Field Emission Characteristics of Double Walled TiO$_2$ Nanotubes


Abstract

Double walled TiO$_2$ nanotubes have been synthesized by two probe anodization method on highly pure Titanium (Ti) substrate. FESEM and XRD analyses revealed the morphological and structural properties of the as-synthesized double walled TiO$_2$ nanotubes. Investigation of their field emission characteristics in a planar diode configuration at a base pressure of 1 x 10$^{-8}$ mbar has been done. The turn-on field defined for the emission current density of 10 µA/cm$^2$ is found to be 2.1 V/µm. As the field is increased further to 2.95 V/µm maximum, a current density of 890 µA/cm$^2$ is achieved. Current-time (I-t) measurement at a preset value of 1 µA emission current for the duration of 3 h demonstrates a robust emission current stability. The observed low turn-on field and stable electron emission makes the double walled TiO$_2$ nanotubes a suitable emitter for various electronics devices applications.

Keywords: TiO$_2$; Double walled nanotubes; Density functional theory; Current stability; Field emission.

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1. Introduction

One-Dimensional (1D) nanostructures have attracted significant research interest in the last few decades.[1] 1D nanostructures proved themselves as potential candidate for various materials science applications due to promising electrical, mechanical and optical properties.[2] Anodic oxidation is simple and low cost method to synthesized self-organized 1D nanostructures.[3] Particularly, the formation of self-aligned and organized titanium dioxide (TiO$_2$) nanotube arrays is possible by using two probe anodic oxidation method.[4] TiO$_2$ is an inorganic semiconductor material with large band gap of 3.2 eV.[5] It exhibits a wide range of application as electrochromic material,[6] biomedical devices,[7] gas sensors,[8] photocatalysis,[9] photo-electrochemistry,[10] dye-sensitized solar cells,[11] and field emission.[12] In recent times, the tremendous efforts have been made by scientific community to synthesis various TiO$_2$ nanostructures such as, nanowires,[13] nanotubes,[14] nanosheets,[15] and nanorods[16] etc. Field emission is quantum mechanical tunneling phenomenon in which electron from the materials has been extracted under the action of strong electrostatic field.[12] Various applications such as X-ray generation techniques, space research, electronic displays, electron microscopes and medical devices depends on electron emitter source of field emission technology.[17] Field emission is highly geometry dependent and a surface-sensitive phenomenon. Emitter materials that possess a high areal density, good electrical conductivity, low work function, very fine tip radius and sharp-edged nanostructures generally show superior field emission characteristics material.[3] TiO$_2$ nanotubes array possess geometrical/morphological features similar to highly aligned CNTs. They can also be made as a tightly adherent layer on the surface of Ti substrate by simple anodization process, which makes them suitable as electron percolation pathways for free electron transfer between interfaces. Aligned TiO$_2$ nanotubes array with high packing density can significantly enhance the field emission properties of the materials, so it can become one of the ideal candidates for field emission applications.[3] In the present work, double walled TiO$_2$ nanotubes were synthesized by simple and economic method of anodization. The structural, morphological, and field

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emission properties of the as-synthesized double walled TiO$_2$ nanotubes were systematically characterized and discussed.

2. Synthesis

The double walled TiO$_2$ nanotubes were synthesised by the anodization method as per previous report.$^{[10]}$ In brief, prior to anodization, a high purity titanium foil (99.7% purity, 0.25 mm thickness, Sigma Aldrich) was cleaned in an ultrasonic bath for 10 min with ethanol and 10 min with acetone sequentially. By taking titanium foil (1 cm × 2 cm) as the working electrode and platinum foil (1 cm × 2 cm) as the counter electrode, anodization was performed in a two-electrode configuration under constant potential at room temperature (25 °C). The reaction was carried out by adding 0.1 M of NH$_4$F and 1 M of H$_2$O in 50 ml of Ethylene glycol. During reaction constant voltage of 30 V was applied for 30 min. Finally, the as-anodized Ti foil was rinsed in deionized water and used for further characterization. Annealing of the Ti foil was carried out at 530 °C for 3 h in air. A double layer oxide, which is double walled TiO$_2$ is formed over the Ti metal substrate due to the coupling of cation and anion migration during oxide growth. For tube formation of the double layer finally turns into an outer- and inner-shell in morphology. The anodic potential causes oxidation of the metal.$^{[11]}$

