Improvement the wastewater purification by TiO$_2$ nanotube arrays: The effect of etching-step on the photo-generated charge carriers and photocatalytic activity of anodic TiO$_2$ nanotubes

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ABSTRACT

The current study demonstrates how the etching step in anodization process effects on the photocatalytic activity of TiO$_2$ nanotubes. In this regard, the TiO$_2$ nanotubes were made by one-step and two-step anodization process on two different substrates Ti and etched-Ti foils, respectively. The results revealed that two-step anodization process is a beneficial way to prepare highly well-organized structure and regular surface. The two-step anodization by an enhancement in the fluoride ions diffusion led to a decrease in nanotubes’ porosity and an increment in the nanotubes' surface area, a factor of roughness, and the ratio of length to diameter, respectively. As a consequence of the improvement in geometrical properties, the two-step TiO$_2$ nanotubes led to the intensification of photocurrent density (from 0.383 to 0.677 mA cm$^{-2}$) and photoconversion efficiency (from 0.18% to 0.29%) in comparison with the one-step nanotubes, respectively. Further, a synergetic impact of the photoelectrochemical measurement and photocatalytic process was observed. The degradation efficiencies of 2,4-dichlorophenol by two-step nanotubes increased from 47 to 55% under visible light, and from 58 to 72% under UV irradiation, which it was attributed to more light harvesting, more photo-generated electrons, higher separation efficiency and improvement in geometrical properties. Furthermore, the kinetic study showed that the reactions follow first-order kinetics and the reaction rate constants by two-step nanotubes are 1.25 and 1.44 times as great as those of one-step nanotubes under visible and UV irradiation, respectively. Moreover, the reusability tests showed that 2-step TiO$_2$ nanotubes has good stability and is active even up to the Fifth run.

1. Introduction

TiO$_2$ is an intensively studied material due to its excellent physicochemical properties and fascinating economic advantages, which could widely be applied in the fields of air purification, wastewater treatment, solar energy conversion and bactericide [1,2]. In particular, due to its high photocatalytic ability, nontoxicity, chemical inertness, and photo-stability over other semiconductors, the nano-sized TiO$_2$ catalyst has attracted numerous attentions for usage in the photocatalytic oxidation processes [3,4]. The rationales of photocatalytic oxidation processes are based on the in situ generation of highly reactive transitory species (i.e. H$_2$O$_2$, OH and O$_2^-$), which to achieve the steady state, react with the undesirable contaminants from water and result in the mineralization of the refractory organic compounds in water [5,6]. Typically, TiO$_2$ nano-catalysts are fabricated in two different types: 1- TiO$_2$ nanoparticles as traditional photocatalyst and 2-immobilized TiO$_2$ thin films as a developed photocatalyst [7]. However, the serious drawbacks of TiO$_2$ nanoparticles are the low surface area, high recombination efficiency of photogenerated electron-hole pairs, easy aggregation during the reaction, and difficult separation from a slurry system after photocatalytic reaction [8-10]. To overcome these drawbacks, fabrication immobilized TiO$_2$ photocatalyst on solid support substrates, have been suggested as an appropriate solution.

For any photocatalyst to create a maximum efficiency, surface trapping and charge separation are very crucial issues. Therefore, nanostructuring of the material (resulting in a short carrier diffusion length to the surface) and in particular using 1D geometries is a popular remedy to minimize recombination losses [11]. Among various nano forms of immobilized TiO$_2$, nanotube array structure has better photocatalytic performance due to the larger specific surface area, strong adsorption effect, excellent light trapping, enhanced electron-hole separation and much slower deactivation of nanotubes during the photocatalytic reaction [12-14]. Therefore, the nanotubular TiO$_2$ has been intensively studied and various methods have been adopted to prepare...
TiO$_2$ nanotube arrays in recent years, the commons are a template-assisted method, hydrothermal synthesis technique, and electrochemical anodic oxidation process (anodize) [15,16]. Among these methods, the simple and quick anodic oxidation procedure is known as the most efficient method to produce TiO$_2$ nanotubes because of creating a larger specific surface area, notable fast and long distance electron transport ability, greater light absorption as a result of the high ratio of length to tube diameter, low cost, fabrication aligned and orderly TiO$_2$ nanotube arrays as well as the ability to easily control the length, diameter and thickness of the nanotube [17–19].

In recent years, various approaches have been considered for enlightening the photocatalytic performance of the TiO$_2$ nanotube arrays. One of which is fabricating highly aligned, very smooth and very ordered TiO$_2$ nanotube arrays by two-step anodization process. The two-step anodization process that firstly reported by Masuda and Fukuda for aluminum [20], has been widely adopted for the creation of highly ordered TiO$_2$ nanotubes [21,22]. We have recently shown that through eliminating the relatively disordered nanotubes grown in the first-step anodization, precise ordered hexagonal imprint patterns are etched on Ti substrates, which have key role in the template for the generation of new nanotubes, and then greatly improve the uniformity and orderliness of the TiO$_2$ nanotubes during the second-step anodization [23]. Considering the fact that electron transport is a restrictive factor in the photocatalytic performance, therefore, the highly ordered and aligned TiO$_2$ nanotubes structures that obtained by two-step anodization process, provides the potential for improved electron transport resulting in higher photo-efficiency [19]. Furthermore, the precise control of the regularity degree of anodic TiO$_2$ nanotubes is very important in the fields of photonic crystals. This is due to that highly ordered nanotube structures are crucial for reasonable control of the propagation of incident light [24].

Although only some limited papers published within the last years have concentrated on the impacts of anodization steps on the orderliness and photocatalytic activity of the TiO$_2$ nanotubes [25–27], they have been largely ignored to evaluate the impacts of the anodization steps on structural properties (length, wall thickness, and surface area), geometrical features including surface area, porosity, roughness factor and ratio of length to diameter. According to our prior study [23,28], the photocatalytic activities of TiO$_2$ nanotubes depend strongly on their morphology, dimensionality and geometrical properties, so it is imperative to comprehensively study the relation between anodization steps, structural and geometrical features, and photocatalytic activity of TiO$_2$ nanotubes as well as their orderliness.

Therefore, the present work is aimed to investigate the correlation between the anodization steps, structural properties, and geometrical features. In the following, this study focuses on investigating the impact of this relationship on the photoelectrochemical performance and photocatalytic activity of TiO$_2$ nanotubes. For this purpose, comparing to the TiO$_2$ nanotubes provided in conventional one-step anodization (1-step TiO$_2$ nanotubes), the highly well-organized structure, tube orderliness and surface smoothness of TiO$_2$ nanotubes are fabricated by two-step anodization (2-step TiO$_2$ nanotubes) process. Subsequently, their photoelectrochemical property and photocatalytic activity are investigated in water splitting and degradation of 2,4-dichlorophenol as a resistant organic pollutant under both UV and Vis irradiation, respectively.

2. Experimental

2.1. Chemicals and materials

All chemicals in the analytical reagent grade were used as received without further purification, and all solutions throughout experiments were prepared with deionized water. Ethylene glycol (≥99%), ammonium fluoride, nitric acid 65%, absolute ethanol, acetone, hydrofluoric acid 40%, methanol, and sodium sulfate were all Merck chemicals. Pure titanium foil with a thickness of 0.25 mm and a purity of 97% was used for making the TiO$_2$ nanotubes. High-purity 2,4-dichlorophenol (Merck No. 803774) was utilized as a probe molecule for catalytic tests.

