



Effect of Ti^{n+} defects on electrochemical properties of highly-ordered titania nanotube arrays

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ABSTRACT

In this paper, highly-ordered TiO_2 nanotube (TNT) electrodes fabricated by anodization at 20 V in 0.1 M F^- -based solution were annealed in O_2 , N_2 and CO respectively. The surface properties of the TiO_2 electrodes after annealing treatment by different gases were studied by means of photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical properties of the TNT electrodes were investigated by cyclic voltammetry, steady-state polarization and photocurrent response measurements. The results showed that Ti^{n+} ($n=0-3$) cations and oxygen vacancies existed in the TNT electrode after annealing in CO , leading to a very efficient electron transfer rate of $1.34 \times 10^{-3} \text{ cm/s}$. Steady-state polarization measurement and photocurrent response demonstrated that the electrode potential of oxygen evolution reaction (OER) reduced by 20% and the photocurrent response increased by 50% for CO -annealed TNT electrode compared with O_2 -annealed TNT electrode.

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1. Introduction

Since the early work of Fujishima and Honda [1] demonstrating for the first time hydrogen generation by the photoelectrolysis, many various metal oxides have been proposed for electrodes for the application of photoelectroanalysis and photoelectrocatalysis [2–5]. However, the general conclusion is that titanium dioxide is the most promising material due to its excellent chemical stability and resistance to corrosion.

Among many important requirements for these electrode materials, there are only two that are not fulfilled by TiO_2 . The first one concerns the energy band gap, e.g., of about 3.2 eV, too high to provide a good match between the adsorption of spectrum of the electrode with the solar spectrum. The second factor which limits the application of TiO_2 is its high electrical resistivity. One considerable decrease in the electrical resistivity can be achieved by annealing TiO_2 under reducing atmosphere [6]. The annealing treatment may help to form different point defects, such as oxygen vacancies, titanium interstitial and more complex structures, which will increase the conductivity and have great effect on the properties of the electrode. Houlihan et al. [7]

reported on the photoresponse of ceramic TiO_2 photoanodes reduced in CO/CO_2 atmospheres and attributed the observed changes in the spectral dependence of photocurrent to the different defect states.

Another way which can improve the photoelectrochemical performance of TiO_2 electrode is to optimize its architecture. Recently, nanostructured TiO_2 electrodes, such as nanoparticles film [8,9], non-oriented one dimensional nanoarchitected electrode [10,11] and oriented one dimensional nanotube electrode [12,13] as shown in Fig. 1, have attracted considerable interest due to their enhanced surface area and nanosize effect. Compared with nanoparticles films and non-oriented nanoarchitected electrodes, oriented one dimensional nanotube electrode exhibits unique electrochemical properties because their oriented tunnels provide direct path for electron or ion transmission. The highest hydrogen generation rate has been observed by replacing TiO_2 nanocrystalline films with oriented titania nanotube arrays [14].

Here, we report on the preliminary results on the effect of surface defects modification on the photoelectrochemical properties of oriented titania nanotube (TNT) electrode. The titania nanotube electrode was fabricated by anodization. Three typical gases, oxidizing gas (O_2), inert gas (N_2) and reducing gas (CO), were chosen as the annealing ambient to generate surface defects, the influence of annealing gases on the defects and surface chemistry of TiO_2 nanotube electrode was studied by means of scanning electron microscopy (SEM), photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and photoelectrochemical method. The aim of this paper is to fabricate an oriented titania nanotube electrode that could provide

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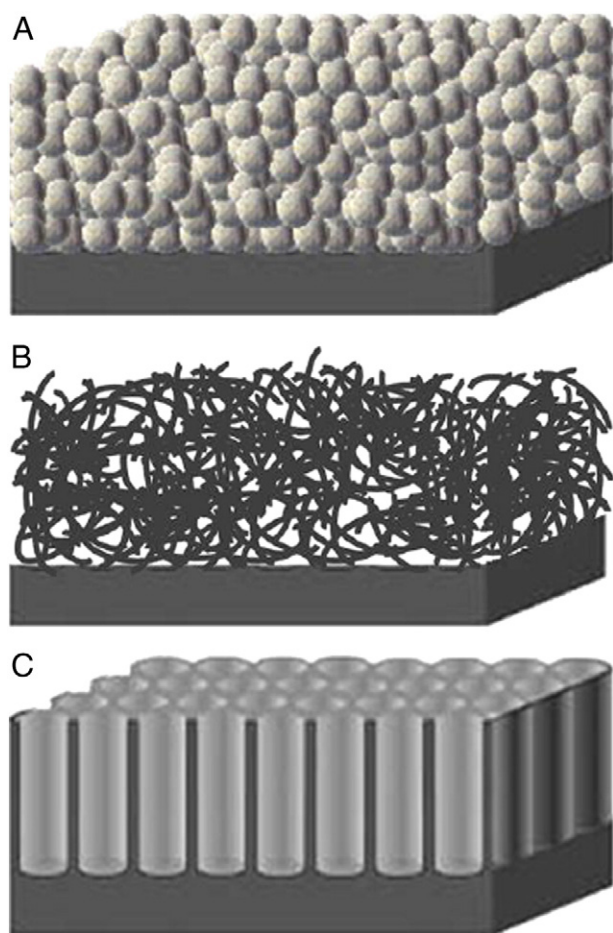


