mechanism is given to understand the excellent stability, which is conducive to their practical applications.

2. Experimental

Ti foils (99.9% purity) were degreased ultrasonically in acetone and ethanol for 15 min, respectively, followed by eroding in a mixture of HF solution and hydrochloric acid [$V(\text{HF}), V(\text{HCl}) = 1, 8$] for 15 s until a mirror finish was exposed. After rinsing with deionized water and drying in a nitrogen stream, they were anodized in an ethylene glycol solution containing NH_4F (0.25 wt.%) and HF (0.05 wt.%) at 40 V at room temperature for 40 min, followed by annealing in air at 450°C for 1.5 h, labeled as pristine TNAs. The pristine TNAs were embedded with 1 g of NaBH_4 in a glovebox (<1 ppm $\text{H}_2\text{O}/\text{O}_2$), 0.5 mL absolute alcohol was added into the mixture to guarantee homogeneous mixing. Then, the mixture was heated in Ar at various temperatures ranged from 340 to 400°C for 20 h in a tube furnace. This temperature range was selected to avoid the formation of NaTiO_2 from the reaction of TiO_2 with NaH , which is formed due to the thermal decomposition of NaBH_4 . Finally, the product was washed with pure water and acetone.

The surface morphologies of as-prepared samples were examined by a field emission scanning electron microscopy (FESEM, JSM-6701F, operated at 5 kV). The structure of the nanotubes was analyzed by X-ray diffraction (XRD) using a Rigaku D/max-2400 diffractometer (with $\text{Cu K}\alpha_1$ 0.154056 nm radiation at 40 kV and 150 mA). Micro-Raman measurements were carried out using a Horiba HR800 Raman system at room temperature, and a 632.8 nm line from a He-Ne laser was used as the excitation laser. Electron transport properties of the samples were measured using the two-probe method on a Keithley 4200 SCS at room temperature in ambient air. The reference electrode was connected to the metallic substrate and the working electrode was connected to the TNAs film under the gold contact with the contact area of $6.0 \times 10^{-7} \text{ m}^2$. The FE properties of as-prepared samples were measured with a diode structure in a vacuum chamber at a base

pressure of 9.0×10^{-5} Pa. The vacuum system was consisted of a vacuum chamber, a compound molecular pump with the ultimate pressure of 6.0×10^{-6} Pa, and a mechanical pump. The cathode consisted of samples and a polished copper rod served as the anode that was kept $40 \mu\text{m}$ away from the samples by a mica spacer containing a hole ($\sim 1 \text{ mm}^2$) in the center. To guarantee the outgassing in the small space, we employ a two-layer mica spacer. The bottom one contains a circular hole ($\sim 1 \text{ mm}^2$) in the center and the top one contains a rectangle hole (1 mm in width and 5 mm in length) in the center. The emission current was measured under varying applied voltage (up to 3500 V).

3. Results and discussion

Fig. 1 shows the photograph of the as-prepared samples, it is evident that after the reduction the color of TNAs converted from bluish green to bluish black, finally black, retaining the original shape without any visible cracks and detachment. To investigate the crystal structure and possible phase changes during the reduction, XRD measurement was performed, and the corresponding XRD spectra are shown in Fig. 2. It is clear that pristine TNAs exhibit obvious tetragonal system with anatase TiO_2 phase (tetragonal, $I4_1/amd$) except for the existence of typical diffraction peaks of metallic titanium. The XRD pattern of TNAs reduced at 340°C was almost identical to that of pristine TNAs, however, after reduction at 370°C and 400°C , the corresponding XRD pattern significantly changed; all major peaks of the product were readily assignable to orthorhombic system with $\text{Ti}_{2.5}\text{O}_3$ phase (orthorhombic, $Immm$). Moreover, the intensity of the XRD peaks of $\text{Ti}_{2.5}\text{O}_3$ obtained at 400°C is stronger than that of $\text{Ti}_{2.5}\text{O}_3$ obtained at 370°C , that is to say, $\text{Ti}_{2.5}\text{O}_3$ with higher crystallinity can be obtained at a higher reduction temperature. These results indicate that the TNAs precursor was successfully reduced to be $\text{Ti}_{2.5}\text{O}_3$, and the crystal structure transformed from the tetragonal to the orthorhombic system. Interestingly, possible intermediates, namely, Magnéli phase $\text{Ti}_n\text{O}_{2n-1}$ ($n > 4$), were not observed, and both the crystallinity and the homogeneity of the $\text{Ti}_{2.5}\text{O}_3$ obtained at 400°C seemed high. Since the intermediates are reported to have significantly larger entropies than $\text{Ti}_{2.5}\text{O}_3$ [26], the absence of such entropically favored Magnéli phases means that enthalpy dominated the Gibbs energy of the system [24]. That is to say, the use of the strong reducing agent NaBH_4 not only enhanced the reaction rate but also made the reduction reaction more enthalpically favorable, that is, decreased the amount of intermediates. Therefore, low-temperature reduction of TNAs precursor resulted in such relatively homogeneous $\text{Ti}_{2.5}\text{O}_3$ products, which is an important aspect of this reduction method.

Because the XRD is a bulk analysis technique and cannot reflect the surface properties. So Raman scattering was conducted to examine the surface structure of investigated samples. As shown in

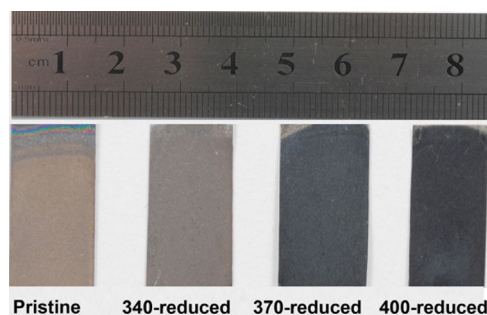


Fig. 1. Photograph of pristine TNAs and reduced TNAs obtained at 340, 370, and 400°C .

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