Hierarchical mesoscale assembly of PbO$_2$ on 3D titanium felt/TiO$_2$ nanotubular array electrode for anodic decolourisation of RB-5 dye

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Abstract
Hierarchical PbO$_2$ nanoparticles (NPs) were grown by hydrothermal method on TiO$_2$ nanotubes (NTs) at 3D titanium felt, which is simple and scalable method. TiO$_2$ NTs were formed on titanium felt by anodising at 25 °C in environmentally friendly methanesulphonic acid solution. The growth of PbO$_2$ on the TiO$_2$ NTs depended on immersion time during hydrothermal synthesis and followed a LaMer-Dinegar burst kinetic model of nucleation and growth. PbO$_2$ formation began with rapid nucleation, followed by mesoscale assembly due to organic capping of poly(vinylpyrrolidinone). The electrochemical performance of 3D electrode was recorded in pH 3 sodium sulphate solutions containing Reactive Black 5 (RB-5) azo dye at 25 °C. The resulting hierarchical 3D electrode achieved 98% decolourisation after 50 min of anodic oxidation with a first order batch decay rate of 0.0875 min$^{-1}$.

Keywords: 3D electrode, electrocatalyst, hierarchical, lead dioxide, TiO$_2$ nanotube
Classification numbers: 2.00, 4.00, 5.06, 5.11, 5.12

1. Introduction
In recent years, degradation of organic matter residue (OMR) in solution by anodic oxidation has been used to treat wastewater. New electrocatalysts and supports are needed to improve the process efficiency and there is a need to develop low-cost materials which remain stable during the electrochemical water treatment [1]. Research has centred on materials that are effective for generation of active oxidising species with sufficient electrical conductivity and a high electrocatalytic activity for in-situ generation of oxidants, notably hydroxyl radicals. Due to their unique architecture, hierarchical 3D electrodes offer improvements over conventional electrodes in providing extensive active sites [2], better electrolyte infiltration and ease of bubble release [3]. The hierarchical architecture of composite electrode has been exploited in water splitting [4], energy storage such as flow batteries [5], and industrial catalyst [6]. The increasing
interest in hierarchical electrodes signifies efficient design and applications have diversified in electrocatalysis.

The use of titanium as an electrode has been reported due to its moderate cost, robustness, acceptable electrical conductivity and chemical stability [7]. Titanium can form a surface oxide layer which can be functionalised and provides corrosion protection. Under certain conditions, titanium oxides can act as photocatalysts [8], composite coatings [9, 10], sensors [11, 12], antibacterial surfaces [13] and ionic diodes [14]. In addition to the above properties, TiO₂ provides hydrophobicity during deposition of metal oxides such as PbO₂ from aqueous solution. The use of TiO₂ coated electrodes is restricted due to the possibility of passivation and limited electrocatalytic activity for electrooxidation of organic compounds. Over the last two decades, it has been recognised that the electrocatalytic properties can be enhanced by the presence of active and unreactive materials, making it feasible to achieve catalytically active oxide coatings, such as Cu₂O, PbO₂ from aqueous solution. The use of TiO₂ coated electrodes, providing an active support for the coating having applications in electrocatalytic degradation of contaminants under controlled operating conditions to grow TiO₂ nanotubular arrays can be grown by anodising pure titanium sheets, providing an active support for the deposition of electroactive species, such as PbO₂. PbO₂ is particularly the most attractive oxide for electrochemical water treatment with an approximate electrical conductivity of 2.5 × 10⁵ Ω⁻¹ cm⁻¹ [19].

In this work, titanium felt was anodised in fluoride-containing aqueous methanesulphonlic acid (MSA) electrolytes under controlled operating conditions to grow TiO₂ nanotubes (NTs) which were then decorated with PbO₂ by immersion and hydrothermal treatment to produce a novel 3D coating having applications in electrocatalytic degradation of Reactive Black 5 (RB-5) dye. Due to its water solubility and its ability to produce a covalent bond with fibre, RB-5 dye is commonly used in textile industry [20]. The results provide important information on interfacial surface transitions between TiO₂ and PbO₂ layers.

