WO$_3$ Deposited TiO$_2$ Nanotube Arrays by Thermal Evaporation Method for Effective Photocatalytic Activity

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Abstract: Titania (TiO$_2$) nanotube arrays were fabricated by anodising Ti foil in glycerol (HOC$_2$CH(OH)CH$_2$OH) containing 0.7 g of ammonium fluoride (NH$_4$F). The crystal structure was studied by X-Ray Diffraction (XRD) analysis and the morphology was observed via Field Emission Scanning Electron Microscopy (FSEM). The average inner diameter of the TiO$_2$ nanotubes was 90 nm, and the length was approximately 2 µm. Tungsten (W) of various thicknesses was then thermally evaporated onto the TiO$_2$ nanotubes and annealed at 400°C in an O$_2$ atmosphere to form tungsten trioxide (WO$_3$). The effect of various thicknesses of W on the degradation of methyl orange (MO) was investigated. The sample with a 2.5 nm thick layer of W showed the best performance. The deposited W layer of that thickness is believed to provide a shallow trap for photo-generated e$^-$ and h$^+$, inhibiting the recombination and extending the lifetime of the charge carriers. Thus, this sample resulted in high degradation of methyl orange (MO) as compared with other samples.

Keywords: titania nanotube, tungsten trioxide, thermal evaporation, photocatalytic activity

1. INTRODUCTION

In the last few decades, TiO$_2$ has been studied extensively because of its excellent properties such as low cost, nontoxicity, high stability against corrosion, self-cleaning properties and strong oxidation ability.$^1$ Therefore, it is widely used in photocatalysis, photovoltaics, gas sensors, biological coatings and photoelectrolysis applications. Studies have indicated that for such applications, well-arrayed TiO$_2$ nanotubes are of great importance because of their one-dimensional (1D) nature, ease of handling and simple preparation.$^{1,2}$ Furthermore, the band gap of nanotube materials can be altered because of the quantum confinement effect.$^2$ Usually, a higher ratio of diameter to length of the tubes (aspect ratio) is preferred because this provides a larger surface area for photon absorption. Moreover, TiO$_2$ nanotubes contain free spaces in their interiors that can be filled with active materials such as chemical compounds,
enzymes, and noble metals, enabling them to be engineered to produce advanced multifunctional materials.\textsuperscript{3}

To date, there are a number of preparation routes that have been reported to fabricate TiO\textsubscript{2} nanotubes. Techniques such as the sol-gel method, hydrothermal method, anodisation, metal-organic chemical vapour deposition (MOCVD) and templating have been reported.\textsuperscript{4-8} However, there has been a growing interest in the anodisation method because of the resulting vertically oriented and highly ordered TiO\textsubscript{2} nanotube arrays, which is the most remarkable property of this method.\textsuperscript{9,10} In 2008, Xiao et al. suggested that TiO\textsubscript{2} nanotubes with WO\textsubscript{3} deposited by a facile hydrothermal method exhibit higher photocatalytic activity.\textsuperscript{16} Modification of TiO\textsubscript{2} nanotubes with cationic deposition is believed to enhance the photocatalytic activity by reducing the recombination of photogenerated electron-hole pairs.\textsuperscript{11-16} Therefore, in this work, the effect of different thicknesses of W deposited by the thermal evaporation method onto TiO\textsubscript{2} nanotubes for effective photocatalytic activity was investigated.

2. EXPERIMENTAL

High purity (99.6\% purity with 0.127 mm thickness) titanium (Ti) foils from STREM Chemicals were used in this study. Prior to anodisation, Ti foils were degreased in an ultrasonic bath containing ethanol for 30 minutes. The foils were then rinsed in deionised water and dried in a nitrogen stream. The anodisation was performed in a two-electrode configuration bath with the Ti foil as the anode and a platinum electrode as the counter electrode. The electrolyte consisted of 100 mL of glycerol with 0.7 g of NH\textsubscript{4}F added. The anodisation voltage was kept constant at 40 V for 1 hour at room temperature (27°C). During the anodisation process, the fluorinated electrolyte was agitated using a magnetic stirrer. The as-anodised Ti foils were cleaned using distilled water and were dried in a nitrogen stream.