2.2. Preparation of vertically aligned TiO$_2$ nanotubes

The path to producing vertically aligned TiO$_2$ nanotube arrays are schematically illustrated in Fig. 1. Before electrochemical anodization, commercial titanium foil was cut into pieces of $3 \times 9$ cm$^2$. Initially, the sheets were submerged in acetone, ethanol and deionized water for about 10 min, respectively, for degreasing. After a thorough washing and chemical polishing by a mixture of nitric acid (HNO$_3$) and hydrofluoric acid (HF) solutions with a volume ratio of 3:1 (2 min), the smooth and sleek titanium sheets underwent anodization on two sides,
in a conventional two electrodes electrochemical cell, as both anode and cathode, connected to a DC power supply. The distance between the anode and cathode was maintained at 3 cm. All experiments were carried out using an ethylene glycol-based electrolyte with 0.5 wt % ammonium fluoride and 2 vol% deionized water. To fabricate 1-step TiO₂ nanotubes, the 1-step anodizing was performed in the mentioned electrolyte at the room temperature under the constant applied voltage of 40 V during 6 h. To synthesize the 2-step TiO₂ nanotubes, the first-step anodizing was performed as a 1-step anodization in the similar conditions, while during 1.5 h. Then, to etch titanium substrate, the formed TiO₂ nanotubes from the first-step was removed by acid treating process using diluted hydrofluoric acid. Subsequently, the etched Ti substrates were anodized for the second time in the same condition as the first-step for 6 h under the constant applied voltage of 40 V. Finally, these obtained samples were annealed in air for 2 h at 450 °C to induce crystallization (the heating and cooling rate were both 3 °C/min).

2.3. Characterization

The surface morphology, length, and diameter of the as-synthesized samples were determined by a field-emission scanning electron microscope (FESEM; Hitachi S4160, Japan) and the elemental composition was estimated by energy dispersive X-ray spectroscopy (EDX). To characterize the crystal structure of the annealed free-standing TiO₂ nanotubes, X-ray diffraction (XRD; Philips PW1840) measurement with Cu Kα radiation was utilized. The optical feature of FSNTs was studied by Diffuse Reflectance UV–vis Spectrophotometer (DRS, Shimadzu, Japan). Also, to determine the functional groups available in the photocatalysts, the Fourier transform infrared analysis (FTIR; Bruker alpha-2000) was performed over a wavenumber range of 500–4000 cm⁻¹.

2.4. Photoelectrochemical experiments

The photoelectrochemical performance was measured using potentiostat/galvanostat (PGS-8, Sharif Solar, Iran) in 0.01 M Na₂SO₄ electrolyte with a standard three-electrode cell consisted of the achieved TiO₂ nanotubes, platinum foil, and Ag/AgCl as the working, counter and reference electrodes, respectively. The potential and photocurrent density of the photoelectrode was controlled by an electrochemical workstation and were reported against the reversible hydrogen electrode (RHE) via the following equation [22]:

\[ E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + 0.059 \, \text{pH} + E^0_{\text{Ag}/\text{AgCl}} \]  

(1)

where \( E_{\text{Ag}/\text{AgCl}} \) equal to 0.198 V at 25 °C. The working electrode (active area: 9 cm²) was illuminated by a UV light source (315–400 nm) with the light intensity of 100 mW cm⁻². All the photoelectrochemical measurements were performed for general presentation under air condition.

2.5. Photocatalytic activity tests

In this work, 100 ml of 2,4-dichlorophenol with the primary concentration of 30 ppm was utilized as a model of pollutant to assess the photocatalytic activity of free-standing TiO₂ nanotubes. After 30 min of immersion the photocatalyst with an active area of 9 cm² in 2,4-dichlorophenol solution, the UV (400 W, Kr lamp Osram, Germany) and visible light (Halogen, ECO OSRAM, 500W, Germany) were served as irradiation source, respectively. The photocatalytic experiments were performed under magnetic stirring during 2 h irradiation. During the experiment, 3 mL sample solution was drawn from the system at certain time intervals and changes in the concentration of 2,4-dichlorophenol during the photocatalytic degradation process were measured by changes in the 2,4-dichlorophenol absorption spectrum at 227 nm wavelength obtained from UV-vis spectrophotometer device (Rayleigh, UV-2601 UV–vis, China). The stability of the fabricated samples during the photocatalytic process was assessed by reusing the catalysts for five runs. After each run, the catalysts were separated, washed thrice with deionized water and dried at 80 °C.

Using an Agilent 190915-433 instrument equipped with an HP-5MS capillary column (30 m × 0.25 mm), the reaction intermediates were recognized by GC–MS in. The column temperature was set at 50 °C for 2 min, and a rate of 10 °C min⁻¹, it was set from 50 to 250 °C at. The samples utilized for GC–MS analysis were prepared based on the following procedure: The achieved degradation product was acidified to pH = 1, then extracted with dichloromethane. Following evaporating the dichloromethane to dryness under vacuum, 10 mL methanol was added to dissolve the deposit. After that, 1 mL concentrated sulfuric acid was added and the obtained solution was refluxed for near 3 h. Followed by concentrating to about 1 mL under decreased pressure, the solution was more extracted using dichloromethane. The released chloride ions initiating from the degradation of 2,4-dichlorophenol were recognized and determined by the AgNO₃ method.

2.6. Free radical capture studies

To exploration of the photocatalytic pathways, free radical capture studies were performed. In these experiments, ammonium oxalate (AO), tert-butanol (t-BuOH), silver nitrate (AgNO₃) and benzoquinone (BZQ) was used as e⁻, OH, e⁻ and O₃ scavengers, respectively [6]. The details of experimental procedures were similar to the photocatalytic experiments, which the difference was the addition of 1 mM scavengers.

3. Results and discussion

3.1. Characterization of synthesized TiO₂ nanotubes

The structure and morphology of the TiO₂ nanotubes are shown in Fig. 2. The FESEM images of original and etched titanium foil are presented in Figs. 2(a-1) and 2(b-1), respectively. From Figs. 2(a-1), it can be observed that after chemical polishing treatment, Ti foil with relatively smooth surface can be acquired. Based on etched titanium foil (Figs. 2(b-1)), it is evident that after removing the TiO₂ nanotubes formed in the first-step anodization, very regular hexagonally distributed imprint patterns are left on the Ti substrate which can greatly improve the uniformity and orderliness of the TiO₂ nanotubes during the second-step anodization. Fig. 2(a-2) and 2(b-2) depict FESEM results of the TiO₂ nanotubes’ surface prepared by 1-Step and 2-Step anodization, respectively. Based on Fig. 2(a-2), it can be found that the 1-Step TiO₂ nanotubes have disorder patterns with a bundle arrangement on the top surface. By contrast, the top view of 2-step TiO₂ nanotubes (Fig. 2(b-2)) presents a highly ordered and regular surface with a honeycomb structure and a well-defined open mouth. FESEM results for the cross-section of the TiO₂ nanotubes which are fabricated by 1-Step and 2-Step anodization are indicated in Figs. 2(a-3), 2(a-4), 2(b-3) and 2(b-4), respectively. As it is observed in Figs. 2(a-3), the 1-step TiO₂ nanotubes have a non-uniform arrangement with small protuberances on the outside the nanotubes walls. According to Figs. 2(b-3), 2-step TiO₂ nanotubes have highly smooth and ordered nanotube walls without any protuberances on the structure. By comparing Figs. 2(a-3) and 2(b-3), it is found that after eliminating the nanotubes grown in the first-step anodization, many ordered hexagonal imprint patterns remain on Ti substrates, which significantly improve the orderliness and uniformity of the TiO₂ nanotubes within the second-step anodization.