2. Experimental details

Reagent grade 70% methanesulphonic acid (MSA), ammonium fluoride, ammonium persulphate, 99% oxalic acid, poly (vinylpyrrolidinone) (PVP, relative molar mass = 55000) and Reactive Black 5 dye were obtained from Sigma Aldrich, while lead nitrate, sodium hydroxide, sulphuric acid, sodium hydroxide, sodium sulphate, ethanol (98%) and acetone were obtained from Fischer Scientific and used as received.

2.1. Anodising of titanium felt

The Ti felt (NV Bekaert SA) was pre-treated in a 10 wt.% oxalic acid solution at 70 °C for 20 min. The Ti felt was washed with ethanol and deionised water, then dried overnight at 90 °C in air. Anodising was carried out in an undivided glass cell of 100 cm³ volume. The Ti felt was connected as an anode with dimensions of 2 cm × 2 cm × 0.15 cm. A graphite plate of 1.5 cm × 6 cm × 1.2 cm dimensions was used as a cathode. The electrolyte was magnetically stirred at 300 rev min⁻¹ using a 0.06 cm diameter, 0.25 cm long PTFE-coated steel, cylindrical stirring bar (Fischer Scientific). The Ti felt was anodised in 1 M MSA electrolyte containing 1 wt.% ammonium fluoride. The anode and cathode were separated at 1 cm apart and applied a cell potential difference of 10 V and 20 V for 1 h at 25 °C.

2.2. Synthesis of lead dioxide

The PbO₂ was deposited hydrothermally in the presence of PVP as a catalyst support, which served as a structure directing agent. 0.015 M Pb(NO₃)₂ and 1 M NaOH were mixed at 25 °C. 0.1 g of PVP was added to 75 cm³ of the above mixture and allowed to stir overnight until complete dissolution has taken place. 3 cm³ of 1.5 M (NH₄)₂S₂O₈ was dissolved in the resultant solution, transferred to an autoclave and heated at 60 °C with samples of Ti felt/TiO₂ NTs for 1 min, 5 min, 15 min, 6 h, and 12 h. The resultant samples were cooled down overnight, to produce an adherent PbO₂ coating on the substrate.

2.3. Heat treatment or calcination

The resulting Ti felt/TiO₂ NTs/PbO₂ composite samples were annealed at 450 °C for 1 h in air using an electric furnace. The calcined samples were later used in decolourisation studies.

2.4. Characterisation of coated substrate

A field emission scanning electron microscope (FESEM, JEOL 6500F) was used to characterise all anodised samples. A Raman confocal microscope (Renishaw, RM 2000) was used to obtain Raman spectra employing light source of 632.8 nm wavelength with 10% laser intensity. The exposure time was approximately 30 s. A Rigaku SmartLab x-ray diffractometer (XRD) operated at 9 kW with Cu target was used for phase characterisation.

2.5. Electrochemical experiments

The electrochemical studies were accomplished by using computer aided PGSTAT302N potentiostat/galvanostat from Autolab (Eco Chemie, Netherlands) utilising Nova 1.11 software. All samples (Ti felt, Ti felt/TiO₂ NTs, and Ti felt/TiO₂ NTs/PbO₂) were used as an anode for electrochemical decolourisation of RB-5 dye. A 100 cm³ solution containing 20 ppm of RB-5 dye in 0.5 M sodium sulphate as a background electrolyte was electrolysed at a constant potential 1.5 V versus Hg/HgO (0.6 M NaOH) at pH 3 and 25 °C.
The pH of the electrolyte was stable throughout the electrochemical studies. Platinum mesh (1.5 cm × 1.5 cm) and mercury/mercuric oxide (Hg/HgO in 1.0 M NaOH) were used as a counter and reference electrode respectively.