Fig. 1. Different structure of nanomaterial electrode (A) nanoparticle films electrode (B) non-oriented one dimensional nanoarchitected electrode and (C) oriented one dimensional nanotube electrode.

low electrical resistivity combined with an efficient photoelectron-response via the modification of surface defects.

2. Experimental details

Titania nanotube arrays were grown from a starting titanium foil (0.5 mm thick, 99% purity purchased from VWR) by potentiostatic anodization at 20 V in an electrolyte of 0.1 M KF + 1.0 M NaHSO₄ for 2 h using a platinum counter electrode (99% purity VWR). NaOH solution was added to adjust the pH value of electrolyte to 4.0, the anodization process was as same as the reference [15]. The as-anodized TNT were amorphous, then, they were annealed at 500 °C under oxygen, nitrogen and carbon monoxide respectively in a tube furnace for 3 h with heating and cooling rates of 5 °C/min.

For characterizing TiO₂ nanotubes morphology, diameter and length, a scanning electron microscope (FESEM, Philips, JEOL JSM7000) was employed with an accelerating voltage 10 kV. Oxygen vacancies and Ti^{n±} defects of the nanotube were measured by X-ray photoelectron spectroscopy (XPS, SSL-300 system, Surface Science Laboratory Inc.) using achromatic AlK α radiation (1486.6 eV) with Ar[±] sputtering to remove the surface layer of the sample. All spectra were obtained under vacuum at a pressure of about 2.7×10^{-7} Pa (2.0×10^{-9} Torr). The analyzer pass energy was set to 50 eV, and the contact time was 40 ms. Prior to tested, the spectrometer was calibrated by setting the binding energies of Au 4f_{7/2} and Cu 2p_{3/2} to 84.0 and 932.7 eV, respectively. Binding energies for the samples were normalized with respect to the position of the C 1s peak resulting from adsorbed hydrocarbon fragments. Electrochemical and photoelectrochemical experiments

were performed in a standard three-electrode configuration with a Pt foil counter electrode and a saturated Ag/AgCl reference electrode.

3. Results and discussion

Titania properties and its potential application depend on its crystallinity, hence crystallization and phase transformation are essential for as-prepared titania nanotube, this process usually occur when annealing amorphous titania nanotube at elevated temperature. Fig. 2 illustrate the Ti 2p XPS spectra and XRD patterns of TNT electrode annealing in O₂, N₂ and CO at 500 °C for 3 h respectively. For the O₂-annealed TNT electrode, the XPS spectra only present two characteristic peaks of Ti 2p_{1/2} at 465 eV and Ti 2p_{3/2} at 459 eV. For the N₂-annealed TNT, these two peaks shift to low energy positions, which means the formation of oxygen vacancies. While for the CO-annealed TNT, there are two extra peaks found at 455 eV and 453 eV which imply the formation of Tiⁿ⁺ ($n=0-3$) cations. From the XRD patterns, it shows that the anatase phase is the main crystalline phase in both samples annealed in O₂ and N₂, while the rutile phase is found in the XRD pattern for the CO-annealed sample. Using the Scherrer formula, the size of anatase crystallites was calculated to be 14 nm for TNT annealed in O₂ and 17 nm for TNT annealed in N₂ and CO. The bigger grain size for TNT annealed in CO may be attributed to the formation of Tiⁿ⁺ ($n=0-3$) defects which promote the rutile grain growth which make the phase transformation relatively easy and the tube structure unstable.

