Controllable preparation of TiO₂ nanotubes and their photocatalytic performance

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Abstract
Ethylene glycol aqueous solution containing 0.5% NH₄F was used as the electrolyte and the Ti foil was oxidized at 40 V for 30 min to obtain TiO₂ nanotube arrays with an inner diameter of about 85 nm. After heat treatment at 450 °C for 2 h, the TiO₂ nanotubes transformed from an amorphous phase to anatase, and a small percentage of the nanotubes collapsed. The Pt loaded by electrodeposition appeared at the nozzle of the nanotubes in a flake morphology. The best catalytic effect on methylene blue degradation was achieved by Pt loading with electrodeposition for 120 s. The methylene blue degradation rate reached 50% after 10 h of ultraviolet irradiation.

1. Introduction
Metal catalytic supports have many advantages over ceramic catalytic supports, such as thin walls, light weight, larger specific surface area, good ductility, and high catalytic efficiency. For example, the metal carrier materials currently used in automobile exhaust catalytic converters mainly include three different alloys: Ni-Cr, Fe-Cr-Al, and Fe-Mo-W. According to a comprehensive consideration of processing performance and economic efficiency, Fe-Cr-Al has very good application prospects in automotive catalysis [1]. Many studies have shown that Fe-Cr-Al alloy has good high-temperature oxidation resistance and that γ-Al₂O₃ film can be formed on its surface, improving its specific surface area and mechanical strength. However, the durability and stability of these Al₂O₃ films need to be improved. The Al₂O₃/316L monolithic catalyst carrier prepared by Ren et al [2] using a two-step pre-coating and secondary coating method had a uniform and smooth surface with a specific surface area of 234 mm² g⁻¹ and good gap connectivity.

Although nanomaterials have attracted much attention in the field of catalysis due to their specific properties [3, 4]. However, metals such as Ti and stainless steel can also be used as metal supports, but there are few studies on using Ti as a metal support and almost no research on the preparation of TiO₂ nanotubes on the surface of Ti for use as photocatalysts. Studies have shown that neatly structured TiO₂ nanotube arrays prepared on the surface of Ti foil have better efficiency for the catalytic degradation of methyl orange [5]. TiO₂ nanotubes are a semiconductor material with no toxicity, stable chemical properties, good biocompatibility, easy preparation, and good photocatalytic performance. Due to their excellent properties, TiO₂ nanotubes have been widely used in biomedicine, sewage treatment, solar cells, and national defense applications [6–12]. The length, diameter, and structure of TiO₂ nanotubes fabricated by anodic oxidation are influenced by many factors, including the chemical composition and pH of the electrolyte, the voltage and time of anodization, the temperature of the electrolyte, and the calcination temperature [13–15]. Some of these influencing factors have been studied by researchers. For example, Roman et al used ethylene glycol and glycine as raw materials to prepare TiO₂ nanotubes by anodization on different substrates (Ti, Ti₆Al₄V, and Ti₆Al₇Nb alloys). Their study showed that the applied potential and processing time had a certain influence on the diameter and length of their obtained nanotubes. Mohamed et al prepared nano TiO₂ by anodic oxidation in electrolytes with different viscosities such as glycine and ethylene glycol. Their results showed that the anodic oxidation voltage, oxidation time, chemical composition of the electrolyte, and pH of the electrolyte affected anodic oxidation. They reported that in the glycerol electrolyte, at least 5% water content is crucial for preparing nanotubes and that a pH value of 6 is
beneficial for preparing highly ordered and continuous nanotube arrays with a length of up to 900 nm. Xiao et al. prepared TiO$_2$ nanotube arrays by anodizing Ti foil in different electrolytes followed by calcination in dry nitrogen at different temperatures. After calcination, the conductivity and capacitance of their nanotube arrays were modified [16].

Generally, TiO$_2$ nanotubes prepared by anodic oxidation are amorphous and can be converted into anatase or rutile phases after heat treatment. However, if the heat treatment temperature is too high, the TiO$_2$ nanotubes will collapse. Nevertheless, in many potential applications, TiO$_2$ nanotubes with specific diameters, morphologies, and phases are required. So far, only a few systematic studies on the control of TiO$_2$ nanotube form and morphology on the surface of Ti foil have been reported. In addition, most existing research on TiO$_2$ nanotubes remains at the basic laboratory-scale research stage, and there are few large-scale applications in actual production and for industrial applications. The main obstacle to their practical application is the solid loading of nanotubes and the problem of product molding.