3. Results and discussion

3.1. Surface characterisation of TiO$_2$ nanotubes

Morphological and elemental analysis of the titanium felt was conducted by means of SEM and EDX, as shown in figures 1(a)–(e). Surface TiO$_2$ NTs were achieved by anodising Ti felt which was pre-treated with oxalic acid at 80 °C for 20 min SEM images of pre-treated Ti felt (figure 1(a)) and hierarchical nanotube arrays on anodised Ti felt (figure 1(b)) reveal that the NTs have a hexagonal pattern with a smooth surface as reported in literature [21]. The NTs have a vertical arrangement of close packed NTs.

TiO$_2$ NTs can act as nucleation site and container of nanostructures, so it is feasible to decorate each anodised nanotube with an oxygen transferring metal oxide, such as PbO$_2$. The formation of TiO$_2$ NTs on 3D Ti felt can be observed in the SEM images (figures 1(b)–(d)). The images

![Figure 1](image_url)
# Table 1. Comparison of discolouration rate by TiO₂ and PbO₂ for degradation of model dye from selected literature.

| Method/type of dyes | Parameters and conditions | \(k/\text{min}^{-1}\) | Colour removal/ % | Time/min | References |
|---------------------|---------------------------|---------------------|-------------------|----------|------------|
| Anodic oxidation of methyl orange | P25 TiO₂/PbO₂, pH 2.5, \(E_{\text{anode}}\) 1.5 V versus Ag/AgCl/saturated KCl | — | 66.4 | 120 | [27] |
| Anodic oxidation of Acid Blue 113 | Pb/PbO₂, current density \(j = 60 \text{ mA cm}^{-1}\), 25 °C | — | 93.6 | 360 | [28] |
| Anodic oxidation of Acid Blue 113 | Ti/TiO₂/PbO₂ disc electrode, \(j = 60 \text{ mA cm}^{-1}\), 25 °C | — | 98 | 60 | [28] |
| Anodic oxidation of Acid Red 27 | Stainless steel/PbO₂, pH 2, current density \(j = 20 \text{ mA cm}^{-1}\), 25 °C | 0.0575 | 97 | 300 | [29] |
| Anodic oxidation of Reactive Black 5 | RVC/TiO₂ nanosheets/PbO₂, pH 3, \(E = 2.5 \text{ V versus Hg/HgO}\), current density, \(j = 2 \text{ mA cm}^{-1}\), 25 °C | 0.060 | 98 | 60 | [30] |
| Anodic oxidation of Reactive Black 5 | 3D Ti felt, \(E = 1.5 \text{ V versus Hg/HgO}\), pH 3, 25 °C | 0.0012 | 7 | 60 | This study |
| Anodic oxidation of Reactive Black 5 | 3D Ti felt/TiO₂ nanotubes, \(E = 1.5 \text{ V versus Hg/HgO}\), pH 3, 25 °C | 0.0058 | 36 | 60 | This study |
| Anodic oxidation of Reactive Black 5 | 3D calcined Ti felt/TiO₂ nanotubes/PbO₂ (\(t_i = 12 \text{ h}\)), \(E = 1.5 \text{ V versus Hg/HgO}\), pH 3, 25 °C | 0.0875 | 98 | 50 | This study |
also showed that the Ti NTs were dispersed uniformly on the Ti felt. The Ti felt anodised at a cell voltage of 20 V appeared darker in colour, due to the longer TiO₂ NTs formed. It is noticeable that the diameter of nanotubes produced using a cell voltage of 20 V (figures 1(c), (d)) was ~100 nm which was larger than samples anodised at a cell voltage of 10 V with ~50 nm in diameter (figure 1(b)). Pore widening in the nanotubular array could be controlled by adjusting the potential distribution over the 3D electrode. The nanotubes produced at a cell voltage of 20 V for 1 h showed a close packed, vertical arrangement with a length ~230 nm and a closed cap at the bottom of the nanotubes (figure 1(e)), which was in agreement with our previous work on 2D Ti foil [22].