Fig. 3 is the top view and side view SEM images of as-prepared TNT, and TNT annealed in O₂, N₂ and CO at 500 °C for 3 h respectively. The as-prepared TNT arrays are 1.5 μ m long and the average pore size

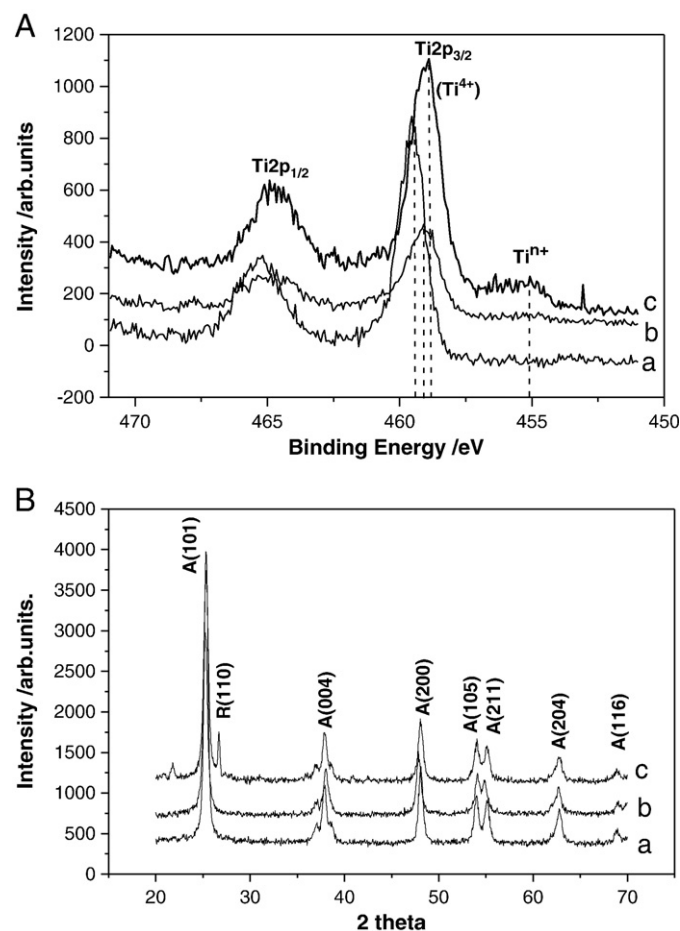


Fig. 2. (A) Ti2p XPS spectra and (B) XRD patterns of TNT electrode annealing in O₂ (curve a), N₂ (curve b) and CO (curve c) respectively at 500 °C for 3 h.