Therefore, the goal of this research was to systematically adjust the oxidation voltage, oxidation time, and heat treatment process of an anodizing oxidation method to prepare the TiO$_2$ nanotubes with controllable morphology and crystal phase on the surface of extremely easy-to-process and shape Ti foil. A cathodic deposition method was then used to load Pt on the surface of a modified foil sample to further improve its photocatalytic performance and provide a corresponding reference for its further catalytic application.

### 2. Experimental materials and methods

#### 2.1. Nanotubes preparation

A Ti foil (0.05 mm $\times$ 10 mm $\times$ 15 mm) with a purity of 99.9% was ultrasonically cleaned with acetone, absolute ethanol, and deionized water for 10 min to remove surface stains. After cleaning, the Ti foil was dried for further use. A WYK-6005K DC power supply was used for electrolysis, where the Ti foil was used as the anode, a graphite sheet was used as the cathode, the spacing was about 30 mm, and the electrolyte was an aqueous ethylene glycol solution containing 0.5 wt% NH$_4$F (volume ratio of 4:1). Anodizing voltages of 20 V, 30 V, 40 V, and 50 V were used, and the oxidation times were 0.5 h, 1 h, 2 h, and 4 h. After each reaction, the obtained sample was immediately removed from the electrolyte, rinsed with a large amount of deionized water, and naturally air-dried for further use.

#### 2.2. Heat treatment

The anodized samples were heated in a muffle furnace to 450 °C for 2 h, followed by natural cooling to room temperature.

#### 2.3. Pt loading on the surface of the sample

150 ml of 1 g l$^{-1}$ chloroplatinic acid solution was prepared as the electrolyte for the electrodeposition experiment. Unmodified Ti foil, modified Ti foil, and modified heat-treated foil were used as the cathode and graphite was used as the anode. Electrodeposition was performed at a constant current of 2 mA cm$^{-2}$ for 2 min. Each Pt-loaded sample was then removed from the electrolyte, washed with deionized water, and dried under shade at room temperature for further use.

#### 2.4. Photocatalysis

An initial methylene blue solution was adjusted to an absorbance of 1.5–1.8 using a spectrophotometer. A graduated cylinder was used to measure 50ml of the prepared methylene blue solution, which was then poured into glassware with a Ti foil sample. Covered with a glass lid, the glassware was placed into a closed environment and subjected to irradiation by ultraviolet light. The absorbance of the solution was measured every 30 min. The photocatalytic effect of each sample was characterized by the change of absorbance, as shown in equation (1).

$$\text{Photocatalytic degradation rate(\%)} = \frac{(\text{initial absorbance} - \text{absorbance after measurement})}{\text{initial absorbance}} \times 100\% \quad (1)$$

#### 2.5. Sample testing and characterization

A field emission scanning electron microscope (FESEM, Gemini, BRUKER, Germany) was used to analyze the morphology and size characteristics of the sample surfaces. An x-ray diffractometer (XRD; D8-Advance, BRUKER, Germany) was used to characterize sample phases.
3. Experimental results and discussion

3.1. TiO$_2$ nanotube arrays and its growth mechanism

The formation of TiO$_2$ nanotubes mainly goes through the following four stages: the formation of oxide layer (barrier layer), electrochemical etching process, electrochemical dissolution process and chemical dissolution process. The growth process of nanotube arrays were shown in figure 1. First of all, formation of oxide layer (barrier layer): due to the interaction between metal and O$^{2-}$ and OH$^-$. A layer of TiO$_2$ dense oxide layer is formed on the surface of Ti metal, which is the barrier layer; After the barrier layer is formed, these anions move to the metal oxide interface and react with the internal metal. Secondly, electrochemical etching process: under the action of electric field, Ti$^{4+}$ ions migrate out of the metal and reach the metal oxide interface; Then, under the action of electric field force, Ti$^{4+}$ moves from metal oxide interface to oxide electrolyte interface. And then, electrochemical dissolution process: under the action of electric field, Ti-O bond is polarized and weakened, which promotes the dissolution of Ti$^{4+}$ ions; Ti$^{4+}$ is dissolved in the electrolyte, while O$^{2-}$ migrates to the metal oxide interface and continues to react with the metal; Finally, chemical dissolution process: under the action of acid electrolyte, the metal or oxide is chemically dissolved. Chemical dissolution plays a key role in the formation of TiO$_2$ nanotubes.

