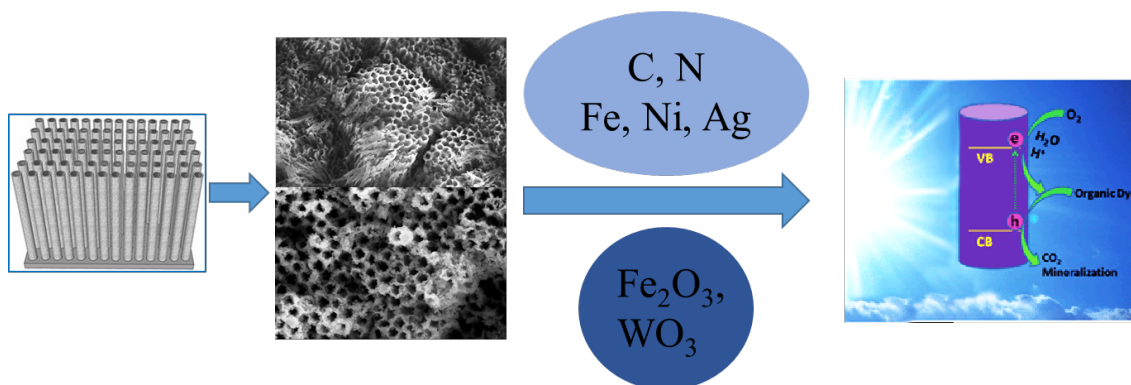


1 Graphical abstract

2 Graphic abstract mainly focuses on the preparation and modification of
3 photocatalytic degradation of organic pollutants by anodized TiO₂
4 nanotubes. The TiO₂ nanotubes have higher photocatalytic activity under
5 visible light after heat treatment or water-assisted treatment, and then
6 modification methods such as doping and surface modification.



7

1 **Recent progress in anodic oxidation of TiO₂ nanotubes and enhanced**
2 **photocatalytic performance: a short review**

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1 **Recent progress in anodic oxidation of TiO₂ nanotubes and enhanced** 2 **photocatalytic performance: a short review**

3 **ABSRTACT**

4 By adjusting the oxidation voltage, electrolyte, anodizing time and other
5 parameters, TiO₂ nanotubes with high aspect ratio can be prepared by oxidation
6 in organic system because anodic oxidation method has the advantage of simple
7 preparation process, low material cost and controllable morphology. Low
8 material cost and controllable morphology by anodizing. This review focuses on
9 the influence of anodizing parameters on the morphology of TiO₂ nanotube
10 arrays prepared by anodizing. In order to improve the photocatalytic activity of
11 TiO₂ nanotubes under visible light and prolong the life of photo-generated
12 carriers, the research status of improving the photocatalytic activity of TiO₂
13 nanotubes in recent years is reviewed. This review focuses on the preparation and
14 modification of TiO₂ nanotubes by anodic oxidation, which is helpful to
15 understand the best structure of TiO₂ nanotubes and the appropriate modification
16 methods, thus guiding the application of TiO₂ nanotubes in practical
17 photocatalysis. Finally, the development of TiO₂ nanotubes is prospected.

18 **KEYWORDS**

19 TiO₂ nanotubes; anodizing; Photo-generated carriers; photocatalytic; Modified

20 **1 Introduction**

21 TiO₂ is nontoxic, acid and alkali resistant, high in chemical stability and excellent in
22 biological phase. Since Fujishima and Honda first reported light-induced water splitting
23 on the surface of TiO₂ in 1972,¹ it has been widely used in photocatalysis, dye-
24 sensitized cells, biomedicine and other fields. The TiO₂ is easy to generate electron-hole
25 pairs when it is excited by external energy. Therefore, most of the organic pollutants
26 could be degraded into CO₂ and H₂O without secondary pollution. Thus, TiO₂ has
27 become a common catalyst for treating organic pollutants. P25, a commonly used
28 photocatalyst in the market at present, has high photocatalytic activity, but TiO₂ powder