3. Characteristics

Field Emission Scanning Electron Microscope (FESEM) (Model Hitachi S-4800) was used to study surface morphology of the double walled TiO$_2$ nanotubes and X-ray diffraction (XRD) by D8 Advance, Bruker instrument was used for phase identification of the double walled TiO$_2$ nanotubes. Field emission characteristics have been investigated in a planar diode configuration at the base pressure of 1 × 10$^{-8}$ mbar. Further details of the field emission measurement is given in reference.$^{[18]}$ The density functional theory (DFT) calculations were carried out using the Vienna Ab initio Simulation Package (VASP).$^{[19]}$ The interactions between the core and valence electrons were described using the Project Augmented Wave (PAW) method.$^{[20]}$ An energy cut-off of 600 eV, and 7 × 7 × 3 Monkhorst-Pack k-point mesh,$^{[21]}$ was used to sample the Brillouin zone of bulk anatase TiO$_2$, whereas the (001) and (101) surfaces were modelled using 5 × 5 × 1 and 5 × 3 × 1 k-point meshes, respectively. All calculations were deemed to be converged when the forces on all atoms were less than 0.001 eV/Å. For accurate determination the electronic structure and bandgap, the screened hybrid functional (HSE06)$^{[22]}$ was employed with the exact exchange value of 25% and a screening parameter of μ = 0.2 Å$^{-1}$. The (001) and (101) surfaces of TiO$_2$ were created from the optimized bulk material using the METADISE code.$^{[23]}$ In order to align the energies to the vacuum level, a slab-gap model was constructed and the corresponding electrostatic potential was averaged along the c-direction, using the Macro Density package.$^{[24]}$ The work function (Φ) was calculated as

$$\Phi = V_{\text{vacuum}} - E_F,$$

where $V_{\text{vacuum}}$ is the $V_{\text{vacuum}}$ level and $E_F$ is the Fermi level.

4. Results and discussion

4.1 Crystal structure and morphological analyses

XRD pattern of the annealed doubled walled TiO$_2$ shown in Fig. 1 reveals the polycrystalline nature of predominant anatase TiO$_2$ peak centred at 20 value of 25.32. In present study the lattice constants have been evaluated from (h k l) planes by using the following equation of interplaner spacing for a tetragonal unit cell as,

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Where, $h$, $k$, and $l$ are the miller indices, $d$ is interplaner spacing, $a$ and $c$ are the lattice constant of unit cell. The reflections due to the TiO$_2$ peaks can be indexed to anatase TiO$_2$ with lattice constants $a = 3.7884$ Å and $c = 9.5190$ Å, which is consistent with the literature (JCPDS Card No. 84-1286). The other peaks are related to the Ti substrate and are assigned as T. Fig. 2 shows the FESEM images of the doubled walled TiO$_2$ nanotubes. The doubled walled TiO$_2$ nanotubes have an average inner tube diameter of 46 nm, an outer tube diameter of 74 nm, and areal density of $29 \times 10^8$/cm$^2$ (see Fig. 2a). The average tube length is calculated at 1.3 µm (Fig. 2b).