\[
\begin{align*}
2H_2O & \rightarrow O_2 + 4e^- + 4H^+ \\
Ti + O_2 & \rightarrow TiO_2 \quad \text{(Electrochemical oxidation that is field assisted oxidation)} \quad (2) \\
4Ti - e^- & \rightarrow Ti^{4+} \quad \text{(Electrochemical dissolution that is field assisted dissolution)} \quad (3) \\
TiO_2 + 6F^- + 4H^+ & \rightarrow TiF_6^{2-} + 2H_2O \quad \text{(Chemical dissolution process)} \quad (4)
\end{align*}
\]

At the initial stage of the anodizing process, a strong electric field passes through the thin oxide layer. At this time, field assisted dissolution is dominant relative to chemical dissolution. Locally dissolved oxides form small pits, which become the formation center of holes. This process can be represented by reaction formulas (4) and (5). Then, the small hole formed by the concave point gradually grows, and the hole density also increases. After that, the same hole continues to expand so as to cover the whole film surface. The growth of pores is due to the inward migration of the oxide layer at the bottom of the pores, that is, the barrier layer. At the same time, Ti$^{4+}$ are removed from the metal to the oxide electrolyte interface and finally dissolved in the electrolyte. Processes was shown from (2)–(4). When the growth rate of the oxide at the metal oxide interface and the dissolution rate of the oxide at the bottom of the hole electrolyte interface reach a basic balance, the thickness of the barrier layer will not change, but with the progress of the reaction, the barrier layer advances deeper into the metal and the
length of the tube increases. When the chemical dissolution rate of the oxide at the nozzle is equal to the rate of the inward advancement of the metal oxide interface at the bottom of the pipe, the length of the pipe will not increase.

3.2. Influence of oxidation voltage on the surface morphology of TiO₂ nanotubes

The microscopic morphologies (100000×) of TiO₂ prepared after 4 h anodization at different oxidation voltages (20 V, 30 V, 40 V, and 50 V) in an aqueous solution of ethylene glycol containing 0.5 wt% NH₄F (volume ratio of 4:1) are shown in figure 1. As can be seen, a layer of uniform and regular nanotubes were formed after 4 h of oxidation at the different voltages and the nanotubes are vertically distributed on the Ti matrix. The 20 V oxidation voltage resulted in the generation of nanotubes with the smallest diameters (figure 1(A)), about 40–70 nm. The nanotubes generated under 40 V have the largest diameters of these samples. The surface of this sample is covered with many broken nanotubes. This is potentially due to the long electrolysis time increasing the dissolution time of the pits, causing the length of the nanotubes to continuously increase. However, the walls of these nanotubes may be too thin to support very long nanotubes, leading to segregation and fracture. Figures 1(B), (C) shows ring structures at the nozzles of the tubes, which might be due to the high concentration of F⁻ ions leading to slow diffusion in the ethylene glycol organic electrolyte and insufficient F⁻ ion diffusion in the nanotube micropores. This would lead to an inconsistent dissolution rate, causing the nozzles of the TiO₂ nanotubes to slightly dissolve and form a ring structure [17]. Figures 1(A)–(D) shows that as the voltage increases, the diameter of the nanotubes also increases and the structure arrangement becomes more orderly. When the voltage reaches 50 V (figure 1(D)), no nanotube structures are observed. This is because the nanotubes collapsed due to the excessively high voltage and formed a sponge-like porous structure. This is because with the increase of oxidation voltage, the dissolution rate in the reaction process is faster than that of oxidation, breaking the state that can form a tube and causing the tube to be dissolved and destroyed.

This shows that the oxidation voltage directly affects the formation of TiO₂ nanotube structures in this electrolyte. High voltages excessively increase the dissolution speed, leading to the formation of sponge-like structures.