Based on FESEM images of Fig. 2, the length, diameter, and wall thickness of the fabricated TiO₂ nanotubes were obtained and presented in Table 1. According to Table 1, 2-step TiO₂ nanotubes have approximately the same inner diameter and wall thickness (57 nm and 14 nm, respectively) in comparison to the 1-step TiO₂ nanotubes (55 nm and 13 nm, respectively). Based on Table 1, it should be stated that the 2-step anodization is adequate to result in more than the two-fold
increment in the length of the nanotubes from 2 μm for 1-step TiO2
nanotubes to 4 μm for 2-step TiO2 nanotubes. To gain a more profound
understanding regarding how the steps of anodization effect on the
nanotubes’ length, it is better to investigate the mechanism of nano-
tubes formation and growth.

The formation of TiO2 nanotubes can be briefly described as a
competition between metal oxide formation, represented by the reac-
tion (2):

\[ Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^+ \] (2)

And metal oxide dissolution, as a soluble fluoride chemical compound,
e.g.:

\[ TiO_2 + 4H^+ + 6F^- \rightarrow [TiF_6]^{2-} + 2H_2O \] (3)

Correspondingly, direct complexation of high-field transported ca-
tions at the oxide electrolyte interface:

\[ Ti^{4+} + 6F^- \rightarrow [TiF_6]^{2-} \] (4)

Reaction (2) describes the oxide growth on an anodized titanium
metal surface. According to this reaction, oxidation process with O2-
ions (from H2O), starts on the anode when the external voltage applied
between anode and cathode electrodes in an electrolyte. Moreover,
oxide growth is controlled by field-aided ion transport (O2- and Ti4+
ions) through the growing oxide. Reactions (3) and (4) explain the
chemical dissolution of the oxide layer and formation of the titanium
hexafluoride complex ([TiF6]2−), respectively. In the presence of
fluoride ions, by aid of an electrical field, a small radius of fluoride ions
makes them suitable to enter the growing TiO2 lattice and alongside the
reaction with metal oxide (Reaction (3)), react with the transported
metallic ions (Ti4+) at oxide/electrolyte interface (thus competing with
O2- transport) to form the water-soluble [TiF6]2 complexes according to
reaction (4). Continuation of the fluoride ions attack on TiO2, inside the
pores, results in pore growth and parallel tube formation [29,30].

Therefore, based on the formation mechanism of TiO2 nanotubes, it
can be concluded that the existence of fluoride ions in the electrolyte
plays the main role in the continuous growth of porous forming TiO2
nanotubes. As presented in Fig. 2, since the 2-step TiO2 nanotubes have
the more orderliness than 1-step TiO2 nanotubes, so the fluoride ions
can easily diffuse to the nanotubes bottom. Thus for the 2-step anodiza-
tion, the chemical dissolution rate increases and the longer tube can
be achieved as compared to the 1-step anodization. Furthermore, the
reason of V-shape and thinner wall in the top of the tube than at the
bottom of 1-step TiO2 nanotubes is as a result of the fluoride ions role.
The 1-step TiO2 nanotubes take this form because the availability of
fluorine ions is higher at the tubes mouths (due to the disorder ar-
angement), which enhances the dissolution of the tube walls at the top

<table>
<thead>
<tr>
<th>Samples</th>
<th>Length (µm)</th>
<th>Average inner diameter (nm)</th>
<th>Wall thickness (nm)</th>
<th>Outer diameter (nm)</th>
<th>Length to diameter ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-step</td>
<td>2</td>
<td>55 ± 0.05</td>
<td>13 ± 0.05</td>
<td>81 ± 0.05</td>
<td>24.69</td>
</tr>
<tr>
<td>2-step</td>
<td>4</td>
<td>57 ± 0.05</td>
<td>14 ± 0.05</td>
<td>85 ± 0.05</td>
<td>47.05</td>
</tr>
</tbody>
</table>

Fig. 2. FESEM images of (a-1) surface of Ti and (b-1) etched Ti substrate, (a-2) surface of 1-step and (b-2) 2-step TiO2 nanotubes, (a-3, a-4) cross section view of 1-step and (b-3, b-4) cross section of 2-step TiO2 nanotubes, and EDX analysis of (c-1) Ti, (c-2) etched Ti (c-3) 1-step and (c-4) 2-step TiO2 nanotubes.
(please see Fig. 2).

To identify the elements that exist in the as-prepared photocatalysts, the EDX analysis was done and the results are exhibited in Figs. 2(c-1)-2(c-4), respectively. It is clear from Figs. 2(c-1) and 2(c-2), the Ti peaks are the only dominate peaks in pure Ti substrates. The EDX analysis confirmed that both prepared TiO$_2$ nanotubes by 1-step and 2-step-anodization mainly consist of Ti and O with some dopants including C and F species. The origin of carbon and fluorine species come from the electrolyte precursors i.e. ethylene glycol and ammonium fluorid, respectively.

By using structural parameters, porosity of the TiO$_2$ nanotubes, \( P \), i.e. surface area occupied by pores divided to the total surface area) and roughness factor of the TiO$_2$ nanotubes \( G \), i.e. the ratio of the total area to the projected area), can be estimated using equations (5) and (6), respectively [28]:

\[
P = 1 - \frac{2\pi w (w + d)}{\sqrt{3} (d + 2w)^2} \tag{5}
\]

\[
G = 1 + \frac{4\pi L (w + d)}{\sqrt{3} (d + 2w)^2} \tag{6}
\]

where \( L \), \( d \), and \( w \) are the respective, length, pore inner diameter and a wall thickness of the TiO$_2$ nanotubes.

Also, total surface area \( (SA) \) of the TiO$_2$ nanotubes can be obtained from the nanotubes structural properties by applying the equations as follows [23]:

\[
SA = \frac{4L(D_{int} - D_{ext})}{D_{ext}^2} \tag{7}
\]

where \( L \), \( D_{int} \), and \( D_{ext} \) are the average nanotube length (\( \mu \)m), inner diameter (nm) and outer diameter (nm), respectively. Based on the equivalent size parameters obtained from the FESEM analysis in Table 1 and equations (5)-(7), the porosity, the roughness factor and total surface area are calculated and presented in Table 2.

According to Table 2, although the anodization step doesn’t have a drastic effect on the porosity of the TiO$_2$ nanotubes, it has an efficient impact on roughness factor and surface area of the TiO$_2$ nanotubes. Fabrication TiO$_2$ nanotubes by 2-step anodization leads to an evident increment in the roughness factor from 151 to 286 and surface area from 69 to 128 m$^2$, respectively.