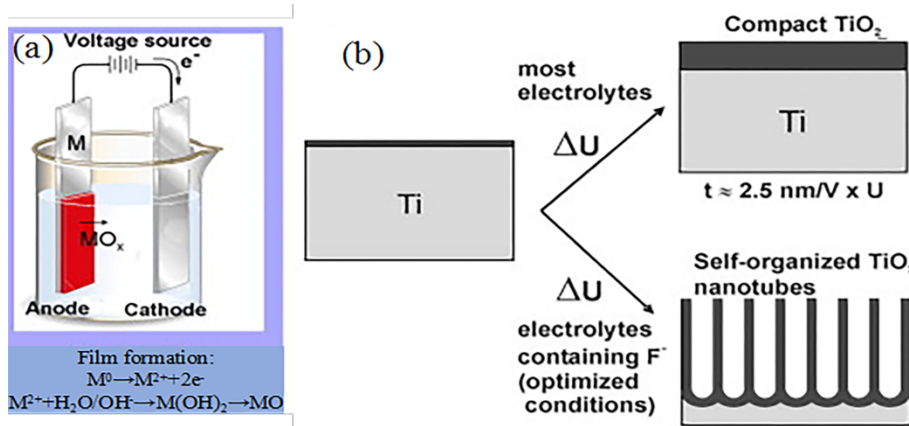
1 and photocatalytic activity are difficult to recover and further improve, respectively.
2 Due to quantum size effect and surface effect of nano-materials, nano-TiO₂ exhibits
3 better performance than conventional TiO₂.

4 One-dimensional TiO₂ nanotube array is easy to separate photo-generated carriers
5 due to its special morphology, such as large aspect ratio and specific surface area,²
6 which has become a promising photochemical/photoelectrochemical material.³⁻⁵
7 Therefore, TiO₂ nanotubes are widely used in photocatalytic degradation.^{6, 7} TiO₂ is a
8 wide band gap N-type semiconductor (≥ 3.0 eV), the electron-hole pair can be generated
9 only after TiO₂ absorbs photons with wavelength less than 387.5 nm. TiO₂ has high
10 photocatalytic activity only under ultraviolet light, so the utilization rate of solar energy
11 will be reduced, and only about 7 % of the solar spectrum will be absorbed. In addition,
12 photo-generated carriers generated by TiO₂ excitation are easy to recombine, which
13 limits the application of TiO₂ nano-photocatalyst.

14 **2 Factors Affecting Structure and Morphology of TiO₂ Nanotubes by** 15 **Anodizing**

16 There are various methods for preparing One-dimensional TiO₂ nanotubes, such as sol-
17 gel method,^{8, 9} template-assisted method,^{10, 11} hydrothermal/solvothermal method,^{12, 13}
18 and electrochemical method.^{14, 15} Since Zwilling et al.¹⁶ initially reported the
19 preparation of TiO₂ nanotube arrays, the preparation of TiO₂ nanotubes by anodic
20 oxidation has become a hot research topic among researchers in recent years. The
21 experimental principle setting is shown in Fig. 1a.¹⁷ Moreover, the dense oxides or TiO₂
22 nanotubes can be formed according to different electrolytes (Fig. 1b). The diameter and
23 length of the nanotubes can be controlled by different parameters through the anodic
24 oxidation method, which provides a better solution for controlling the morphology of
25 nanotubes. In general, the diameter of TiO₂ nanotubes prepared by anodic oxidation

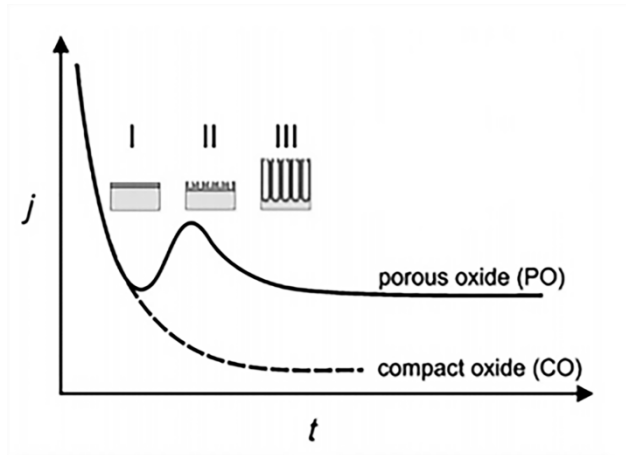
1 (tens of nanometers to hundreds of nanometers) is larger than that of TiO₂ nanotubes
 2 prepared by hydrothermal method (more than ten nanometers). Therefore, it is
 3 necessary to adjust various process parameters to prepare nanotubes with high aspect
 4 ratio and preferable regularity and uniformity.