Figure 2 shows the changes in inner diameter and wall thickness of the nanotubes prepared under different voltages (20 V, 30 V, and 40 V). As the voltage increases, the diameter of the nanotubes increases while their wall thicknesses do not significantly change. When the anodic oxidation voltage is low, the force of F⁻ ions directly impacting the Ti surface in the electrolyte is also very low, and only small pits are formed on the Ti surface. As the oxidation time increases, the pits gradually corrode to form nanotubes [13]. When the voltage increases, the pits formed by the impact of F⁻ ions in the electrolyte on the Ti surface become larger under the action of the electric field, and larger nanotubes are formed over time. Li et al reported a linear relationship between the anodic oxidation voltage and TiO₂ nanotube pore size under the condition of 0.24 wt% HF [17]. After fitting, the relationship between TiO₂ pore size (d) and oxidation voltage (U) can be described by the following equation:

\[ d = k \times U + b \]  

where the intercept \( b = 2.2 \) nm, the slope \( k = 5.2 \) nm V⁻¹, and \( 0 \leq U \leq 25 \) V.
In general, the oxidation voltage has a significant influence on the morphology of the nanotubes. Based on the results of this experiment, it can be concluded that in an aqueous solution of ethylene glycol containing 0.5 wt% NH₄F (volume ratio of 4:1), a voltage of 20 V results in nanotubes with the smallest diameter and a voltage of 40 V results in nanotubes with the largest diameter. Therefore, 40 V was determined to be the optimal oxidation voltage, and this voltage was used in subsequent experiments.

3.3. Influence of oxidation time on the surface morphology of TiO₂ nanotubes

The microscopic morphologies (200000×) of TiO₂ prepared after anodic oxidation at an oxidation voltage of 40 V for different oxidation times (0.5 h, 1 h, 2 h, and 4 h) are shown in figure 3. Neat and compact nanotube arrays were obtained under all four oxidation times. After 0.5 h (figure 3(A)), the walls of the nanotubes are relatively thick and no broken nanotube fragments are visible on the surface of the sample, unlike the samples shown in B, C, and D (representing 1 h, 2 h, and 4 h oxidation times, respectively). Figure 3(B) shows that the nanotube walls become thinner with increasing oxidation time. A small number of flake nanotube fragments are visible on the surface of these nanotubes. This is because the TiO₂ was not rinsed with distilled water after the oxidation process or because the TiO₂ was excessively dissolved due to the long oxidation time. Generally, these nanotubes had a better appearance than those shown in figure 3(A). Figure 4(C) shows that 2 h oxidation causes the nanotubes to segregate. The nanotubes of this sample are sparsely arranged, have very thin walls, show the formation of nozzle rings, and large broken nanotube pieces are visible on the surface. This is potentially because the length of the nanotubes and degree of corrosion both increase with increasing oxidation time. Therefore, the segregated nanotubes can no longer support themselves. Compared with figure 3(C), the TiO₂ nanotubes shown in figure 3(D) generated after 4 h oxidation are not significantly different, indicating that the growth rate and dissolution rate of the nanotube layer is similar for oxidation times between 2 h and 4 h.

Figure 4 shows the changes to the inner diameter and the wall thickness of the nanotubes generated under 40 V with different oxidation times. The inner diameters of the nanotubes increase from 85 nm to 120 nm with increasing oxidation time, while their wall thicknesses change in a small range of about 18–28 nm. Therefore, oxidation time has a small influence on the nanotube inner diameter but a large influence on the wall thickness of the nanotubes. This result is in good agreement with results reported by Shang et al [18]. This is because after the initial formation of nanotubes, increasing the oxidation time slightly increases the inner diameter of the nanotubes and decreases their wall thickness due to the dissolving effect of F⁻ in the electrolyte on the inner nanotube wall. However, as shown in figure 4, an oxidation time of 4 h leads to a slightly thicker tube wall, which

Figure 3. SEM images of TiO₂ nanotube samples prepared at 40 V under different oxidation times: (A) 0.5 h, (B) 1 h, (C) 2 h, and (D) 4 h.
might be caused by TiO2 residues or particles in the corroded nanotubes sticking to the tube nozzles after a long oxidation time.