### 3.2. Evaluation crystal phase

The crystal structure of the as-prepared samples is investigated using XRD analysis. Fig. 3 indicates the XRD patterns of 1-Step and 2-Step TiO$_2$ nanotubes. XRD data reveal that the main phase of all the samples can be identified as the anatase phase of TiO$_2$ (JCPDS card 21-1272). In detail, as indicated in Fig. 3, the main diffraction peaks at 2\( \theta \) = 25.5°, 37.3°, 38.1°, 48.2°, 54.2° and 55.2°, which are corresponded to the Miller indexes (101), (103), (004), (200), (105) and (211), respectively, can be interpreted as characteristic peaks of anatase phase to the Miller indexes (101), (103), (004), (200), (105) and (211), respectively.

The angular 2\( \theta \) = 25.5° for anatase and 2\( \theta \) = 27.5° for rutile and by applying the equations as follows [23]:

\[
f_1 = \frac{K_4 \times I_4}{(K_4 \times I_4 + I_0)} \tag{8}
\]

Where \( f_1 \) is the volume fractions of the anatase phases, respectively, \( I_4 \) and \( I_0 \) correspond to the diffraction peak intensities of anatase (101) and rutile (110), respectively, and \( K_4 \) is a constant equaling to 0.886. According to Fig. 3 and based on equation (8), all calcined nanotubes have approximately 88% anatase phases. It is worth noting that the studies conducted by Yu and Bo [9] and Zhang et al. [17] revealed the photocatalytic activity of TiO$_2$ nanotubes are substantially increased when sample containing both anatase and rutile crystalline phases compared to single crystal sample. Since anatase is well known for its better photocatalytic activity and rutile is well known to have smaller band gap than anatase (3.2 eV for anatase and 3.0 eV for rutile), so the composite of two crystalline phases can be beneficial in reducing the recombination of photo-generated electrons and holes and enhancing photocatalytic activity [18].

#### 3.3. Determination optical absorption

Fig. 4(a) shows the UV-vis diffuse reflectance absorption spectra (DRS) of 1-Step and 2-Step TiO$_2$ nanotubes. DRS studies help to understand the band gaps of the material. The band gaps change during the photoreaction as the catalysts are exposed to photons with different energies. The chemistry involved could be highlighted by these changes. Seen from Fig. 4, both as-fabricated 1-step and 2-step TiO$_2$ nanotubes exhibited typical UV light absorption spectrum, based on the electronic transition from O$^2-$ anti-bonding orbital to the lowest empty orbital of Ti$^{4+}$ (O$^2-$ Ti$^{3+}$) [23,31]. In addition, both samples showed strong visible light absorption, that probably caused by the trapped charge carriers or some color centers, as well as the absorption of incident light by the nanotubes [31,32]. The value of band gap of the samples can be estimated through equation (9) [23]:

\[
(\alpha h\tilde{\nu})^{1/2} = A(h\tilde{\nu} - E_g) \tag{9}
\]

where \( E_g \) is the band gap energy of the material, \( h \) is Planck's constant, \( \tilde{\nu} \) is the frequency of vibration, \( h\nu \) is the energy of the incident photon, \( A \) is a proportional constant and \( \alpha \) is the coefficient of absorption per unit length (cm$^{-1}$). Fig. 4(b) shows the plots of \((\alpha h\tilde{\nu})^{1/2}\) versus photon energy (h\( \tilde{\nu} \)) plot to \( \alpha \to 0 \), \( E_g \) of the samples was obtained. According to Fig. 4(b), the calculated band gap value for 1-step and 2-step TiO$_2$ nanotubes are 3.1 eV and 3.05 eV, respectively. This result demonstrates that compare to the band gap of commercial TiO$_2$ which is ~3.2 eV [33], the nanotubular structure of TiO$_2$ decreases TiO$_2$ band gap. The visible light responsive ability of 1-step and 2-step TiO$_2$ nanotubes can be ascribed to two reasons. First, the coexistence of different crystal phases that mainly involving anatase and rutile, can reduce the recombination of photo-generated electrons and holes due to the rutile smaller band gap of 3.0 eV. As a result, the composite of two crystalline phases with extending wavelengths into visible light can enhance photocatalytic activity under visible light irradiation. Second, the fabrication of TiO$_2$ nanotubes by anodization process leads to introduce some species such as carbon and fluorine into the structure of the TiO$_2$ nanotubes. As a consequence of the presence of such elements, the recombination of electron-hole pairs can be suppressed and accordingly the photocatalytic activity can be improved under both UV and visible light irradiation. Therefore, both 1-step and 2-step TiO$_2$ nanotubes not only promote UV adsorption but also should possibly be responsive to the visible light.

### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Porosity</th>
<th>Roughness factor</th>
<th>Surface area (m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-step</td>
<td>0.51</td>
<td>151</td>
<td>69</td>
</tr>
<tr>
<td>2-step</td>
<td>0.50</td>
<td>286</td>
<td>128</td>
</tr>
</tbody>
</table>
3.4. Functional group analysis of \( \text{TiO}_2 \) nanotubes

The functional groups that present in synthesized photocatalysts can be determined by FTIR as shown in Fig. 5. The peaks observed at around 3420 and 2925 cm\(^{-1} \) are ascribed to the Ti-OH bond \([34]\). The spectra indicate comparatively robust band at around 1630 cm\(^{-1} \) shown for both samples resulted from the OH bending vibration of chemisorbed and/or physisorbed water molecule on the surface of the catalysts \([35]\). The broad absorption peak from 800 cm\(^{-1} \) to 500 cm\(^{-1} \), with maximum absorption at around 645 cm\(^{-1} \), is attributed to the asymmetric stretching, symmetric stretching, and the bending modes of Ti–O–Ti bond, respectively \([36]\). Also, the band peaking at around 1400 cm\(^{-1} \) appeared in both spectra are respectively allocated to the stretching and bending modes of the hydroxyl groups surfaces \([36]\). For both samples, a small peak at around 3780 cm\(^{-1} \) which is assigned as O-H stretching of the hydroxyl group to Ti atoms was observed \([33]\).