For the W deposited TiO\textsubscript{2} nanotube arrays, a thermal evaporation process was conducted using a K950X Turbo Evaporator thermal evaporator by EMITECH. The thickness varied from 2.5 nm to 10 nm. After the thermal evaporate process, the TiO\textsubscript{2} nanotube samples were annealed at 400°C for 4 hours in an oxygen (O\textsubscript{2}) atmosphere. The morphological properties of the TiO\textsubscript{2} nanotubes were characterised using a Zeiss SUPRA 35VP field emission scanning electron microscope (FESEM) at working distances down to 1 mm and extended accelerating voltages ranging from 30 kV down to 100 V. The FESEM model was capable of energy dispersive X-ray (EDX) spectroscopy. To obtain the length of the nanotube layer, cross-sectional measurements were
carried out on mechanically bent samples. The actual length of the tubes was divided by \( \cos 45^\circ \). The crystal phase of the TiO\(_2\) nanotubes was studied by X-ray diffraction using a Bruker D8 powder diffractometer operating in the reflection mode with Cu K\( \alpha \) radiation (40 kV, 30 mA) and a diffracted beam monochromator. A step scan mode with a step size of 0.1° in the range of 20°–70° was also used. The photoluminescence spectra were recorded at room temperature using an LS 55 luminescence spectrometer (Jobin-Yvon HR).

The photocatalytic degradation studies were performed by dipping 4.0 cm\(^2\) of Ti foil into 100 mL of 30 ppm methyl orange in a custom-made quartz glass photoreactor. A blank sample (without TiO\(_2\)) was also prepared to eliminate the effect of the light on the degradation of methyl orange. Both samples were left in the reactor for 30 minutes in a dark environment to achieve adsorption/desorption equilibrium. The samples were then photoirradiated at room temperature with a TUV 18W UV-C Germicidal light. Every hour, 5 mL of solution was withdrawn from each quartz tube to monitor the degradation of methyl orange after irradiation. The concentration of the degraded methyl orange was determined by using a UV spectrometer.

3. **RESULTS AND DISCUSSION**

3.1 **Formation of TiO\(_2\) Nanotube**

Figure 1 shows the illustrative top view and cross-sectional FESEM image (the inset in Figure 1) of the TiO\(_2\) nanotube arrays, which were grown by the potentiostatic anodisation of Ti foil at 40 V in glycerol for 1 hour. As shown in Figure 1, the anodised Ti had a complete porous structure with a well-aligned and smooth nanotube array. The average length of the tubes was 2 \( \mu \)m, and the diameter of the tubes was 90 nm. The aspect ratio (tube length / tube diameter) of these TiO\(_2\) nanotube arrays was approximately 25. EDX was employed to investigate the quantity of the elements Ti and O in the anodised and annealed sample. From Figure 2, it can be concluded that the atomic ratio of Ti to O was 1:2, which confirms that this sample consisted of pure TiO\(_2\) nanotubes without any impurity. The data are summarised in Table 1. The corresponding XRD pattern for this TiO\(_2\) nanotube array is shown in Figure 3(a). Major peaks were detected at 25.37°, 35.67°, 48.21°, 54.10° and 55.26°, corresponding to the (101), (004), (200), (105) and (211) planes, which match with the reference pattern of anatase TiO\(_2\), with an ICDD number of 00-021-1272.
Figure 1: FESEM image of the TiO$_2$ nanotubes grown by anodisation in glycerol electrolyte containing 0.7 g of NH$_4$F.

Figure 2: EDX spectra of the pure TiO$_2$ nanotubes.