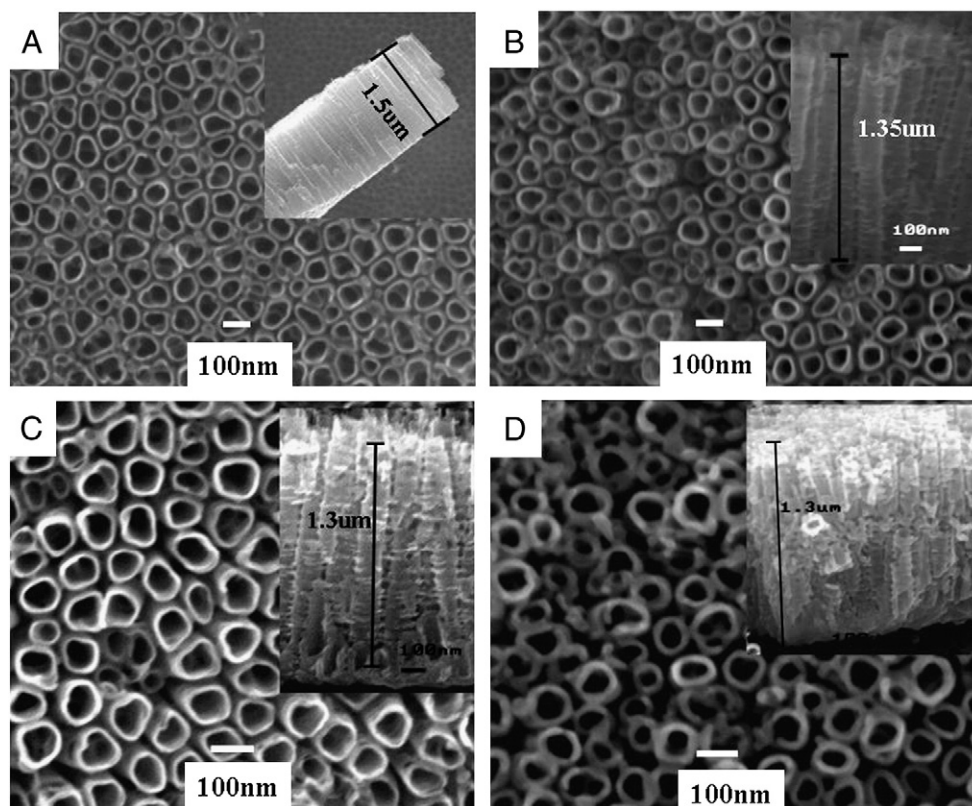


Fig. 3. SEM images of (A) as-prepared TNT electrode, and TNT electrode annealing in (B) O_2 (C) N_2 (D) CO at 500 °C for 3 h (insets are the cross-sections of the TNT).

is 100 nm. After annealed in O_2 , the TNT arrays have a length of 1.35 μm due to the sintering effect. While after annealed in N_2 or CO, the length of the nanotubes decreased to 1.3 μm . The shrinkage of the nanotube is ascribed to the phase transformation or mass transport of the nanotube at elevated temperatures. The phase transformation or crystallization takes place through nucleation, grain growth and densification [16]. Oxygen vacancies exist in the nanotubes after annealed in N_2 or CO according to the XPS spectra, which can enhance the volume transport in nanotube walls and lead to the shrinkage of the nanotube. It is also found that annealing in CO results in the $Ti^{n\pm}$ cations in the nanotubes, the oxygen vacancies and $Ti^{n\pm}$ cations will rapid the grain growth of anatase phase to rutile phase, make the nanotube a little bit broken from the SEM side view as shown in Fig. 3 (D). To obtain a stable nanostructure CO-annealed TNT, decreasing the annealing temperature to 450 °C is an effective way. But the $Ti^{n\pm}$ cations peaks in XPS spectra were not as obvious as that of the sample annealed at 500 °C.

The electrochemical properties of TNT electrodes annealed in different ambient were examined by cyclic voltammetry (CV) with 10 mM $K_3[Fe(CN)_6]$ as probe at a scan rate 0.1 Vs^{-1} . Fig. 4 presents the CV results. For TNT electrode annealed in O_2 , there is a reduction peak at 0.1 V and no oxidation peak is observed in this scan range, this indicates that the electrochemical reaction of the electrode is irreversible. However, for the TNT electrodes annealed in N_2 and CO, both the oxidation peak and reduction peak are observed during the scan process, the peak separation are 0.21 V and 0.136 V respectively, which shows that the two electrodes reaction are quasi-reversible. According to the peak separation, the average apparent heterogeneous electron transfer rate constant (k) were calculated to be 2.18×10^{-3} cm/s for N_2 -annealed TNT electrode and 1.34×10^{-3} cm/s for CO-annealed TNT electrode. These results can be matched with the electron transfer rate constants of carbon nanotube electrode (7.53×10^{-4} cm/s) and boron-doped diamond electrode (1.06×10^{-5} cm/s) [17,18]. It was found that TNT electrode annealed in CO at 500 °C was more inclined to peel off

from the substrate after cycling 200 times, not as stable as O_2 -annealed TNT electrode. To improve its reliable, one effective way is to decrease the annealing temperature to 450 °C.

Steady-state polarization curves and photocurrent response of the three TNT electrodes were measured in 0.01 M Na_2SO_4 solution using a 150 W lamp simulating a solar spectrum, the results are shown in Fig. 5 (A) and (B). Fig. 5 (A) demonstrates that the electrode potential of oxygen evolution reaction (OER) for TNT electrodes annealed in different ambient are quite different. The OER potential is 1.72 V for O_2 -annealed TNT electrode, while for N_2 and CO-annealed sample, the OER potential are 1.54 V and 1.37 V respectively. The decrease of OER potential indicates the improving of electro-catalytic activity of both TNT electrodes. From Fig. 5(B), we can also get the same results, the photocurrent of O_2 -annealed TNT electrode is 11 $\mu A/cm^2$, smaller than photocurrent of N_2 -annealed TNT electrode and CO-annealed TNT