3.5. The adsorption capacity of photocatalysts

The photocatalytic process needs first to transfer the pollutants to the catalyst surface, so the adsorption capacity is the important index of the photocatalyst degradation ability \([3]\). UV-vis absorbance spectra of 2,4-dichlorophenol adsorption by 1-step and 2-step \( \text{TiO}_2 \) nanotubes arrays are shown in Fig. 6(a). As we can see in Fig. 6 (a), the adsorption was followed by UV-vis spectroscopy at 227 nm corresponding to the maximum absorption peak of 2,4-dichlorophenol. According to the Beer-Lambert law \([15]\):

\[
\text{Abs} = \epsilon b C
\]

where \( \text{Abs} \) is the measured absorbance, \( b \) is the path length, \( \epsilon \) is the wavelength dependent molar absorptivity coefficient, and \( C \) is the analyte concentration, thus \( C/C_0 = A/A_0 \) can be easily obtained, where \( C_0 \) is the preliminary concentration of the 2,4-dichlorophenol, \( A_0 \) is the absorbance value at 227 nm of the 2,4-dichlorophenol aqueous solution before UV irradiation. Consequently, based on \( C/C_0 = A/A_0 \), the percentage of the degradation of 2,4-dichlorophenol (or adsorption) against irradiation time can be calculated as follow \([28]\):

\[
X_{\text{DCP}} = (1 - C/C_0) \times 100 = (1 - A/A_0) \times 100
\]

where \( X_{\text{DCP}} \) is the percentage of the degradation of 2,4-dichlorophenol. The adsorption capacity of 2,4-dichlorophenol on as-fabricated photocatalysts are shown in Fig. 6(b). According to Figs. 6(b), 30% and 23% of the 2,4-dichlorophenol molecules were adsorbed on 2-step and 1-step \( \text{TiO}_2 \) nanotubes, respectively. According to Fig. 2, since the 2-step \( \text{TiO}_2 \) nanotubes have the more orderliness structure than 1-step \( \text{TiO}_2 \) nanotubes, so the 2,4-dichlorophenol molecules can easily diffuse and adsorbed on the nanotubes inner surfaces.

3.6. Photoelectrochemical measurement

Photocurrent measurement was used to evaluate the charge separation in the as-prepared photocatalysts. In this regard, larger photocurrent means higher separation efficiency and more photo-generated electrons. Therefore, several photoelectrochemical measurements are performed to assess the water splitting on 1-step and 2-step \( \text{TiO}_2 \) nanotubes.

The characteristics of the photocurrent density-voltage (j-V) curves were recorded in dark, under UV and visible light illumination, and are demonstrated in Fig. 7(a). In the dark, current is so low that can be negligible and the photocurrents are determined from the measured currents subtracting the respective dark one. Also, the dark result indicated that no electrochemical oxidation happened in the darkness. As shown in Fig. 7(a), anodization steps have a significant effect on the photoelectrochemical properties. Under illumination, the saturated photocurrent density of 2-step \( \text{TiO}_2 \) nanotubes is much higher compared to 1-step \( \text{TiO}_2 \) nanotubes in the linear-sweep voltammograms. This result indicates that the photo-generated electrons on the 2-step \( \text{TiO}_2 \) nanotubes can be faster transported to the counter electrode, and greater water splitting efficiency can be expected. Since the photo-energy of UV irradiation is further than photo-energy of visible light, so it is evident that more photocurrent density and electron-hole pairs generate under UV illumination as compared to the visible light illumination \([33]\).

The flat band potential \( (E_0) \) for the \( \text{TiO}_2 \) nanotube was estimated using the modified Gärtner-Butler equation as follow \([37]\):

\[
j_p = \left( \frac{2q\varepsilon_0\lambda^2}{N_d} \right) \left( E - E_0 \right)
\]

where \( j_p \) is the photocurrent density, (\( q \) is the electron charge, \( \varepsilon \) is the dielectric constant, \( \varepsilon_0 \) is the permittivity of free space, \( I_0 \) is the photon flux, \( \alpha \) is the absorption coefficient, \( N_d \) is the effective density of states.
at the conduction band edge, $E$ is the bias potential and $E_{fb}$ is the flat band potential, respectively. According to equation (12), linear plot of the square of the photocurrent density versus bias potential allows to determination of the flat band potential as the intercept with the potential axis at $(j_p)^2 = 0$. The calculated flat-band potentials for all samples are represented in Table 3. By comparison, the $E_{fb}$ obtained for the 2-step TiO$_2$ nanotubes under both UV and visible illumination is more than the $E_{fb}$ obtained for the 1-step TiO$_2$ nanotubes. Notably, compared to 1-step TiO$_2$ nanotubes, a positive shift of $E_{fb}$ in 2-step TiO$_2$ nanotubes demonstrates a decrease in bending of the band edge, thereby facilitating the photo-generated electron separation and transfer [38].

**Fig. 7(b)** shows the transient photocurrent density of 2-step and 1-step TiO$_2$ nanotubes photoelectrodes by several on-off cycles under the UV and visible light illumination. It should be indicated that the photocurrent went down to zero as soon as the irradiation of light was stopped, while subsequently shifted to original value as soon as the light was switched on again, indicating that the photo-generated current was completely caused by the activity of the as-fabricated TiO$_2$ nanotubes photoelectrode. Additionally, the 2-step TiO$_2$ nanotubes photo-anode exhibits higher photocurrent (0.677 mA cm$^{-2}$ under UV and 0.306 mA cm$^{-2}$ under visible) compared to the 1-step TiO$_2$ nanotubes (0.383 mA cm$^{-2}$ under UV and 0.121 mA cm$^{-2}$ under visible), demonstrating that 2-step TiO$_2$ nanotubes possess higher separation efficiency of photo-generated charge carriers and photocatalytic performance.
Fig. 5. FTIR spectra of the 1-step and 2-step TiO$_2$ nanotubes.

Fig. 6. (a) UV–vis absorbance of 2,4-dichlorophenol during adsorption on 1-step and 2-step TiO$_2$ nanotubes, and (b) Adsorption capacity of 1-step and 2-step TiO$_2$ nanotubes.
The hydrogen production efficiency (photoconversion efficiency) of the prepared samples is determined by the following equation [38]:

$$\eta(\%) = \frac{j_p \left[E_0^0 - |E_{app}|\right]}{I_0} \times 100$$ (13)

where $\eta$ is the photoconversion efficiency, $j_p$ is the photocurrent density (mA.cm$^{-2}$), $I_0$ means the intensity of the incident light, $E_0^0$ represents the standard changeable potential (1.23 V vs. RHE), and $|E_{app}|$ denotes the absolute value of the applied voltage which is obtained from $E_{app} = E_{meas} - E_{aoc}$, where $E_{meas}$ is the electrode potential (vs. Ag/AgCl).

### Table 3

The photoelectrochemical properties recorded on 0 V vs. Ag/AgCl reference electrode.

<table>
<thead>
<tr>
<th>Illumination</th>
<th>Samples</th>
<th>Photocurrent (mA.cm$^{-2}$)</th>
<th>Photoconversion efficiency (%)</th>
<th>$E_{fb}$ (V vs. RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>1-step</td>
<td>0.21</td>
<td>0.18</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>2-step</td>
<td>0.33</td>
<td>0.29</td>
<td>0.68</td>
</tr>
<tr>
<td>Visible</td>
<td>1-step</td>
<td>0.05</td>
<td>0.04</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>2-step</td>
<td>0.10</td>
<td>0.09</td>
<td>0.50</td>
</tr>
</tbody>
</table>

### Fig. 7

Photoelectrochemical properties of the 1-step and 2-step TiO$_2$ nanotubes: (a) linear-sweep voltammograms, (b) the transient photocurrent response, and (c) photoconversion efficiency.

### Fig. 8

Photocatalytic degradation of 2,4-dichlorophenol by 1-step and 2-step TiO$_2$ nanotubes under (a) visible light irradiation, and (b) UV irradiation.
2-step TiO2 nanotubes.

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open mouth (please see Fig. 2 and Table 2). By contrast, the synthesized area, roughness factor, and very orderliness structure and well-de

1-step TiO2 nanotubes exhibit very disorder patterns on the upper surface and weak ordered structure, hence generate the lowest photocurrent density.

