Estimating the degradation of methylethionium chloride dye on nanotubular TiO\(_2\) structure

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**Introduction**

The great importance of titanium and its alloys due to their good properties and excellent performance in broad spectrum applications i.e. fuel cells, photo-catalysis, gas sensors, semiconductors, biomaterials, special coatings, and manufacturing of optical devices, etc. [1]. Formation of uniform, stable and adherent passive film at the surface of titanium provides protection from many hostile environments where other metal/alloys could be adversely affected. The formation of titanium dioxide (TiO\(_2\)) film can be tuned to variable thickness, morphologies and structures by changing the process parameters during electrochemical anodizing \([2,3]\).

In TiO\(_2\) the overlap of 3d\(^2\) conduction band in ‘Ti’ and 2p\(^2\) state in oxygen forms valence state which results in the formation of band gap of 3.2 and 3.0 eV in anatase and rutile respectively \([4,5]\). The oxygen deficient or distorted structure of TiO\(_2\) results in the formation of additional energy levels within band gap of TiO\(_2\) semiconductor. These energy levels are located within the band gap and are known as sub-bands or trap states. These sub-bands are created due to the disorder in the crystal structure and can trap electrons and holes. Photocatalytic reactions occur at the surface of the TiO\(_2\) nanoparticles when they are exposed to ultraviolet or visible light. The electrons excited from the valence band to the conduction band leave behind holes in the valence band. These holes can react with water to form hydroxyl radicals, which can then react with organic pollutants to break them down into simpler substances. The process of photocatalysis is described by the following reactions:

\[ \text{TiO}_2 + h\nu \rightarrow \text{TiO}_2^* \]

\[ \text{TiO}_2^* + e^- \rightarrow \text{TiO}_2 + \text{O}_2 \]

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The oxide species in the environment (water) are decomposed electrochemically at TiO\(_2\)/environment by charge carriers. The generation of peroxo ions (O\(^2^-\)) reacts with organic species to produce water and carbon dioxide by exchanging charge with water. Due to excellent semi-conductive properties of high aspect ratio, highly ordered and self-organized; the titanium oxide nanotubes (TNTs) are preferred over nanoparticles due to rapid charge transportation and limited retention time \([8–10]\).

**Experimental**

The synthesis of nanotubular structure and optimization of anodizing conditions are already explained by Deen et al. \([11]\). Briefly, Ti6Al4V specimens (30 L × 10 W × 4 T) mm were first mechanically polished by grinding successfully from 180 to 2500 grit size papers followed by chemical cleaning in acetone, ethanol and deionized water (DI) respectively, before air drying.

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Mechanically polished specimens were electrochemically anodized in electrolyte for 2 h at 45 V in a two electrode cell system (graphite rod as cathode and Ti6Al4V as anode) which is connected to a DC power supply (Matrix-MPS-300L-3). The electrolyte used in this study contains 0.5 M ammonium di-hydrogen phosphate (NH₄H₂PO₄) + 0.1 ml ethylene glycol + 0.1 ml glycerol + 0.15 M ammonium fluoride (NH₄F) + water (Bal.). The nanotubular structure obtained after anodizing process is shown in Fig. 1. The crystal structure was modified by heat treatment in air at 350 °C (heating rate 10 °C/min) for 3 h in muffle furnace (Wise Therm). The as-anodized and heat treated specimens are designated as ‘AN’ and ‘AN-HT’ respectively in this study. X-ray diffraction (XRD, Philips and pro X-Pert software) patterns were obtained using Cu-Kα radiation of wavelength 1.540598 Å and Raman spectroscopy analysis was performed to investigate microstructure of ‘AN’ and ‘AN-HT’.

The photocatalytic activity of both ‘AN’ and ‘AN-HT’ was estimated in a methylethionium chloride (methylene blue, MB, 2 mM solution) by potentiodynamic polarization and Electrochemical impedance spectroscopy (EIS) under dark and illumination of various light intensities in three electrode cell system placed in a box having changeable light sources at fixed position over the cell. In this system the saturated calomel electrode (SCE) was reference, graphite rod was used as auxiliary and anodized specimens acted as working electrode. This cell assembly was connected to Gamry potentiostat (PC14/750). The potentiodynamic polarization scans were obtained (scan rate was 10 mV/s connected to Gamry potentiostat (PC14/750). The potentiodynamic polarization scans were obtained (scan rate was 10 mV/s).

Results and discussion

X-ray diffraction

The XRD pattern of anodized sample (Fig. 2a), although, showed similar peaks as that of Ti, however, their intensity has decreased slightly while a new peak (2 0 0) at 40.58° appeared which was due to Ti₃O₄ as it is matching to reference pattern of Ti₃O₄.