![Fig. 1 XRD pattern of doubled walled TiO$_2$ nanotubes.](image)

4.2 Field emission studies

Fig. 3 (a) shows the current density-electric field (J-E) plot of the double walled TiO$_2$ nanotubes. The turn-on field defined at a current density of 10 µA/cm$^2$ is found to be 2.1 V/µm. Compared to other TiO$_2$ nanostructures reported in the literature (as summarized in Table 1),$^{[25-28]}$ the observed low turn on field of the double walled TiO$_2$ nanotubes is found to be superior. The observed low turn-on field for the double walled TiO$_2$ nanotubes may be attributed to the well-aligned nature, nanometric size, and high density of the double walled TiO$_2$ nanotubes. High emission current density of 890 µA/cm$^2$
has been achieved upon the application of an applied electric field of 2.95 V/µm. The field emission characteristic is further analyzed by the Fowler–Nordheim (F–N) plot, i.e. ln(J/E^2) versus (1/E), derived from the observed J–E characteristic as shown in Fig. 3b. The F–N plot shows a non-linear behavior for the doubled walled TiO₂ nanotubes. The stability of the emission current of the doubled walled TiO₂ nanotubes was ascertained from the current-time (I-t) plot at a preset value of 1 µA emission current for the duration of 3 h as shown in Fig. 4. The emission current remained fairly stable for the entire duration of measurement with only small instabilities/fluctuations in the form of “spikes”. The observed fluctuations in the emission current may occur due to adsorption, desorption of the residual gas molecules and phenomenon of ion bombardment.[29]

### 4.3 Density functional theory

The field emission characteristics are influenced by the work function (Φ) of the emitter material, we have carried out density functional theory calculations to gain atomic-level insight into the electronic structure bulk anatase TiO₂ and predict the work function of the two most stable and commonly observed (001) and (101) surfaces of TiO₂.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Turn-on field (V/µm) (for J= 10 µA/cm²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double walled TiO₂</td>
<td>2.1</td>
<td>Present Work</td>
</tr>
<tr>
<td>nanotubes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aligned TiO₂ nanotubes</td>
<td>7.8</td>
<td>25</td>
</tr>
<tr>
<td>TiO₂ nanowires</td>
<td>5.7</td>
<td>26</td>
</tr>
<tr>
<td>N₂ doped TiO₂</td>
<td>11.2</td>
<td>27</td>
</tr>
<tr>
<td>TiO₂ nanotubes</td>
<td>23.8</td>
<td>28</td>
</tr>
</tbody>
</table>
The optimized lattice constants of the bulk anatase TiO$_2$ (Fig. 5a) were obtained at $a=b=3.803$ Å, $c=9.517$ Å, in good agreement with the experimental lattice constants ($a=b=3.782$ Å and $c=9.502$ Å). The electronic band gap of anatase TiO$_2$ is predicted at 3.21 eV (Fig. 5b), in good agreement with experimental estimate of 2.23 eV. The valence band edge consists mainly of O-$p$ states whereas the conduction band edge is dominated by Ti-$d$ states. The (001) facet has a higher surface energy predicted at 0.88 Jm$^{-2}$ than the (101) surface, which has a lower surface energy of 0.45 Jm$^{-2}$. These results are consistent with previous theoretical calculations. We have also consistently predicted a lower work function for the most stable (101) surface at 5.10 eV than for the less stable (001) surface at 5.52 eV. The lower work function for the most stable (101) surface is promising for the field emission applications, as it favours efficient electron emission capability of the TiO$_2$ material.
5. Conclusions
In summary, we have successfully synthesized doubled walled TiO$_2$ nanotubes by a simple anodization method. FESEM analysis confirmed the formation of doubled walled TiO$_2$ nanotubes with an average inner and outer tube diameter of 46 nm and 74 nm, respectively. The doubled walled TiO$_2$ nanotubes show promising field emission behavior in terms of low turn-on field and stable field emission current. A low work function of 5.10 eV is predicted to the most stable TiO$_2$(101) surface from first-principles DFT calculations, making it suitable to attain good field emission characteristics. These results demonstrate that doubled walled TiO$_2$ nanotubes are promising next generation field emission electron sources.

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Conflict of Interest
There is no conflict of interest.

Supporting Information
Not applicable

References

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