Table 4
Fitting parameters of the photocatalytic kinetics for determination the reaction rate order.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reaction rate order</th>
<th>Correlation coefficient (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Visible light</td>
</tr>
<tr>
<td>1-step</td>
<td>n = 0</td>
<td>0.9844</td>
</tr>
<tr>
<td></td>
<td>n = 1</td>
<td>0.9876</td>
</tr>
<tr>
<td></td>
<td>n = 2</td>
<td>0.9696</td>
</tr>
<tr>
<td>2-step</td>
<td>n = 0</td>
<td>0.9820</td>
</tr>
<tr>
<td></td>
<td>n = 1</td>
<td>0.9836</td>
</tr>
<tr>
<td></td>
<td>n = 2</td>
<td>0.9626</td>
</tr>
</tbody>
</table>

at which j_p is measured and E_moc is the electrode potential (vs. Ag/AgCl) at open circuit under illumination. Plots of photoconversion efficiency with applied potential are presented in Fig. 7(c). A maximum photoconversion efficiency of 0.29% (under UV) and 0.09% (under visible) are obtained for 2-step TiO2 nanotubes electrode, while they are only 0.18% (under UV) and 0.04% (under visible) for 1-step TiO2 nanotubes electrode at 1 V (vs. RHE). Based on the above results, we confirmed that the highly ordered 2-step TiO2 nanotube intensifies its photocurrent density and photoconversion efficiency in both UV and visible regions.

Following the above results, to have a clear insight about the relation between photoelectrochemical measurements and photocatalytic activity of TiO2 nanotubes, the photocurrent density and photoconversion efficiency on 1-step and 2-step TiO2 nanotubes are recorded on 0 V against Ag/AgCl reference electrode and are presented in Table 3. The reason for choosing this voltage (0 V) is that the photocatalytic processes are basically performed in the absence of external potential. According to Table 3, the photocurrent and photoconversion efficiency under UV illumination on 2-step TiO2 nanotubes are 1.57 and 1.61 times more than on 1-step TiO2 nanotubes, respectively. Also, under visible illumination, the photocurrent and photoconversion efficiency on 2-step TiO2 nanotubes are 2 and 2.25 times more than on 1-step TiO2 nanotubes, respectively. So in the photocatalytic process, the 2-step TiO2 nanotubes can have the efficient performance compared to the 1-step TiO2 nanotubes.

To sum up, the photoelectrochemical results revealed that the 2-step TiO2 nanotubes have the best performance to generate electron-hole (e⁻/h⁺) pairs and charge carrier separation as in comparison with the 1-step TiO2 nanotubes under both UV and visible illumination. This is mainly because that the 2-step TiO2 nanotubes have the larger surface area, roughness factor, and very orderliness structure and well-defined open mouth (please see Fig. 2 and Table 2). By contrast, the synthesized 1-step TiO2 nanotubes exhibit very disorder patterns on the upper surface and weak ordered structure, hence generate the lowest photocurrent density.

3.7. Performance of photocatalytic degradation

Fig. 8(a) and (b) show employing the 1-step and 2-step TiO2 nanotubes in degradation of 2,4-dichlorophenol under visible light and UV irradiation, respectively. Based on Fig. 8, it should be mentioned that from the irradiation time the photocatalytic degradation started (zero time), and before that, it is related to the existence of samples in the pollutant solutions in the dark place. The slight concentration variations in the dark place are as a result of the penetration of pollutants into the nanotubes and their adsorption by the nanotubes’ surface. As shown in Fig. 8, examination of the self-degradation of 2,4-dichlorophenol with no photocatalyst under visible light and UV irradiation showed that the photolysis of 2,4-dichlorophenol was negligible, and only decreased by 4% without the photocatalyst under UV irradiation for 240 min. Based on Fig. 8(a), it can be seen that under visible light irradiation, the TiO2 nanotubes have the photocatalytic ability. Under visible light irradiation, the 2-step TiO2 nanotubes showed a 2,4-dichlorophenol removal efficiency of 55%, higher than 47% over 1-step TiO2 nanotubes. This is caused by the narrow-band-gap of 2-step TiO2 nanotubes in comparison with the 1-step TiO2 nanotubes (please see Fig. 4). The narrow-band-gap not only promotes UV adsorption but also should possibly be responsive to the visible light.

Fig. 8(b), represents the photocatalytic degradation of 2,4-dichlorophenol by 1-step and 2-step TiO2 nanotubes under UV irradiation. As shown in Fig. 8(b), the 72% degradation efficiency of 2,4-dichlorophenol achieved on the 2-step TiO2 nanotubes, which is greater than 58% over 1-step TiO2 nanotubes under UV irradiation. In the general mechanism of photocatalytic degradation, electron transport is a restraining factor for the photocatalytic performance of TiO2 materials, however, the TiO2 structure is a critical factor in the efficiency of electron transport [19]. The light penetration and pollutant diffusion into TiO2 nanotubes, which prepared by 1-step and 2-step anodization, are schematically illustrated in Fig. 9. The amount of holes and electrons available in the TiO2 nanotubes surface is obviously related to the light absorbed by the TiO2 nanotubes [39]. Whatever the more light be absorbed by TiO2 nanotubes, charge carriers are photogenerated in the TiO2 layer that have to be rapidly transferred to the solution species before recombination. So by checking the process of recombination, more active sites will be available for reacting with pollutants to degrade them [22,27]. As shown in Fig. 9, 2-step TiO2 nanotubes improve the charge transfer in addition to the enhanced light absorption in comparison with the 1-step TiO2 nanotubes. In contrast, it is obvious that the more orderliness structure of 2-step than 1-step TiO2 nanotubes leads to 2,4-dichlorophenol molecules can easily transfer to the active cationic sites and trap the entire surface holes [14,39]. Thereby 2-step TiO2 nanotubes by decreasing the charges accumulate, lead to increased photocatalytic efficiency as a result of the recombination process.

Furthermore, based on Table 2, it can be seen that the surface area,
porosity, and length to diameter ratio of the TiO2 nanotubes increased with the creation of TiO2 nanotubes by 2-step anodization. The increment of the length to diameter ratio in the TiO2 nanotubes results in greater light absorption, thus, it leads to the greater photocatalytic degradation rate. Indeed, the roughness factor expresses the real surface area developed by the photocatalyst. So the increment in the roughness factor and surface area provide more active sites for the photocatalytic reactions progress and finally improves the catalytic efficiency. Moreover, based on Table 2, the decrease of the 2-step TiO2 nanotubes’ porosity is another reason for the increase in the photocatalytic efficiency, as compared to the 1-step TiO2 nanotubes’ porosity. The low porosity of the TiO2 nanotubes not only provides an effective electron transfer path, but also an effective blocking layer, which prevents the recombination of photo-generated electrons [28]. Retarding the recombination process leads to the creation of more active sites for the oxidation and reduction reactions, therefore, it increases the photocatalytic efficiency.