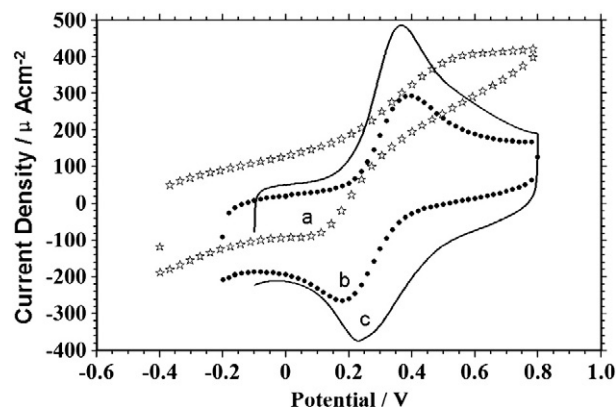


Fig. 4. CV curves for TNT electrodes annealed in O_2 (curve a), N_2 (curve b) and CO (curve c) at 500 °C for 3 h. The measurements were taken in 1 M KCl solution at 0.1 Vs^{-1} in the presence of 10 mM $K_3[Fe(CN)_6]$.

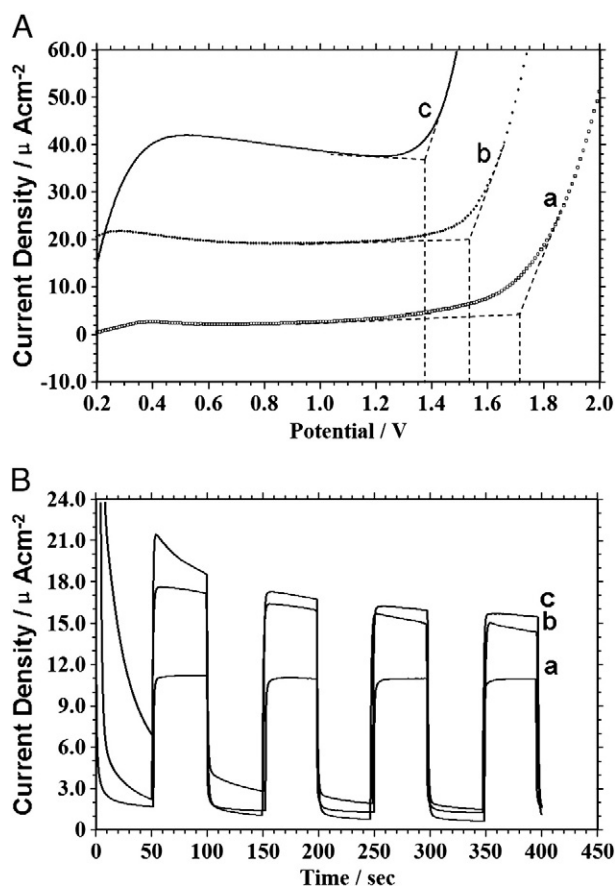


Fig. 5. (A) Steady-state polarization curves and (B) photocurrent response for TNT electrode annealed in O₂ (curve a), N₂ (curve b) and CO (curve c) at 500 °C for 3 h. The measurements were taken in 0.01 M Na₂SO₄ solution at 0.1 V s⁻¹.

electrode which the photocurrent response are about 16 $\mu\text{A cm}^{-2}$ and 17 $\mu\text{A cm}^{-2}$ respectively. The photocurrent density reflects the generation, separation and transfer efficiency of photo-excited electrons from valence to conduction band of TNT. The higher the photocurrent response, the higher the photoelectrochemical reactivity. The improvement of the photoelectrochemical reactivity of the TNT is related to the formation of oxygen defect and titanium cations with low valence after annealed in N₂ or CO. The formation of these surface defects has a direct effect on the electronic structure and decrease the work function of the TNT, thus, they could enable excitation with photon energy lower than the band gap and hence improve the photoelectron density.

4. Conclusion

Titania nanotube arrays prepared by anodization of titanium foils were subjected to anneal treatments in O₂, N₂ and CO respectively. It

was demonstrated that annealing TNT electrode in CO have resulted in the formation of oxygen vacancies and titanium cations with low valence, as compared to the as-grown and O₂-annealed TNT electrode. The presence of Ti^{n±} ($n=0-3$) and oxygen vacancies appreciably enhanced the electrochemical properties of the TNT electrode, leading to very efficient electron transfer rate 2.18×10^{-3} cm/s for N₂-annealed TNT electrode and 1.34×10^{-3} cm/s for CO-annealed TNT electrode. Steady-state polarization measurement and photocurrent response demonstrated that the electrode potential of oxygen evolution reaction (OER) reduced by 20% and the photocurrent response increased by 50% for CO-annealed TNT electrode compared with O₂-annealed TNT electrode. Good electrical conductivity and the reducing of the work function due to the formation of surface defects were believed to be responsible for the improved electrochemical properties of CO-annealed TNT electrode.

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