5
 6 **Fig. 1** (a) Schematic device of anodic oxidation experiment. (b) Anodic oxidation leads to oxidation
 7 of metal substances, forming solid oxides on the metal surface.¹⁷

8 At present, there are various controversies about the formation mechanism of TiO₂
 9 nanotube arrays. Nonetheless, the formation mechanism of this ordered nanotube array
 10 structure has not been perfectly explained. The generally accepted mechanisms of
 11 porous structure formation are field-assisted dissolution theory and field-assisted
 12 injection theory.¹⁸ The theory of "field dissolution" was first applied to explain the
 13 formation mechanism of anodic oxide film on aluminium surface.¹⁹ The typical current-
 14 time (j-t) curve is plotted and demonstrated in Fig. 2. The whole oxidation process
 15 consists of three stages: the initial oxidation film formation, porous oxide film
 16 formation, and nanotube arrays formation and stable growth. Firstly, when the voltage is
 17 applied, Ti⁴⁺ and O²⁻ are produced by dissolution and water, respectively. Meanwhile,
 18 the electricity separation near the anode forms a dense TiO₂ initial oxidation film, the
 19 loop current decreases exponentially.²⁰ After the initial oxide film is formed, O²⁻ near

1 the anode passes through the oxide film and reaches the interface between the oxide
2 film and titanium substrate under the action of electric field force, which leads to realize
3 field oxidation growth. On the other hand, F^- in the electrolyte combines with Ti^{4+} in the
4 TiO_2 film to generate TiF_6^{2-} . In addition, TiF_6^{2-} is also produced by chemically attack of
5 the formed $TiO_2(TiO_2+4H^++6F^-= [TiF_6]^{2-}+2H_2O)$, which leads to realize field-induced
6 dissolution.²¹ Stress and crystallization in the film layer lead to uneven energy
7 distribution and F^- distribution, resulting in uneven oxide film surface, pore nucleus
8 formation and subsequent pore formation. The un-oxidized Ti matrix bulge at the
9 bottom of the small hole enhances the electric field, accelerates the dissolution of the
10 top oxide film, and turns the small hole into a small cavity.²² The current gradually
11 increases with the field-induced oxidation increases. At the end, the small cavities
12 gradually deepen to form continuous and independent nanotube arrays. With the
13 extension of oxidation time, the nanotube array grows stably and the current tends to be
14 stable when the growth rate and dissolution rate reach equilibrium.²³ According to the
15 theory of "field dissolution", porous anodic oxide are formed at metal/oxide interface,
16 while dissolution occurs at the electrolyte/oxide interface. However, the reason of the
17 metal ions migrated from metal/oxide interface to electrolyte/oxide interface before the
18 formation of oxide can't be explained. To solve this problem, the field-assisted injection
19 theory was developed. Under the condition of high current efficiency, oxide grows on
20 two interfaces, while under the condition of relatively low current efficiency, metal ions
21 moving outward are directly injected into electrolyte at electrolyte/oxide interface.²⁴

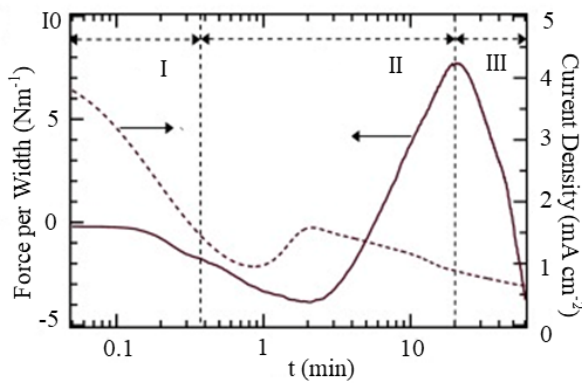


1
2 **Fig. 2** Typical current-time (j - t) characteristics after voltage step in the absence of (---) and the
3 presence of (—) fluoride ions in the electrolyte. Dense oxides (fluoride-free) or porous/tubular metal
4 oxides (fluoride-containing) are formed through different morphological stages (I–III).¹⁸