The surface of anodised felt contains uniform films. The formation of ordered nanotubes is due to the presence of fluoride ions as reported [23, 24]. The fluoride ion can be used in the form of sodium fluoride, ammonium fluoride or hydrofluoric acid, we preferred the ammonium salt for relative safety in handling.

The mechanism is related to the electrochemical development of oxide layer on the Ti felt substrate according to the following reaction:

\[
\text{Ti} + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- ,
\]

and subsequent dissolution with fluoride ions [25, 26]:

\[
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O}. \tag{2}
\]

Initially, anodising forms a dense layer of TiO₂ on the Ti felt substrate. In the presence of ammonium fluoride, the TiO₂ film can dissolve, forming an anionic fluorotitanate complex. Fluoride ion migration is controlled by the potential gradient, leading to selective dissolution and formation of an ordered array of nanotubes. The oxide layer dissolves at the pore mouth and oxide formation held at the bottom pores. The nanotubular structure separates from the substrate due to the barrier layer of residual oxide. This compact layer of nanotubes depends upon factors such as acid concentration, fluoride ion intake and applied potential [26], as shown in table 1.

### 3.2. Decoration of TiO₂ nanotubes with PbO₂

The nanotubular arrangement of TiO₂ NTs is more hydrophilic in nature compared to Ti metal. Therefore, these modified surfaces are able to take in liquid and absorb the aqueous phase inside the TiO₂ NTs on immersion to a solution. This wetting characteristic enables filling of the tubes with aqueous solution of lead nitrate as metal source, ammonium sulphate as oxidant and PVP as a structure directing agent of PbO₂ [31]. Hence, PbO₂ accumulates on the TiO₂ NTs grew over the surface of the Ti felt on immersion during hydrothermal treatment in figures 2(a)–(d).

The deposition of PbO₂ on nanotubular arrangement on Ti felt was proved by Raman and FESEM studies. Figures 2(a)–(c) reveals SEM images for a deposited lead dioxide during 1, 5, and 15 min of immersion on the TiO₂ NTs, which showed rapid nucleation of PbO₂ NPs in which the surfaces of 3D felt have been concealed at 15 min (figures 2(c), 3(a) and (b)). Some of the uncovered nanotubes can still be seen at low immersion times (e.g. 1 and 5 min) in figures 2(a), (b). The quantity of deposited PbO₂ in the nanotube arrays could be increased by tuning the immersion time. The surface coverage was approximately improved from 20%, 60% to 90% respectively for 1, 5, and 15 min of immersion. In the first one minute, the precursors went into the pores of nanotubes, followed by nucleation over the top of nanotubes due to larger size of PbO₂ compared to TiO₂ NTs. The PbO₂ NPs have an oval shape of approximately 100 nm, showing monodispersed spontaneous nucleation at hydrothermal temperature of 60 °C. The kinetics of spontaneous nucleation may be controlled by adjusting temperature, the concentration of precursors and the strength of oxidising agent, i.e., ammonium persulphate, as postulated by LaMer-Dinegar [32].

The LaMer-Dinegar theory could be applied for colloidal monodispersed condition which was used to predict further crystal growth (figure 2(d)). In this case, the PVP was used as a surface directing agent [31] which capped the surface of PbO₂ restricting further growth. The negatively charged PVP then acted as new nucleation centres of Pb²⁺ ions, resulting in local aggregation of nanoparticles in figures 3(c), (d). This aggregation resembled diffusion-controlled growth in LaMer-Dinegar theory with assisted aggregation due to the structure direction and interlinking bridges by PVP [32]. Lead oxide and PVP became inorganic-organic building block of spherical mesocrystal formation. This non-classical crystallisation usually leads to high surface area functional materials [33, 34]. Coalescence of microspheres occurred at long reaction times since the space for growth was limited in figures 3(e) and (f). PVP continued to maintain the particle size of PbO₂ as shown in the inset of figure 3(f). The decoration of nanotubes with PbO₂ on the nanotubular arrays over Ti felt substrate was expected to increase the electrochemical properties of the coating.