Figure 3: XRD patterns of the TiO$_2$ nanotubes (a) pure TiO$_2$ nanotubes (b) TiO$_2$ nanotubes deposited with 2.5 nm of W (c) TiO$_2$ nanotubes deposited with 5.0 nm of W (d) TiO$_2$ nanotubes with 10 nm of W [A = Anatase TiO$_2$, T = Titanium].
Table 1: Element composition for pure TiO$_2$ nanotubes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti (wt%)</th>
<th>O (wt%)</th>
<th>W (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ nanotube</td>
<td>66.66</td>
<td>33.34</td>
<td>–</td>
</tr>
</tbody>
</table>

3.2 Formation of WO$_3$ Deposited TiO$_2$ Nanotube

The TiO$_2$ nanotube arrays coated with various thickness of W were studied to evaluate the effect of W incorporation on the photocatalytic activity. Figure 4(a–c) shows the FESEM images of TiO$_2$ nanotubes with various thicknesses of W. A hazy, thin layer of WO$_3$ was found covering the wall of the TiO$_2$ nanotubes. The openings of the nanotubes were not covered with WO$_3$. EDX was performed on the thermally evaporated TiO$_2$ nanotube sample to determine the wt% of W incorporated on the surface of the annealed TiO$_2$. It can be concluded that the samples contain Ti, O and W.

The wt% of W was found to increase with the thickness of the deposited W, as shown in Figure 5. The data are summarised in Table 2. The wt% of W for 2.5 nm, 5 nm and 10 nm were 2.55, 7.07 and 13.07 wt%, respectively (Tables 2). The XRD pattern of each sample is shown in Figure 3(b–d). The majority of the peaks match those expected for the anatase phase (ICDD number 00-021-1272). Moreover, the WO$_3$ peak was difficult to identify in this XRD pattern; this difficulty is probably due to the amorphous nature of WO$_3$.

As can be seen, the intensity of the anatase peak at 25.37° corresponding to the (101) preferential orientation of the TiO$_2$ nanotube was enhanced after the deposition of W. This enhancement be attributed to the W atoms existing as interstitials that shared the oxygen with the Ti atoms, improving the (101) orientation of the anatase phase. This statement is in agreement with Wang et al. in 2007.17
Figure 4: FESEM images of the TiO$_2$ nanotubes as grown by anodisation (a) deposited with 2.5 nm of W (b) deposited with 5.0 nm of W (c) deposited with 10 nm of W.
3.3 Photoluminescence Characteristics

Photoluminescence (PL) has been used widely to investigate the energy levels of materials and to provide fundamental information on the
properties of the energy levels lying within the band gap. To study the influence of the deposited W on the luminescence of TiO$_2$ nanotubes, we measured the PL emission spectra of TiO$_2$ nanotubes deposited with different thicknesses of W in the wavelength range of 330–800 nm. The near band edge (NBE) emission at approximately 396 nm (3.2 eV) and a broad green emission centred at approximately 521 nm (2.4 eV) can be observed in the PL spectra as shown in Figure 6. These PL peaks may be closely related to the luminescence caused by the recombination of photoinduced electrons and holes, which may result from lattice distortions and surface oxygen deficiencies. The emission band centred at approximately 396 nm is assigned to the emission of a bandgap transition with photon energy approximately equal to the bandgap energy of anatase (387.5 nm). The PL signal at 521.3 nm is due to excitonic PL, which is mainly produced by oxygen vacancies. Oxygen vacancies are believed to be the main defect that causes green PL in TiO$_2$ nanotubes.\textsuperscript{18,19}

Table 2: Element composition for W deposited TiO$_2$ nanotube.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti (wt%)</th>
<th>O (wt%)</th>
<th>W (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposited with 2.5 nm of W</td>
<td>63.38</td>
<td>34.07</td>
<td>2.55</td>
</tr>
<tr>
<td>Deposited with 5.0 nm of W</td>
<td>62.38</td>
<td>30.15</td>
<td>7.47</td>
</tr>
<tr>
<td>Deposited with 10 nm of W</td>
<td>55.39</td>
<td>31.53</td>
<td>13.07</td>
</tr>
</tbody>
</table>