5 The theory of "field dissolution" explains the formation of holes and the deepening
6 of channels, but it can't explain the formation mechanism of gaps between nanotubes.²⁵
7 At the same time, TiO₂ nanotube arrays can also be obtained in fluorine-free electrolyte
8 system,^{26, 27} which proves that the "field dissolution" effect of fluorine ions in the
9 growth process of nanotubes is controversial. Moreover, as we know, F⁻ participates in
10 the field-assisted dissolution or ejected reaction to reduce current efficiency and volume
11 expansion coefficient. However, the total volume of nanotubes is basically the same
12 under the given current condition, which has nothing to do with the concentration of F⁻
13 .^{28, 29} Based on the field dissolution theory, the growth of nanotubes is stable. The
14 reason is that the oxide formation rate at the metal/oxide interface is equal to the
15 dissolution rate at the electrolyte/oxide interface, but this balance has not been verified.
16 On the contrary, there is evidence to prove that this balance does not exist.^{30, 31}
17 Therefore, in recent years, the field-assisted dissolution theory has been widely
18 challenged.³²⁻³⁴

19 The theory of "field dissolution" holds that nanotubes are formed in a "top-down"
20 excavation mode, while the tracer atomic method proves that the formation of

1 nanotubes is opposite.³⁵ Based on this result, a new theory “viscous flow and stress
 2 model theory” is proposed,³⁶ which holds that under the stress caused by electrostriction
 3 or volume expansion stress, the barrier oxide fluid grows from bottom to top along the
 4 pipe wall under high electric field, and finally forms the nanotube array structure.²⁴
 5 Moreover, viscous flow caused by the existence of internal stress in oxide during
 6 nanotube growth has been proved.³⁷ Fig. 3 simultaneously shows stress and current
 7 density measurements during the continuous anodizing experiment at 20 V.³⁸ In the first
 8 stage, the initial barrier oxide grows and produces compressive stress at the constant
 9 rate of 0.4 minutes. In the second stage, the compressive force is further increased, and
 10 then the tensile stress is continued for 20 minutes the oxide is separated and nanotubes
 11 are formed at this stage. In the third stage, the stress increases in the compression
 12 direction and the thickness of the nanotube layer increases in the remaining time of the
 13 anodizing cycle.²⁵

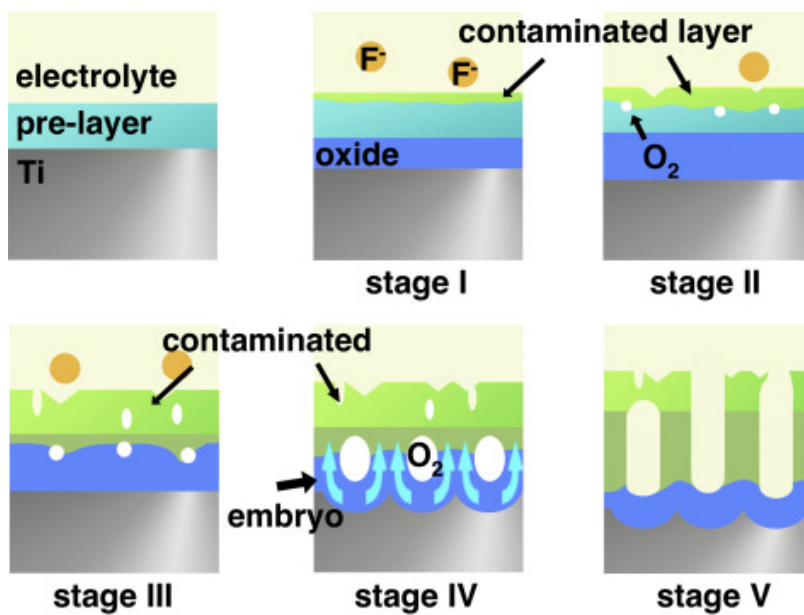


14
 15 **Fig. 3** Stress and current density transients at 20 V in 0.1 M NH₄F and 1.6 wt % water in ethylene
 16 glycol.³⁸

17 However, the viscous flow model can't explain how the nanotube embryo is
 18 formed, nor can it explicitly indicate whether the barrier oxide grows at two interfaces
 19 or one interface at the bottom of the nanotube.