EDX elemental analysis is shown in figure 4 for this coating. The surface contained lead in abundance with titanium and traces of oxygen. This is consistent with uniform adhesion of PbO₂ over the Ti felt strands. However, EDX did not show stoichiometric phases of TiO₂ and PbO₂ due to interference from the Ti felt substrate. Raman spectroscopy revealed the structural properties of coatings related to the presence of PbO₂ and formation of anatase phase after annealing as shown in figure 5(a). The distinct Raman peaks were observed at 428 cm⁻¹ and 137 cm⁻¹ which showed the presence of PbO₂ [35] and the effect of annealing in transforming the substrate to anatase phase, as indicated by previous research [36]. In figure 5(a), no significant anatase peaks were observed before calcination, showing that the hydrothermal synthesis of PbO₂ at 60 °C did not significantly affect the structure of the titanium phase. The anatase phase of the calcined Ti/TiO₂ NTs was also confirmed by XRD in figure 5(b).
3.3. Electrochemical studies of novel coatings containing PbO$_2$

The nanotubes coated with PbO$_2$ NPs on a Ti felt substrate are shown in Figure 3. The 12 h immersion time was used since it contained the most PbO$_2$ after nucleation and growth in Figure 2(d). Such surfaces are suitable for use in the anodic oxidation of RB-5 dye. Linear sweep voltammetry was used to examine the electrochemical characteristics of Ti felt/TiO$_2$ nanotubes and Ti felt/TiO$_2$ NTs/PbO$_2$ electrodes towards RB-5 dye. The main goal of these studies was to detect the electrocatalytic performance towards oxidation of organic molecules and to know the potential at which oxygen evolution began.

Figure 6 shows the polarisation curve obtained in the overpotential range from 0.4 V to 2.0 V versus [Hg/HgO] NaOH (sat.) at a sweep rate of 10 mV s$^{-1}$, in 0.6 dm$^3$ volume solution containing $20 \times 10^{-5}$ M (20 ppm) of RB-5 dye at pH 3 with 0.5 M Na$_2$SO$_4$ in a working electrode compartment while counter electrode containing only 0.5 M of Na$_2$SO$_4$ at pH 3. The scan towards more positive potentials showed a steep rise in anodic current, corresponding to decomposition of RB-5 azo dye into oxygenated products and intermediates, attributed to oxygen evolution and other anodic reactions. This conversion of organic pollutant (RB-5 dye) to oxygenated products was interceded by OH free radical produced at a non-active anode surface due to primary water discharge over Ti felt/TiO$_2$ NTs/PbO$_2$ electrode surfaces. The oxidation peak in voltammogram indicates oxidative degradation of dye at anode via in-situ OH mediation. In case of Ti felt/TiO$_2$ NTs/PbO$_2$ coatings, oxygen evolution started at a potential of 1.5 V versus Hg/HgO (0.6 M NaOH) at a scan rate of 10 mV s$^{-1}$. This corresponds to the most positive potential before anodic oxidation of dye takes place as a primary reaction, followed by the secondary reaction of oxygen evolution at more positive potentials. For Ti felt/TiO$_2$ NTs, oxygen evolution took place at 1.0 V versus Hg/HgO due to water electrolysis at anode [37]. Ti felt/TiO$_2$ NTs/PbO$_2$ surfaces showed electrocatalytic activity for anodic oxidation of RB-5 dye at 1.5 V versus Hg/HgO. Previous reports indicated that mediated OH radicals produced via water discharge act as highly active oxidants and negligible adsorption of these active mediators takes place over the non-active anode [38].