In general, oxidation time influences the morphology of the TiO2 nanotubes, but this influence is not significant. However, longer oxidation times make the TiO2 nanotubes more fragile. An oxidation time of 30 min led to the most orderly TiO2 nanotube array with no visible nanotube fragmentation. Therefore, this was the optimal oxidation time under the studied conditions.

3.4. Influence of heat treatment on the surface morphology and crystal phase of TiO2 nanotubes

The morphologies of the nanotubes prepared under an oxidation voltage of 40 V and an oxidation time of 0.5 h are shown in figure 5. Figures 5(A, B) shows the morphology of the unheated sample under 20000 × and 200000 × magnification, respectively. Figures 5(C, D) shows the morphology of the sample sintered at 450 °C for 2 h at 20000 × and 200000 × magnification, respectively. The nanotube walls of the heat-treated sample are flat without any large-area collapse. The thickness of the nanotube walls increases after sintering at 450 °C. However, the heat-treated nanotube walls are uneven, forming a granular shape, and some of the nanotubes are collapsed. This might be due to an excessively long oxidation time, which would increase the length of the nanotubes and make the tube walls thinner, preventing the nanotubes from being robust enough to withstand the sintering temperature of 450 °C. Nevertheless, the morphology of the nanotubes does not significantly change before and after sintering at 450 °C. Lv et al [19] discussed the effect of heat treatment on nanotubes prepared by anodic oxidation. Their study found that nanotubes heat-treated at 300 °C and 450 °C retained intact structures, but nanotubes heat-treated at 600 °C partially collapsed and nanotubes heat-treated at 700 °C completely collapsed.

Figure 6 shows the XRD patterns of the TiO2 nanotubes before and after sintering at 450 °C. The unheated sample does not show the presence of crystalline anatase or rutile crystalline TiO2, with only a few peaks of the metallic Ti substrate. Because the nanotubes are amorphous after room-temperature anodization, no TiO2 peaks are detected. After heat treatment in a muffle furnace at 450 °C, the characteristic diffraction peaks of anatase TiO2 are visible, with the (101) diffraction peak appearing at 2θ = 25.16°, the (200) peak at 2θ = 48.05°, and the (211) peak at 2θ = 55.06°. In addition, many strong Ti diffraction peaks (the (002) peak at 2θ = 38.46°, the (101) peak at 2θ = 40.25°, and the (102) peak at 2θ = 53.09°) also appear in the heat-treated diffraction pattern due to the Ti substrate. This is because the oxide film is thin in certain areas and because the XRD detection depth ranges from 7 μm to 35 μm, leading to Ti substrate diffraction in addition to TiO2 nanotube diffraction. This shows that under 450 °C heat treatment, the TiO2 nanotubes partly transform from an amorphous phase to the anatase phase. A prior study reported that under the same heat treatment parameters, increasing the oxidation voltage promotes the transformation of rutile phase TiO2 to anatase phase TiO2 [9].

In general, heat treatment did not significantly change the surface morphology of the nanotubes, but the crystal phase of the nanotubes was changed. Anatase-form TiO2 was obtained by heat treatment at 450 °C.

3.5. Influence of TiO2 nanotubes on Pt loading

The morphologies of the TiO2 samples after 120 s of Pt loading by electrodeposition are shown in the SEM images in figure 7. The morphologies of the Pt-loaded samples prepared under the optimal anodizing
parameters (40 V, 0.5 h) are shown in figure 7(A, B) under 20000 × and 200000 × magnification, respectively. Figures 7(C), (D) shows SEM images of a control group Pt-loaded sample prepared under non-anodic oxidation conditions.