To sum up, the consequences of photocatalytic activity of prepared catalysts in degradation of 2,4-dichlorophenol are in good agreement with the achieved results from photoelectrochemical measurements, where presented in Fig. 7. The 2-step TiO2 nanotubes by decreasing the porosity and increasing the surface area, roughness factor, and length to diameter ratio, respectively, lead to further absorption of light, increasing photocurrent density and photoconversion efficiency, retarding the electron-hole pairs recombination and increasing the active sites for photocatalytic degradation. Therefore, the 2-step TiO2 nanotubes can improve the photocatalytic degradation in comparison with the 1-step TiO2 nanotubes.

Fig. 10. First-order kinetic model for degradation of 2,4-dichlorophenol by the 1-step and 2-step TiO2 nanotubes under (a) visible light irradiation, and (b) UV irradiation.
3.8. Kinetics of photocatalytic degradation

In the following equation the generalized rate for degradation of 2,4-dichlorophenol is presented [40]:

\[ r = -\frac{dC}{dt} = kC^n \]  
\[ \text{(14)} \]

where \( r \) is the rate of photocatalytic reaction, \( k \) is rate constant, \( C \) is the concentration of 2,4-dichlorophenol in the bulk solution as a function of time \( t \), and \( n \) is the reaction rate order. If the reaction follows zero-order kinetics (\( n = 0 \)), after separating and integrating of both sides of equation (14), equation (15) which indicates the zero-order kinetics is obtained:

\[ C = -kt + C_0 \]  
\[ \text{(15)} \]

If the reaction follows first-order kinetics (\( n = 1 \)), after separating and integrating of both sides of equation (14), equation (16) which indicates the first-order kinetics is obtained:

\[ \ln\left( \frac{C}{C_0} \right) = kt \]  
\[ \text{(16)} \]

If the reaction follows second-order kinetics (\( n = 2 \)), after separating and integrating of both sides of equation (14), equation (17) which represents the first-order kinetics is obtained:

\[ \frac{1}{C} = kt + \frac{1}{C_0} \]  
\[ \text{(17)} \]

In all of the aforementioned equation, \( C_0 \) is the primary concentration of 2,4-dichlorophenol and is equal to 30 ppm.

Table 4, represents all the fitting parameters of the photocatalytic kinetics. It can be seen from Table 4 that the first-order kinetics for both samples have the highest correlation coefficient value (\( R^2 \)) which is higher than 0.99 under UV irradiation and higher than 0.98 under visible light, respectively. This result indicates that the exponential model can well describe the visible light, respectively. This result indicates that the exponential model can well describe the visible light, respectively.

3.9. Mechanism of 2,4-dichlorophenol degradation

Fig. 11 illustrates the mechanism of 2,4-dichlorophenol degradation by TiO2 nanotubes. Reactions (18)–(23) briefly summarize the photocatalytic reaction to further clarify the mechanism, in Refs. [23,28].

\[ \text{TiO}_2 + \text{Energy (heat or light)} \rightarrow h^+_\text{ads} + e^-_\text{ads} \]  
\[ \text{(18)} \]

\[ h^+_\text{ads} + \text{pollutant} \rightarrow \text{pollutant}^+ \rightarrow \text{degradation products} \]  
\[ \text{(19)} \]

\[ O_2(\text{ads}) + e^-_\text{ads} \rightarrow O_2^- \]  
\[ \text{(20)} \]

\[ H_2O + h^+_\text{ads} \rightarrow \text{OH}^+ + H^+ \]  
\[ \text{(21)} \]

\[ O_2^- + \text{pollutant} \rightarrow \text{degradation products} + CO_2 \]  
\[ \text{(22)} \]

\[ \text{OH} + \text{pollutant} \rightarrow \text{degradation products} + CO_2 \]  
\[ \text{(23)} \]

Where \( e^-_\text{ads} \) and \( h^+_\text{ads} \) are the electron in the conduction band and the positive hole in the valence band, respectively, while the subscripts 'ads' denote the adsorbed forms of the O2 molecule.

Based on the reaction (18), when the radiated light energy is equal to or higher than the TiO2 nanotubes' band gap energy, the valence band electrons are excited. These electrons travel to the conduction band to create electron-hole pairs in TiO2 nanotubes. Actually, photocatalytic reactions are occurred by either the direct or indirect processes. The pollutants are adsorbed on the surface of the photocatalyst through the direct process. They have reaction with the active cationic sites and are degraded (the reaction (19)). In the indirect process, the oxygen and water molecules are adsorbed on the photocatalyst's surface. These molecules react with the electron-hole pairs (the reactions (20) and (21)) to produce the unstable hydroxyl radicals ('OH') and superoxide ions ('O2^-') which oxidize the organic pollutants into the inorganic compounds (the reactions (22) and (23)). To further verify the mechanism of 2,4-dichlorophenol degradation and identify the photocatalytic degradation pathways, free radical capture studies were performed by using AO, t-BuOH, AgNO3 and BZQ as \( h^+ \), 'OH, e^- and 'O2^- scavengers, respectively. The results of this examination are presented in Fig. 12. Based on Fig. 12(a), it can be seen the addition of 1 mM AO dramatically reduced the degradation efficiency from 72% to 30%. It means \( h^+ \) plays an important role in the photocatalytic degradation of 2,4-dichlorophenol by TiO2 nanotubes. As explained in Fig. 11, \( h^+ \) can degrade pollutant in two pathways including direct reaction with \( h^+ \) ('the reaction (19)) or indirect reaction with produced hydroxyl radicals (the reactions (21) and (23)). The effect of the pathway with the participation of hydroxyl radicals was examined by using t-BuOH as 'OH scavenger. The results indicated that 'OH is the main reactive species in the photocatalytic degradation of 2,4-dichlorophenol over TiO2 nanotubes which by it scavenging the

Fig. 11. A depiction of the photocatalytic mechanism for degradation of 2,4-dichlorophenol by highly ordered TiO2 nanotubes.
degradation efficiency dropped up to 42%. Moreover, a significant inhibition of 2,4-dichlorophenol photocatalytic degradation was also observed in the presence of AgNO3. By introduction of 1 mM AgNO3 to the photocatalytic reactor, the degradation efficiency decreased from 72 to 40%. It illustrates the key roles of e− in the photocatalytic degradation and dechlorination process. The addition of 1 mM BZQ exhibited that O2− species have a little effect on photocatalytic degradation of 2,4-dichlorophenol which the degradation efficiency lessened only 7% by capturing of superoxide anion radicals. Now according to obtained result, we can distinguish the contribution of each reactive species in photocatalytic degradation of 2,4-dichlorophenol by TiO2 nanotubes. As shown in Fig. 12(b), the primary photocatalytic degradation of 2,4-dichlorophenol occurred through h+ pathways which 41% of degradation was attributed to the reaction with hydroxyl radicals and 16% of degradation was related to the direct reaction with h+ species. In the next stage, the photocatalytic degradation pathway continued via reaction with e−, which accounts for 35% of the 2,4-dichlorophenol decomposition. Also, superoxide anion radicals play a minor role in 2,4-dichlorophenol degradation over TiO2 nanotubes, which accounts for around 8% of the 2,4-dichlorophenol degradation.