The drop in intensity of anodized sample and absence of typical titanium dioxide peaks showed that the anodized film is very thin and lacks oxygen for the development of proper rutile or anatase phases. The XRD pattern of as anodized (AN) and heat-treated sample (AN-HT) clearly confirmed that the heat treatment in air; aided the formation of more oxidized and regular phases. The spectrum in Fig. 2b showed that many peaks (without asterisk superscript) were the characteristics of anatase phase (01-076-0326), whereas few peaks, labeled with asterisk, were due to rutile phase (01-076-0326). It is clear from the XRD analysis that heat treatment of anodized titanium favors the formation of anatase with very low content of rutile phase.

Raman spectroscopy analysis

To characterize the structure and supporting the results of XRD the Raman spectroscopy was done for ‘AN’ and ‘AN-HT’ specimens as shown in Fig. 3. The as anodized (AN) specimen showed the amorphous Ti₃O₄ phase and exhibited broad bands at 425.28, 610.02 (peak A₁g) and 702.01 cm⁻¹ (weak). These bands were attributed to the Ti–O bonds.

This presence of phase (Ti₃O₄) in as synthesized nanotubes confirmed the oxygen deficient titanium dioxide. The O–O interactions were relatively weak bands at 229.27 cm⁻¹, 264.74 cm⁻¹ and 308.75 cm⁻¹ which represent the distorted and immature form of rutile phase. On heat treating the nanotubular structure in air the Raman spectrum clearly depicted shift in two major bands from 425.28 and 610.02 (for AN) to 417.82 and 624.78 cm⁻¹ respectively. Both shifts in bands corresponded to E₂g mode of rutile and anatase phases respectively. But the presence of anatase phase was dominated in AN-HT
spectrum which was assured by Raman peaks \((E_g)\) at 228.62 and 624.78 cm\(^{-1}\) [12,13].

**Photocatalytic performance**

The photocatalytic behavior of TiO\(_2\) nanotubes depends on the crystal structure and is limited by electron-hole recombination, light absorption characteristics, oxidation and reductions reaction rates as a function of adsorption behavior of species in the environment. In as anodized (AN) specimen which have oxygen deficient TiO\(_2\) crystal structure would have multiple sub band gap electronic states. The energy required by electron to transit in these states would be less than actual band gap energy for n-type TiO\(_2\) NTs. But these could increase the possibilities of charge recombination without giving charge to the environment species for redox reactions [14,15]. The photocatalytic mechanism for dye degradation in aqueous solution is shown in Fig. 4. When the specimen is illuminated with light the electrons in the valence band shift to conduction band leaving behind the holes. The concentration of charge carriers and their separation tendencies depends on the crystal structure and band structure of TiO\(_2\).

**Potentiodynamic polarization scan**

The ability of AN and AN-HT specimen to produce hole–electron pair and corresponding oxidation and reduction of ionic species in the electrolyte was evaluated by potentiodynamic polarization scans as shown in Figs. 5 and 6 respectively. In dark, the cathodic polarization depicted the large reverse current with small change in potential which represented the rapid reduction of oxygen to produce oxygenase (O\(^2^-\)) ions. The ions could adsorb at the NTs...
and may improve the deficiency of oxygen in as anodized (AN) to form crystalline TiO₂ structure during anodic polarization.

The difference between \( E_{\text{OCP}} \) and \( E_{\text{corr}} \) was negative (−1.114 mV) due to charge relaxation (negative) by cathodic polarization. The critical current density \( (I_{\text{crit}}) \) was 0.147 mA/cm² at −602.38 mV beyond which a constant current density 0.114 mA/cm² was observed above 711.9 mV representing degradation of dye in dark. Similarly, the rapid increase in reverse current during cathodic polarization and charge relaxation was observed under 60 W illumination.

But at 60 W there were larger (two) current excursions than 100 and 200 W, the overall photocatalytic activity was correlated with anodic polarization. These kinks in current density during anodic polarization were attributed to the electronic traps within subband energy states due to amorphous nature of as formed structure. The reverse current flow in these excursion corresponded to the recombination of electronic states. The increase in light intensity (at 100 and 200 W separately) resulted in decrease \( I_{\text{crit}} \) value and decrease in overall anodic current density as depicted in Fig. 7. It was deduced that increase in light intensity has little influence on photocatalytic degradation of dye and was higher under 60 W illumination.

In case of AN-HT the critical current density \( (I_{\text{crit}}) \) was increased up to 100 W followed by decrease in magnitude. In dark the increase in anodic current density above \( I_{\text{crit}} \) with small current excursions were attributed to reduction of dissolved oxygen in aqueous medium.