1 Based on the viscous flow model and avalanche breakdown theory,^{37,39} an oxygen
2 bubble model and a double current model are proposed to explain the relationship
3 between the nanotube morphology and current density-time curve. Double current
4 model refers to ion current and electron current model. The ratio of the two currents can
5 be controlled by adjusting the concentration of NH_4F .⁴⁰ Zhu et al put forward the kinetic
6 model of porous anodic oxide,⁴¹ in which ion current was used to form oxide, and
7 electron current was caused by impurity center in oxide, which was used to generate
8 oxygen or spark. For a given electrolyte, electron current depends on impurity center
9 and is independent of ion current. The formation of nanopores can be attributed to the
10 precipitation of oxygen in oxides. Oxygen starts to release at the critical thickness, that
11 is, oxide growth keeps the channel wall lengthening and oxygen evolution keeps the
12 channel unblocking. By controlling the release rate of oxygen under different pressures,
13 the shape of the channel can be adjusted.⁴¹ Regular and uniform thin films can be
14 obtained with the stable current density.⁴² Electron current and oxygen release have a
15 key influence on the formation of porous layer.⁴³ Oxygen bubble model theory can
16 explain the experimental phenomenon that contradicts the field-assisted dissolution
17 theory and has been recognized by many researchers.^{44,45} Especially for some special
18 nanostructures formed by anodic oxidation, the oxygen bubble model has a well
19 explanation.^{46,47} The cavity between the double walls of nanotubes obtained by anodic
20 oxidation in electrolyte containing NH_4F and H_3PO_4 provides direct evidence of pore
21 formation caused by oxygen bubbles.⁴⁸ Under this model, the formation diagram of
22 nanotubes is shown in Fig. 4. In the stage I, a dense layer is formed under the front layer.
23 In stage II–IV, the oxides exposed to electrolyte are usually contaminated by anions
24 (usually fluorine). Once anions are introduced into the contaminated layer, they will
25 soon meet the growth layer to form nanotube embryos. In stage II, the contaminated

1 layer does not reach the grown oxide. At this stage, O₂ bubbles are generated and
 2 trapped between the contaminated layer and the preformed layer. With the pollution in
 3 stage III, the accumulated O₂ may break the pre-layer, thus forming small cracks on the
 4 pre-layer. When the pollution reaches the growth layer, the nanotube embryo begins to
 5 grow in stage IV. In stage V, oxygen bubbles destroy the oxide layer and the electrolyte
 6 enters the nanotube. Oxide and nanotube grow steadily.⁴⁹

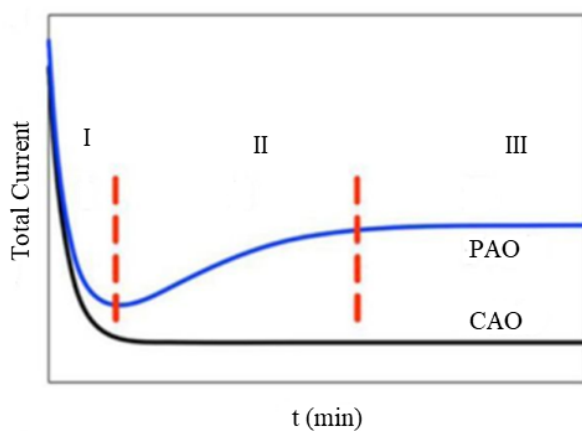


7

8 **Fig. 4** The mechanism diagram of TiO₂ embryo initiation.⁴⁹

9 Fig. 5 shows the typical current-time curves of three stages (I, II and III
 10 respectively). Under the condition of constant voltage anodic oxidation, the initial high
 11 electric field intensity produces relatively high ion current, which decreases with the
 12 increase of oxide thickness, as shown in stage I. With the increase of the thickness of
 13 barrier layer and the accumulation of anions near the oxide surface, the electron current
 14 increases exponentially when the barrier layer grows to the critical thickness and the
 15 electric field intensity drops to the critical value. Due to the sufficient electron current,
 16 the release of oxygen remains in the anion contaminated layer. Closed small bubbles
 17 appear as bubble mold, which leads to the formation of pore embryo in stage II. With

1 the growth of barrier oxide, oxygen bubbles grow and expand upward. Until the oxygen
2 bubble breaks, the electrolyte is allowed to enter, and the total anodic oxidation current
3 reaches quasi-steady state (the stage III).⁵⁰ The larger electron current leads to the rapid
4 overflow of oxygen bubbles on the anode membrane surface, while the barrier oxide
5 produced by the small ion current cannot surround the oxygen bubbles, and only a dense
6 membrane can be obtained. The balance between the ion current and electron current
7 can lead to the formation of nanotubes.⁵¹