According to figure 6, the electrocatalytic performance of electrodes in this work is in the following order: Ti felt/TiO$_2$ nanotubes/PbO$_2$ > Ti felt/TiO$_2$ NTs. This represented the better capability of the substrate decorated with PbO$_2$ to degrade the dye at higher potential. Oxygen evolution started at given applied potential at a specified scan rate by using different electrodes was due to the anodic reactions reveals with the electroactive and transitional species. An oxygen evolution started at higher potential by using Ti felt/TiO$_2$ NTs/PbO$_2$ showed the positive improvement of the substrate by the addition of PbO$_2$ with subsequent OH mediated electrocatalytic oxidation of the dye molecules.

The oxygen evolution reaction (OER) is a secondary anodic process. The free radical generated during electrochemical
oxidation of RB-5 dye is the result of intermediate reaction taking place just before the oxygen evolution reaction. The water discharge is the first step during the course of these intermediate reactions which ultimately generate mediated hydroxyl radicals (·OH) at the anode. The nature of electrode also plays an important role in the impact of hydroxyl radicals over the anode surface as subsequent steps in anodic oxidation. From the above illustration two types of substrates can be categorised for anodic oxidation: active and non-active electrodes [39]. Active electrodes are strongly influenced by hydroxyl radical interaction with the anode [40]. The interaction of active anodes and hydroxyl radical leads to the formation of higher oxides or superoxides which oxidise the organic while competing with oxygen evolution reaction [39, 40]. Pt is one of the active anodes with high adsorption enthalpies which was extensively studied due to its attracting nature towards hydroxyl radicals. Meanwhile, the hydroxyl radical itself is responsible for the oxidation of organic for non-active electrodes. The decorated PbO2 NPs over TiO2 NTs act as a sink for electron removal and have no influence on the anodic oxidation since hydroxyl radicals actively participate in the anodic reaction; PbO2 can be viewed as a relatively non-active electrode.

3.4. Electrochemical removal and discolouration of RB-5 dye

The colour degradation was studied by electrolysis of electrolyte containing RB-5 dye and using novel coating as anode with applied constant potential at 1.5 V versus Hg/HgO in figure 7. An 80 ml of electrolyte containing 20 ppm of RB-5
dye with 0.5 M of Na₂SO₄ at pH 3 was used for electrolysis studies with working electrode (Ti felt/TiO₂ NTs/PbO₂, Ti felt/TiO₂ NTs or Ti felt), counter electrode (Pt) and reference electrode (Hg/HgO (0.6 M NaOH)). The UV-vis spectra measured during constant current electrolysis of the electrolyte for the maximum absorbance band for RB-5 dye in the visible region (λmax = 597 nm) decreased as a function of time. By using calcined Ti felt/TiO₂ NTs/PbO₂ as working electrode, the intensity of visible band was continuously reduced over 60 min of electrolysis (figure 7).

There is no evidence of new bands in the absorbance data, denoting prompt transformation in the dye structure during electrochemical treatment steps which may associate with the oxidation of complex dye structure into elementary molecules (CO₂) [41]. Different elementary aliphatic and aromatic hydrocarbons may arise due to the oxidation of RB-5 dye, this results from the displacement of functional groups (chromophore groups) present in azo dyes and ultimately removal of these groups to carbon dioxide and organic acids (carboxylic acid) [42]. The normalised concentration related to the time for electrolysis studies of dye using Ti felt/TiO₂ NTs/PbO₂, Ti felt/TiO₂ NTs, Ti felt as anode is represented in figure 7. A pseudo-first order decay of the initial concentration of dye, C₀, with time t can be described by:

$$\ln \left( \frac{C}{C_0} \right) = -kt$$  \hspace{1cm} (3)

where k is the apparent first order rate constant, C is the dye concentration. A comparison of observed rate constants is given in table 1.