The AN-HT specimen showed a constant degradation at relatively higher current density \( (169.5 \mu A/cm²) \) under 60 W light source. In contrast with AN specimen the current excursions were relatively small and did not appear at 60 W and 200 W due to crystalline structure of nanotubes after heat treatment and absence of sub band energy states. A peculiar behavior at 100 W was observed by small but continuous current excursions due to activation of sub energy states without giving constant current density value for dye degradation.

**Electrochemical impedance spectroscopy**

Electrochemical impedance spectroscopy (EIS) was used to analyze the photocatalytic behavior of as anodized and heat-treated anodized specimens toward MB dye degradation exposed to various light intensities. This is an efficient technique to monitor kinetics of electrochemical reaction without changing the surface properties due to perturbation of small potential amplitude (10 mVrms). The Nyquist plots of AN and AN-HT specimens in MB dye solutions are shown in Figs. 8 and 9 respectively under varying light intensities within the frequency range of 100 kHz to 10 mHz. Due to decrease in photocatalytic tendency under 200 W the EIS results are not expressed in this study.

The as anodized (AN) TiO₂ nanostructure was deficient in oxygen and is considered as amorphous semiconductor which has transient kinetic behavior due to electronic traps [16]. Table 1 shows the kinetic parameters of AN and AN-HT impedance spectrum which were obtained by fitting the impedance values in equivalent electrical circuit model as shown in Fig. 10. The solution resistance \( (R_s) \) of dye containing electrolyte was lower in

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**Fig. 7.** Critical current density \( (I_{\text{crit}}) \) trends for ‘AN’ and ‘AN-HT’ as a function of light power.

**Fig. 8.** EIS Nyquist plots for ‘AN’ specimens in dye solution under dark, 60 W and 100 W light sources.

**Fig. 9.** Nyquist plots for ‘AN-HT’ specimens exposed to dye solution in dark, 60 W and 100 W light.

**Fig. 10.** Equivalent electrical circuit model for EIS spectrums for both ‘AN’ and ‘AN-HT’ specimens.
dark which increased under illumination due to decrease in charge recombination admittance ($Y_{\text{rec}}$) hence promoting the dissipation of charge by oxidation of water molecules at the valence band and reduction of oxygen at conduction band edge.

This process ultimately degraded the dye molecules and resulted in increase in solution resistance (mechanism as described in Fig. 4). The charge transfer resistance ($R_{\text{ct}}$) ‘AN’ and ‘AN-HT’ specimens decreased to $-84.64 \Omega \text{ cm}^2$ and $-30.19 \Omega \text{ cm}^2$ respectively under illumination by 60 W light intensity. The relatively higher charge transfer resistance decreased the dye degradation tendency under 100 W light source for both specimens by lowering the electronic charge transfer coefficient (B). The value of ‘B’ was higher under 60 W illumination for ‘AN’ and ‘AN-HT’ specimen which corresponded to increased efficiency of charge separation (generation of electrons and holes) which ultimately promote the redox reaction for dye degradation. The lower electronic charge recombination admittance ‘$Y_{\text{rec}}$’ (3.035 and 0.404 mS s$^{1/2}$/cm$^2$) and higher ‘B’ (0.014 and 0.170 s$^{1/2}$) for ‘AN’ and ‘AN-HT’ respectively at 60 W attributed to enhanced degradation tendency of TiO$_2$ nanotubular structure. The relatively higher $Y_{\text{rec}}$ and low value of B for ‘AN’ specimen than ‘AN-HT’ under 60 W light was considered due to lower concentration of charge carriers (electrons and holes) available for redox reaction or in other words it may be evaluated that increased consumption of electrons to produce oxygenase (O$_2$/C_0) ions would decrease the oxygen deficiency in ‘AN’ (Ti$_6$O) crystal structure. This behavior for anodized (AN) specimen was also in support to the potentiodynamic polarization results. Upon further increase in light intensity (100 W) both specimens represented similar behavior as in dark but in this case the increased in temperature at the specimen surface introduced adverse effect for charge transfer events at the semiconductive surface of nanotubes.

### UV–vis photospectroscopy

The known concentration of MB dye solution was irradiated by visible light and it was found that the dye was stable under visible light without interaction with AN-HT surface. The photocatalytic degradation of dye solution when exposed to AN-HT surface was estimated by UV–vis spectroscopy. The absorption spectrums of known concentration dye solutions at various exposure times are shown in Fig. 11. A prominent absorption peak of unexposed dye was observed at $\lambda = 664$ nm which depressed upon extended exposure to AN-HT surface under illumination. It was observed that with the passage of time the absorption intensity had a decreasing trend. The photocatalytic activity of AN-HT to degrade dye was validated by this decrease in light absorption. The degradation tendency of dye solution by AN-HT was evaluated by using Beer’s Lambert Law.