Figure 7(A) shows that a large number of flakes cover the surface of the nanotubes, potentially caused by the adhesion of the nanotubes to the surface of the nanotubes after falling off or insufficient cleaning after oxidation. Figure 7(B) shows that in addition to the nanotube ring structure, flakes formed by the bonding of granular materials cover the nanotube nozzles. Under the action of force, the flakes remain on the surface of the nanotubes, with aggregate sizes of tens of nm. Zhang et al reported a study in which a Ti sheet was anodized in an electrolyte (ethylene glycol + 0.3 wt% NH4F + 2 vol% H2O) at a voltage of 60 V for 3 h, followed by Pt loading.
by electrodeposition. They found that the Pt metal preferentially aggregated in nanotubes with defects and existed in the form of flakes [20]. Figures 7(C), (D) shows the morphologies of the unoxidized sample after Pt loading. The metallic and agglomerated Pt is distributed on the surface of Ti after agglomeration, with a size of 20–80 nm and a relatively uniform distribution. This is potentially because the significantly fluctuating current during preparation caused large Pt particle size differences.

Figure 8(A) shows the morphology and EDS spectrum of the Ti sheet modified by anodic oxidation at 40 V and 30 min after Pt electrodeposition for 120 s, while figure 8(B) shows the morphology and EDS spectrum of the control sample after Pt electrodeposition for 120 s. 0%, 9.89%, 11.34%, and 0% Pt content were detected at points 1, 2, 3, and 4 in figure 8(A), respectively. The EDS spectrum of the nanotube nozzle shows 0% Pt content. The Pt content of the flakes on the surface of the nanotubes is about 10%, probably because the fragments have many defects, allowing the metal Pt to preferentially aggregate on the flakes. Figure 8(B) shows that the surface of the control sample is mainly composed of Ti and Pt. The Pt content values corresponding to points 1, 2, 3, and 4 in figure 8(B) are 60.70%, 94.10%, 0%, and 0%, respectively. The Pt content of the spherical particles is far higher than the Ti content in these locations, but no Pt content is detected at points 3 and 4, further away from the Pt particles. This indicates that the metallic Pt is distributed in the form of particles on the surface of the Ti foil.

3.6. Influences of nanotubes, Pt loading, and heat treatment on photocatalytic performance

The Ti foil that was not anodized or heat-treated is denoted T, the Ti foil sample that was anodized at a voltage of 40 V for 30 min is denoted TN, and the anodized TN sample heat-treated at 450 °C for 2 h is denoted TNH. The non-anodized Pt-loaded sample is denoted Pt/TN and the Pt-loaded TNH sample is denoted Pt/TNH.

Figure 9 presents the catalytic efficiency of the samples for the degradation of methylene blue over 10 h of ultraviolet light irradiation. The catalytic efficiency of the anodized sample TN to methylene blue was 15% after 10 h, higher than that of the blank sample T (10%). This is due to the larger specific surface area of the nanotubes formed by anodic oxidation. The photocatalytic efficiency of sample TNH obtained by anodic oxidation and heat treatment was 25%. After the heat treatment, the TiO2 nanotubes transform from an amorphous phase to anatase TiO2, which has a stronger ability to adsorb H2O, O2, and OH−. This stronger adsorption capacity leads to higher photocatalytic activity. In addition, the anatase TiO2 had smaller crystal grains and a larger specific surface area than the amorphous TiO2, also enhancing photocatalytic activity [21]. This shows that heat treatment can significantly improve the photocatalytic efficiency of the TiO2 nanotubes.
As a semiconductor photocatalyst, the energy band gap of titanium dioxide is 3.2 eV. When irradiated by ultraviolet light with wavelength less than 387.5 nm, the valence band electrons of titanium dioxide are excited and transition to the conduction band, resulting in hole ($h_{VB}$) and photogenerated electron ($e_{CB}$) pairs in the valence band. In aqueous solution, ($h_{VB}$) and ($e_{CB}$) can react with water and oxygen in a series of ways, and then generate hydroxyl radical ($\cdot$OH) and other strong oxidizing radicals, which will completely oxidize and degrade organic matter and form inorganic small molecules. The reaction steps are as follows [22].

(1) Titanium dioxide absorbs effective photons ($hν \geq E_G = 3.2$ eV), and generates conduction band electrons and valence band holes. Due to the presence of oxygen in the reaction, the generated $e_{CB}$ will react with oxygen to produce $O_2^−$.
Therefore, it is obvious that the recombination of $e_{CB}^-$ and $h_{VB}^+$ is prevented, which makes $h_{VB}^+$ de oxidize dye molecules.