The different values of normalised concentration and pseudo first order removal kinetics are influenced by the
electroactive nature of the different substrates used and the architecture of the electrode in which 3D electrode gives more surface area for generation of ·OH radicals. The said performance may arise due to the tendency of Ti felt/TiO2 NTs/PbO2 to transform mediated ·OH radicals to oxidised dye or direct attack of hydroxyl radical to the azo dye instead of promoting oxygen evolution.

The polarisation curves are shown in figure 6 for anodic oxidation of RB-5 dye, comparing the performance of two electrodes i.e. Ti felt/TiO2 NTs/PbO2 and Ti felt/TiO2 NTs. The curves show that Ti felt/TiO2 NTs/PbO2 exhibited a more efficient colour removal with linear pseudo first order degradation at a controlled potential 1.5 V versus Hg/HgO as seen in figures 7 and 8.

Water discharge produces OH free radical mediators which ultimately lead to colour removal. As almost negligible colour removal (40% after 60 min) was observed for Ti felt/TiO2 NTs during anodic oxidation which might be due to the adsorption of dye on nanotubes instead of degradation by radicals. Moreover, the lower results for Ti felt alone were observed, with discoloration of dye of about 7% after 60 min which is quite small while comparing with that of calcined Ti felt/TiO2 NTs/PbO2 which was about 96% and 99% degradation in 50 and 60 min respectively, showing that the potential gives rise to oxidation of Ti felt. For Ti felt/TiO2 NTs/PbO2 the nature of PbO2 assists generation of physically adsorbed OH radicals as explained by reaction (1) and nanotubes can provide a platform to adsorb the dye molecules inside the tubes present on the Ti felt substrate.

Table 1 shows that the rapid degradation of RB-5 dye with 98% colour removal was seen by using 3D Ti felt/TiO2 NTs/PbO2 substrate in about 50 min at constant potential 1.5 V versus Hg/HgO. The calculated rate constant at this constant potential is 0.0875 min⁻¹. The lowest apparent rate constant was seen at titanium felt, approximately 0.0012 min⁻¹. It is 10 times lower than the rate for anodic oxidation of RB-5 dye using the Ti felt/TiO2 NTs/PbO2 substrate. The rate constant for Ti felt/TiO2 NTs was found to be 0.0058 min⁻¹ as dye molecules adsorbed over surface site of negatively charged nanotubes [43].

This hierarchical modification of surfaces could be applied for 3D printed electrode for future work. Several surface pre-treatments, fluid flow, and heat transfer, which may alter diffusion-controlled growth and coalescence [44], are interesting to be studied.

4. Conclusions

TiO2 NTs can be formed on the top surface of titanium felt with nanotubular arrangements using MSA (1 M) containing ammonium fluoride 1.0 wt.% by anodising at an applied cell
potential of 10 V for small nanotubes (diameter ~50 nm) and 20 V for large nanotubes (diameter ~100 nm). The PbO2 can be deposited inside the nanotubes by immersion of anodised titanium felt and hydrothermal treatment in a solution containing Pb(NO3)2 and structure directing agent (PVP). The immersion time (t) plays an important role in the deposition of PbO2 over nanotubular structures following LaMer-Dinegar theory which started with rapid nucleation, followed by mesoscale formation and coalescence of PbO2 microsphere aggregates. Further application of these coatings showed that Ti felt/TiO2 NTs/PbO2 exhibited the electrochemical dye discoloration of about 99% in 60 min at 1.5 V versus Hg/HgO. The electrochemical performance of coating was improved by the presence of PbO2 as a non-active anode capable of mediating the electrogeneration of hydroxyl radical during water discharge. This research points the way to a practical approach to decorate metal oxide structures on TiO2 NTs over inexpensive porous 3D Ti-felt substrate, for environmental remediation of wastewater.

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Conflict of interest

The authors declare that they have no conflict of interest.

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