The percentage degradation of dye was about 5.15% in initial 30 min exposure which gradually reached to 45.05% after 180 min as shown in Fig. 12.

<table>
<thead>
<tr>
<th>Light power</th>
<th>$R_s$ ($\Omega \text{ cm}^2$)</th>
<th>$R_{\text{ct}}$ ($\Omega \text{ cm}^2$)</th>
<th>$Y$ ($\mu S s^2$/cm$^2$)</th>
<th>$n$</th>
<th>$Y_{\text{rec}}$ (mS s$^{1/2}$/cm$^2$)</th>
<th>$B$ ($\times 10^{-3}$ s$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As anodized (AN)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark</td>
<td>50.76</td>
<td>0.747</td>
<td>32.68</td>
<td>0.530</td>
<td>11.02</td>
<td>3.176</td>
</tr>
<tr>
<td>60 W</td>
<td>232.6</td>
<td>-84.62</td>
<td>40.67</td>
<td>0.350</td>
<td>3.035</td>
<td>14.09</td>
</tr>
<tr>
<td>100 W</td>
<td>213.7</td>
<td>35.03</td>
<td>118.0</td>
<td>0.399</td>
<td>0.114</td>
<td>1.730</td>
</tr>
<tr>
<td>Anodized and heat treated (AN-HT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark</td>
<td>60.46</td>
<td>-2.17</td>
<td>752.1</td>
<td>0.579</td>
<td>39.49</td>
<td>104.0</td>
</tr>
<tr>
<td>60 W</td>
<td>94.35</td>
<td>-30.19</td>
<td>587.9</td>
<td>0.546</td>
<td>0.404</td>
<td>170.4</td>
</tr>
<tr>
<td>100 W</td>
<td>57.64</td>
<td>-10.56</td>
<td>560.2</td>
<td>0.544</td>
<td>0.594</td>
<td>101.0</td>
</tr>
</tbody>
</table>

The degradation was pronounced due to formation of hydroxyl (OH$^\cdot$) and oxygenase (O$_2$/C_0) radicals which oxidize dye molecules [17]. Jalalah et al. [18] described the photo-degradation tendency of methylethionium chloride dye on TiO$_2$ nanoparticles doped with sulfur and reported the complete vanishing of blue color in water in 90 min under visible light. The high percent degradation could be achieved by doping of other elements in nanotubes which may be helpful in narrowing down the band gap and hence facilitate the catalytic degradation of organic compounds in water.

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**Table 1**

Kinetic parameters ‘AN’ and ‘AN-HT’ specimen exposed to MB dye solution obtained from impedance spectrums model fitting.

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**Fig. 11.** UV–vis spectrophotometry absorption spectrums of dye solution unexposed to ‘AN-HT’ (Known) and exposed solution after 30, 60, 120 and 180 min.

**Fig. 12.** Photocatalytic degradation of methylethionium chloride dye solution (20 mM) exposed to ‘AN-HT’ specimen.
Conclusion

1. X-Ray diffraction patterns of ‘AN’ and ‘AN-HT’ showed oxygen deficient TiO and rutile/anatase crystal structure.

2. The ‘AN’ specimen exhibited two broad bands at 425.28 and 610.02 (A1g) of amorphous TiO phase. These bands were shifted to 417.62 and 624.78 cm⁻¹ respectively which corresponded to $E_g$ mode of rutile and anatase phases.

3. The potentiodynamic scans of both ‘AN’ and ‘AN-HT’ specimens in MB solution depicted relatively higher $I_{crit}$ values under illumination than in dark. The current excursions in anodic polarization regimes were attributed to sub-energy bands which acted as electron traps in case of ‘AN’. The reverse current flow in these fluctuations was due to recombination of charge (electrons and holes). It was deduced that increase in light intensity beyond 60 W has little influence on photocatalytic degradation of dye.

4. Impedance spectrums of ‘AN’ and ‘AN-HT’ depicted the negative charge transfer resistance (very low) under 60 W illumination also the decreased recombination admittance and increased charge transfer of AN-HT specimen quantitatively represented better photocatalytic behavior than ‘AN’ and these results validated the potentiodynamic polarization findings.

5. During UV–vis spectroscopy of AN-HT specimen in known concentration MB dye solution the depression of adsorption intensity at same wavelength ($\lambda = 664$ nm) for 180 min confirmed total 45.05% dye degradation.

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References