Figure 6: The PL spectra of the TiO$_2$ nanotubes, (a) pure TiO$_2$ nanotubes (b) deposited with 2.5 nm of W (c) deposited with 5.0 nm of W and (d) deposited with 10 nm of W.
Reduction in the PL intensity for the W deposited TiO$_2$ nanotubes compared to the pure TiO$_2$ nanotubes was observed. The observed PL response could be attributed to the high W content; these atoms act as the centres of electron-hole combination rather than facilitating charge transport and decreasing the rate of the radiative recombination process. The variation in PL intensity with the W content may result from the change in the defect state in the shallow level of the TiO$_2$ surface. Furthermore, FESEM images show that the TiO$_2$ nanotubes are covered with WO$_3$ as an independent structure, which would hinder the charge transport process and act as a recombination centre.

### 3.4 Photocatalytic Activity

The photocatalytic activity of TiO$_2$ nanotubes with and without W content was evaluated by the photodegradation of methyl orange under UV light irradiation as shown in Figure 7. From the results obtained, the colour of the methyl orange (MO) changed from orange to pale orange, indicating degradation. It was noted that TiO$_2$ nanotubes deposited with 2.5 nm of W exhibited the highest degree of MO degradation, followed by the pure TiO$_2$ nanotubes and the 10 nm W deposited TiO$_2$ nanotubes.

The enhancement of the photocatalytic activity of the TiO$_2$ nanotubes deposited with 2.5 nm of thermally evaporated W was due to the coupling efficiency of the TiO$_2$ nanotubes and the WO$_3$ particles. The resulting junction between the deposited W and the TiO$_2$ nanotubes plays an important role in the separation of photogenerated electron-hole pairs. After the absorption of light with energy equal to or greater than the band gap, electrons and holes are generated. The photogenerated electrons are transferred from the conduction band of the TiO$_2$ nanotubes to the conduction band of the WO$_3$, and the holes in the valence band of the WO$_3$ are transferred to that of the TiO$_2$ nanotubes under illumination. Therefore, W deposition can provide a shallow trap for photogenerated electrons and holes, inhibiting recombination and extending the lifetime of the charge carriers. The photodegradation rate could consequently be enhanced because more charge carriers are available, and the efficiency of photocatalytic activity has been improved.
Figure 7: Degradation of methyl orange on different TiO$_2$ nanotube samples (a) deposited with 2.5 nm of W (b) pure TiO$_2$ nanotubes (c) deposited with 10 nm of W and (d) blank sample without TiO$_2$ nanotubes.

The poor photocatalytic activity of TiO$_2$ nanotubes deposited with 10 nm of W may be caused by the dilution effect of the inactive W phase. The photocatalytic efficiency is decreased significantly because the inactive W phase (excess WO$_3$ content than optimum value in TiO$_2$ nanotubes) will act as the centres of electron-hole recombination easily. With thicker deposition of W, the W grows to attain independent identity, which is a distinct thin layer of WO$_3$ and was found covering the wall of the TiO$_2$ nanotubes as seen in Figure 4 (b) and (c). Most of the excited UV light is adsorbed by the thick W layer, and therefore, the transfer of electrons and holes is hindered. The photocatalytic activity decreases sharply, resulting in a level lower than that of the pure TiO$_2$ nanotubes. The optimum concentration can be explained by the balance of two factors: an increase in trapping sites leading to efficient trapping, and fewer trapped carriers leading to interfacial charge transfer. Therefore, the optimum concentration of W is important to determine in order to improve the photocatalytic activity for TiO$_2$ nanotubes.

4. CONCLUSION

In conclusion, we report WO$_3$/TiO$_2$ nanotubes with different concentrations of W to enhance the photocatalytic activity. TiO$_2$ nanotubes with an average length of 2 µm and 90 nm diameter were successfully produced in a glycerol electrolyte by the anodisation method. These samples were deposited with W using the thermal evaporation technique and annealed at 400°C in an O$_2$ atmosphere to become WO$_3$. The sample with 2.55 wt% of W was found to show the most effective photocatalytic activity.
5. ACKNOWLEDGEMENT

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6. REFERENCES