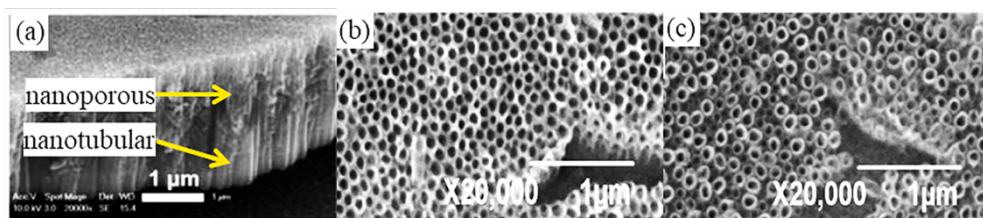
8
9 **Fig. 5** The current-time curve of porous anodic oxide(PAO) or compact anodic
10 oxide(CAO) prepared by constant voltage anodic oxidation.⁵²

11 In fact, because the formation mechanism is hard to be derived by direct in-situ
12 experiments, it is difficult to successfully explain the formation mechanism of
13 nanotubes by a single theoretical model, but well results can be obtained by combining
14 various theories.⁵³ If the plastic flow model is combined with the oxygen bubble model,
15 the formation of gaps and ribs around the anode TiO₂ nanotubes can be successfully
16 clarified.⁵⁴ Based on the oxygen bubble model and oxide flow model, the formation
17 mechanism of lotus-root-like nanostructures is proposed.⁵⁵

18 **2.1 Surface pre-treatment**

19 Nowadays, there are extensive researches on the influence of anodic oxidation

1 parameters on the morphology of TiO₂ nanotubes,^{28, 56} but few researches are focused
2 on the influence of anodic pre-treatment on the morphology of TiO₂ nanotubes. Cold-
3 working Ti plate produces an intermediate structure between self-organized nanotubular
4 and nanoporous morphology(Fig. 6a). The thickness decreases with the increase of
5 cold-working amount. Long-time thermal annealing after cold-working can eliminate
6 the defects of cold-working and form good nanotube morphology.⁵⁷ The residual stress
7 in Ti foil can be eliminated by heat treatment of Ti plate, which is beneficial to reduce
8 the diameter of anodized TiO₂ nanotube array and obtain good morphology with
9 uniform arrangement. With the increase of annealing temperature, the growth rate of
10 TiO₂ nanotubes increases.⁵⁸ Surface roughness of Ti can induce higher growth rate
11 (extended nanotube length) and improved self-organization.⁵⁹ So that the grinding or
12 polishing Ti plate affects the morphology of anodized TiO₂ nanotubes. Surface
13 irregularities caused by grinding make it easier to form nanonuclei, but their growth is
14 more disordered. Therefore, unlike the smooth surface formed by polishing, the
15 distribution of surface nanotubes on the ground surface is sparser and the height is more
16 irregular. The polished surface forms nanotubes with larger outer diameter and wall
17 thickness(Fig. 6b, c).⁶⁰ Different polishing methods (chemical polishing and mechanical
18 polishing) also affect the TiO₂ nanotubes formed by subsequent anodic oxidation.⁶¹