2) $OH^-$ is neutralized by photogenerated holes to produce hydroxyl radicals

$$ (H_2O \leftrightarrow H^+ + OH^-) + h_{VB}^+ \rightarrow \cdot OH + H^+ $$

3) $O_2^-$ is neutralized by protons

$$ O_2^- + H^+ \rightarrow HO_2 $$

4) Transient hydrogen peroxide formation and disproportionation oxidation

$$ 2HO_2 \rightarrow H_2O_2 + O_2 $$

5) $H_2O_2$ decomposition and secondary oxygen reduction

$$ H_2O_2 + e^- \rightarrow \cdot OH + OH^- $$

6) The organic reactant (R) is oxidized by hydroxyl radical

$$ R + \cdot OH \rightarrow R + H_2O $$

7) The organic reactants are directly oxidized by photogenerated holes

$$ R + h^+ \rightarrow R^+ \rightarrow \text{Degradation products} $$

In addition, methylene blue can be used as photosensitizer in TiO$_2$ photodegradation methylene blue system. Under UV irradiation, the system is photosensitized, and the irradiation of base oxygen will produce singlet oxygen ($^1O_2$). It can be seen from the above reaction steps that in the process of TiO$_2$ photocatalytic degradation of methylene blue, the main active species involved in the degradation of methylene blue are, $h_{VB}^+$, $e_{CB}^-$, $\cdot OH$, $O_2^-$ and $^1O_2$ [23].

Figure 10 shows the excitation of an electron form the valence band to the conduction band initiated by light absorption with energy equal to or greater than the band gap of the semiconductor. Figure 11 illustrates some of the deexcitation pathways for the electrons and holes.

In addition, Pt loading also improves the photocatalytic efficiency. After anodization, the Pt/TN sample had a higher catalytic efficiency than sample TN. Furthermore, sample Pt/TNH, with a methylene blue degradation rate of 50% after 10 h, had a higher catalytic efficiency than sample TNH. The photocatalytic activity of TiO$_2$ can be improved after platinum loading. The reason is that the intrinsic light absorption edge of TiO$_2$ has different degrees of red shift after platinum loading, which expands the light response range. Therefore, under the condition of ultraviolet irradiation, the increase in the number of electron hole pairs is conducive to the improvement of catalytic activity. Secondly, the high work function of platinum is higher than that of TiO$_2$ (the work function of platinum is 5.165eV and that of TiO$_2$ is 4.10eV) [25]. Therefore, the loaded metal platinum and TiO$_2$ semiconductor have different Fermi energy levels. In order to match the Fermi energy levels, electrons will migrate from TiO$_2$ to the surface of platinum and form a space charge layer between them. The surface of platinum obtains negative charge and the surface of semiconductor has excess positive charge. The energy barrier formed between metal semiconductors is Schottky energy barrier, which is an effective electron capture well [26]. When electrons move to the surface of platinum, Schottky energy barrier can capture electrons, which reduces the recombination probability of electrons and holes and is conducive to the catalytic reaction. Third, the adsorption performance of platinum can further strengthen the adsorption capacity of photocatalyst, so it can increase the adsorption of degraded products, water and oxygen on the surface of catalyst film, and an appropriate amount of adsorption is conducive to the catalytic reaction.
In summary, the combination of anodic oxidation, heat treatment, and Pt loading enhances the photocatalytic performance of these TiO$_2$ nanotube samples.

4. Conclusion

Highly ordered arrays of TiO$_2$ nanotubes with diameters of about 40–70 nm were prepared on the surface of Ti foil by anodic oxidation followed by heat treatment and Pt loading. Under UV light irradiation, the degradation effects of different samples on methylene blue were investigated. The results showed that good photocatalytic performance was obtained for a sample synthesized with an anodization voltage of 20 V, an oxidation time of 4 h, and a heat treatment temperature of 450 °C. Pt loading further improved the photocatalytic efficiency of this material, leading to the highest performance of the catalysts reported herein. Pt loading was achieved by electrodeposition at a constant current of 2 mA cm$^{-2}$ for 2 min. The Pt-loaded TiO$_2$ nanotube sample had a methylene blue degradation rate of 50% after 10 h of UV irradiation, much higher than that of the other samples.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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