3.10. Identification of 2,4-dichlorophenol degradation products

The intermediate types made during degradation of 2,4-dichlorophenol, were recognized by GC–MS. The major reaction intermediates identified in an aliquot withdrawn after 240 min following a degradation are presented in Fig. 13 and Table 5 under UV irradiation which specified in Fig. 8. The existence of carboxylic acid intermediates in the chromatogram indicates the involvement of hydroxyl radicals in attacking 2,4-dichlorophenol. The degradation process leads to simple
acids such as acetic acid, oxalic acid, etc. as the final products [41, 42]. Some intermediates identified in this study (Table 5) were also reported formerly for the photodegradation of 2,4-dichlorophenol by photocatalysts with phthalocyanines, and without TiO2 nanotubes [43]. Chloride ions were also detected and identified as one of the final products of the photocatalytic degradation, in addition to identifying the organic intermediates. The content of Cl⁻ in the reaction media after the completion of the photocatalytic experiment nearly matches to the amount of chlorine present in 2,4-dichlorophenol, which indicates the essentially complete mineralization.

Based on these findings, a possible process diagram for the degradation of 2,4-dichlorophenol by TiO2 nanotubes was suggested and illustrated in Fig. 14. First, 2,4-dichlorophenol is oxidized by TiO2 nanotubes photocatalysts and transforms into hydroxylated intermediates. Because of the electron-donating behavior of the phenolic OH group and the electrophilicity of the radicals, the attack of hydroxyl radical occurs most favorably at para- and ortho-position of the phenolic ring and leads to its hydroxylation. These intermediates are easy to dechlorinate, forming semiquinones. Finally, by further oxidation the benzene rings are broken and the major products are organic acid such as maleic acid, oxalic acid and formic acid. Eventually all these acids can be degraded completely into CO₂ and H₂O.

### Table 5

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>Identified intermediate</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6</td>
<td>Methyl 2-methoxy acetate</td>
<td>H₃COC(H₂)COOCH₃</td>
</tr>
<tr>
<td>6.48</td>
<td>Methyl oxalate</td>
<td>H₂COOCOOCH₂</td>
</tr>
<tr>
<td>8.96</td>
<td>Dimethyl maleate</td>
<td>H₂COOCCH=CHCOOCH₃(z)</td>
</tr>
<tr>
<td>11.44</td>
<td>Dimethyl succinate</td>
<td>H₂COOCCH₂CH₂COOCH₃</td>
</tr>
</tbody>
</table>

3.11. Stability

Stability is a key parameter for nanostructures in the application of photocatalytic degradation. Five consecutive photocatalytic experiments were conducted under similar experimental conditions, to investigate the stability of the 2-step TiO2 nanotubes under UV irradiation. The changes of 2,4-dichlorophenol concentration and photocatalytic reaction rate constant after five cycles are presented in Fig. 15(a) and (b), respectively. According to Fig. 15, the photocatalytic efficiency and rate constant did not exhibit any significant decline even after five recycles. After five catalytic cycles, the photocatalytic efficiency and rate constant decreased from 72% to 68% and from 0.0046 min⁻¹ to 0.0042 min⁻¹, respectively. These slight changes indicate that 2-step TiO2 nanotubes involve a greater mechanical robustness, low photo-corrosion and good chemical stability during the...
photocatalytic degradation of 2,4-dichlorophenol under UV light irradiation. Therefore, it can be stated that the 2-step TiO$_2$ are stable catalysts and that they could be regarded as versatile candidates for practical use in water and wastewater treatment.

4. Conclusion

In summary, TiO$_2$ nanotubes were made by 1-step and 2-step anodization process on two different substrates Ti and etched-Ti foils. The influence of etching step on the morphology of the surface, geometrical properties, photoelectrochemical features and photocatalytic activity of the obtained TiO$_2$ nanotubes was investigated. The FESEM result demonstrated that the etching step has great influence on the growth mechanism and geometrical properties of TiO$_2$ nanotubes. The 2-step anodization led to a drastic increment in the length of the nanotubes from 2 $\mu$m for 1-step TiO$_2$ nanotubes to 4 $\mu$m for 2-step TiO$_2$ nanotubes. Moreover, the TiO$_2$ nanotubes prepared by 2-step anodization showed the best photoelectrochemical performance among the two samples due to their higher roughness factor, surface area, and length to diameter ratio as well as very orderliness structure and well-defined open mouth. Furthermore, the photocatalytic activity of prepared catalysts in degradation of 2,4-dichlorophenol was in good agreement with the achieved results from photoelectrochemical measurements. The prepared TiO$_2$ nanotubes by 2-step anodization under visible light and UV irradiation had the best photocatalytic activity by 55% and 72% degradation of 2,4-dichlorophenol, respectively. Actually, these improvements are caused by the more light harvesting, increasing photocurrent density and photoconversion efficiency, retarding the recombination of electron–hole pairs and increasing the active sites for photocatalytic degradation. Eventually in this research, the 2-step TiO$_2$
nanotubes with the highest length to diameter ratio (47), surface area (128 m²) and roughness factor (286), and the lowest porosity (0.5%) under visible light and UV irradiation had the highest reaction rate constant in the degradation of 2,4-dichlorophenol with the values of 0.0025 min⁻¹ and 0.0046 min⁻¹, respectively.

Acknowledgments

The authors would like to acknowledge College of Engineering, University of Tehran, and Iran National Science Foundation (INSF) for their esteemed financial support.

References


Nomenclature

UV: Ultra-violet radiation
Δ: Nanotubes inner diameter (nm)
W: Nanotubes wall thickness (nm)
L: Nanotubes length (m)
P: Porosity
R: Roughness factor
V: Volume fraction of the anatase
D: Diffusion peak intensities of anatase
R: Diffraction peak intensities of rutile
C: Concentration of 2,4-dichlorophenol (ppm)
I: Initial concentration of 2,4-dichlorophenol (ppm)
A: Absorbance value of the 2,4-dichlorophenol at 277 nm
A: Initial absorbance value of the 2,4-dichlorophenol at 277 nm
c: Photocatalytic degradation time (min)
κ: Reaction rate constant
x: Percentage of 2,4-dichlorophenol degradation
E: Energy of band gap
H: Planck's constant
B: Path length
SA: Surface area of nanotubes
Dint: Average inner diameter of nanotubes (nm)
Dext: Average outer diameter of nanotubes (nm)
\( R^2 \): Correlation coefficient
\( E_{\text{ERHE}} \): Potential vs. reversible hydrogen electrode
\( E_{\text{Ag/AgCl}} \): Potential vs. Ag/AgCl electrode
\( J_p \): Photocurrent density
\( I_0 \): Intensity of the incident light
\( E_{\text{app}} \): Applied voltage
\( E_{\text{meas}} \): Electrode potential vs. Ag/AgCl
\( E_{\text{eo}} \): Electrode potential vs. Ag/AgCl at open circuit
\( E_{fb} \): Flat band potential

Q: Electron charge
\( N_E \): Effective density of states at the conduction band edge

\textit{Greek symbol}

\( \alpha \): Absorption coefficient
\( \omega \): Frequency of vibration
\( E \): Wavelength of molar absorptivity coefficient
\( \varepsilon \): Dielectric constant
\( \varepsilon_0 \): Permittivity of free space
\( \eta \): Photoconversion efficiency