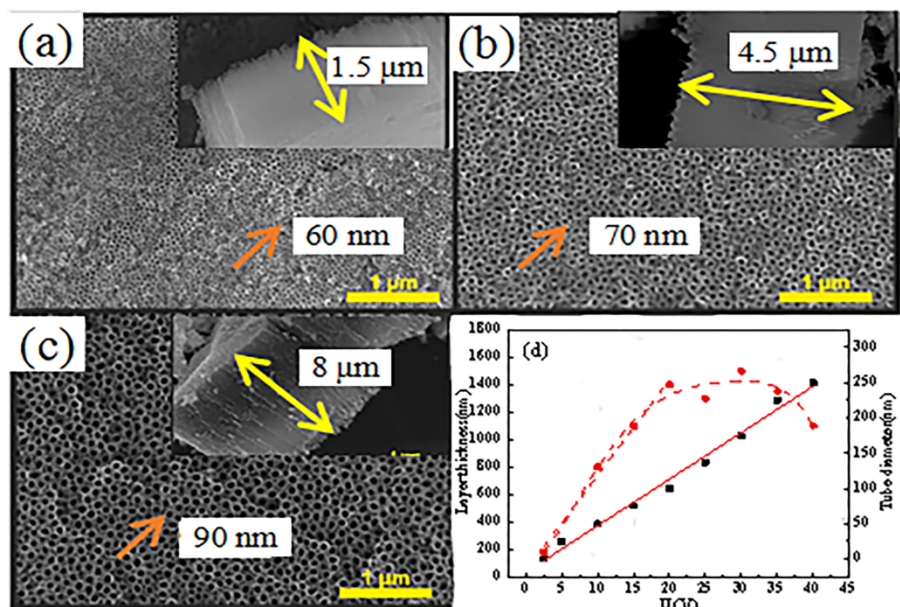


19 **Fig. 6** (a) Intermediate structure of nanotubes and nanopores,⁵⁷ and SEM images of the
20 anodized surfaces (b) ground and (c) polished.⁶⁰
21

1 **2.2 Oxidation Voltage**

2 The research shows that the anodic oxidation voltage has a great influence on the
3 formation of the tube.^{62, 63} Low voltage easily forms a mixed structure both at the top
4 nanopore layer and the bottom nanotube layer.⁶⁴ High voltage leads to rapid dissolution
5 of TiO₂, attenuation or fracture of the formed nanotubes, and even breakdown of Ti
6 plate.⁶⁵ Therefore, TiO₂ nanotube arrays can only be oxidized within a certain voltage
7 range, which is called "voltage window". Mor et al. found that the voltage window was
8 10-23 V when anodizing Ti plates in HF solution system.⁶⁶ For organic electrolyte, the
9 voltage window is generally higher than that of aqueous electrolyte.⁶⁷ In addition, the
10 oxidation voltage is also related to the diameter and length of nanotubes.⁶⁸ The
11 structural characteristics of anodized TiO₂ nanotubes, such as grain size, inner pore size
12 and outer pore size, increase with the increasing anodizing voltage.^{69, 70} As the oxidation
13 voltage increases, the diameter and length of nanotubes increase, and the linearity
14 depends on the oxidation voltage.⁷¹ Furthermore, the voltage also affects the tube
15 spacing and tube morphology of TiO₂ nanotubes. Within the limited voltage range from
16 10 V to 40 V, the self-organized spacing of TiO₂ nanotubes can be obtained from 21
17 nm~168 nm,⁷² and the tube length gradually increases with the increase of voltage(Fig.
18 7a, b, c).⁷³ However, when the applied potential exceeds a critical value (usually higher
19 than 60 V), the diameter of the porous anodized nanostructure decreases(Fig. 7d), and
20 the critical value is determined by the electrolyte,^{74, 75} therefore, the aspect ratio is
21 reduced. While decreasing the voltage can reduce the porosity and increase the
22 roughness coefficient and aspect ratio of TiO₂ nanotubes. At the same time, decreasing
23 the voltage can separate TiO₂ nanotubes prepared by anodic oxidation in the second-
24 step from the titanium substrate, and obtain independent TiO₂ nanotubes with closed
25 end and hexagonal structure.⁷⁶ If square voltage is applied to Ti sheet, the morphology

1 and morphological characteristics of the nanotubes will be changed, and bamboo-knot
2 walls will be formed.⁷⁷



3
4 **Fig. 7** The morphology of surface and cross section of TiO₂ nanotubes obtained at (a) 20 V, (b) 30 V,
5 (c) 40 V for 60 minutes respectively in the solution system of NH₄F/ethylene glycol,⁷³ and (d)
6 variation curve of inner diameter and length of TiO₂ nanotubes with voltage.⁷⁵

7 **2.3 Electrolyte**

8 After continuous development, anodizing electrolytes have experienced four
9 generations of electrolyte types: the first generation is HF-containing aqueous
10 electrolytes,⁷⁸ the second generation is buffered neutral aqueous electrolytes with
11 fluoride salts (such as KF, NaF),⁷⁹ the third generation is viscous organic electrolytes
12 containing fluoride (such as NH₄F/ethylene glycol),⁸⁰ and the fourth generation is non-
13 fluoride-based electrolytes (such as HCl).⁸¹

14 Ethylene glycol containing NH₄F and H₂O is widely used because it can produce
15 nanotubes with uniform diameter and smooth walls.⁸² The pH value, F⁻ concentration
16 and water content in the electrolyte affect the formation and dissolution of oxide film.

1 Temperature mainly affects the migration rate of ions in electrolyte. Therefore,
2 temperature is very important for the formation of TiO₂ nanotubes.⁸³ Anodizing is
3 usually carried out at room temperature, because it is beneficial to the formation of TiO₂
4 nanotubes in this temperature range. However, by changing the electrolyte temperature,
5 it is found that TiO₂ nanotubes can be formed in a large temperature range. In this
6 temperature range, there is no significant change in the diameter of nanotubes, but the
7 wall thickness of TiO₂ nanotubes changes significantly.⁴ At low temperature, the rate of
8 oxide dissolution reaction is slower than that of titanium etching, resulting in the
9 formation of thicker nanotube walls.⁸⁴ At high temperature, the rate of chemical etching
10 is faster than that of anodic oxidation, and no nanotube structure is formed at this time.⁸⁵
11 Elevated temperature accelerates the formation of TiO₂ nanotubes, and at the same time,
12 it also aggravates the chemical corrosion on the top, so it is unfavourable to prepare
13 longer TiO₂ nanotubes. However, if only the Ti surface is heated and the electrolyte is
14 kept at a low temperature, the TiO₂ nanotubes can grow rapidly and a high aspect ratio
15 can be obtained.⁸⁶ The hydrolysis content increases with the increasing pH value,
16 resulting in a large amount of hydrated TiO₂ deposited on the surface of nanotubes.⁸⁷
17 Shorter and cleaner nanotubes are formed with lower pH value, while higher pH value
18 could cause longer nanotubes to suffer unnecessary precipitation. Alkaline solution is
19 not conducive to the formation of self-organized nanotubes.⁸⁸ F⁻ is mainly related to the
20 dissolution of oxide film. The nanotube length increases to the maximum value and then
21 gradually decreases with the increase of NH₄F concentration. If the concentration is
22 very high, the nanotubes become disordered and irregularly arranged, forming a very
23 thick precipitate on the TiO₂ film.⁸⁹ Typical F⁻ concentration is between 0.3 wt% and
24 0.5 wt%.^{90, 91}

1 When the electrolyte contains no water or its content is low, the diffusion of H⁺
2 and F⁻ ions in high viscosity ethylene glycol electrolyte is inhibited. With the increase of
3 water content, the concentration of H⁺ increases gradually, the electrochemical
4 oxidation rate is faster than the chemical dissolution rate, and the tube length of TiO₂
5 nanotubes increases. However, when excessive water is added, the H⁺ concentration
6 increases to the point where the chemical dissolution rate is higher than the
7 electrochemical oxidation rate, which leads to the destruction of the oriented tubular
8 structure, and even completely dissolves to form nanoparticles.⁹² In addition, the
9 solution viscosity of NH₄F and ethylene glycol electrolyte is very unfavourable to the
10 diffusion of various ions in the electrolyte, so the uniformity of electrolyte also has a
11 great influence on the morphology of TiO₂ nanotubes. The morphology of TiO₂
12 nanotubes can be better than that of prepared without stirring before anodic oxidation or
13 during oxidation.^{93, 94} The increase of stirring rate has little effect on the morphology of
14 TiO₂ nanotubes, but the higher the stirring rate, the more serious the fracture of TiO₂
15 nanotubes.⁹⁵ The effects of various electrolyte parameters on the tube diameter, length
16 and wall thickness of anodized TiO₂ nanotubes are shown in Table 1

17 **Table 1** Tube diameter, length and wall thickness of TiO₂ nanotubes prepared with different
18 electrolyte parameters in ethylene glycol system.

Electrolyte parameters	Condition	Tube diameter	Tube length	Wall thickness	References
	2 wt%	52.73 nm	21.8 μm	36.91 nm	
Water content	3 wt%	111.5 nm	25.6 μm	15.75 nm	96
	4 wt%	121.2 nm	24.2 μm	31.9 nm	
Temperature	5 °C	Premature pores	No	No	97

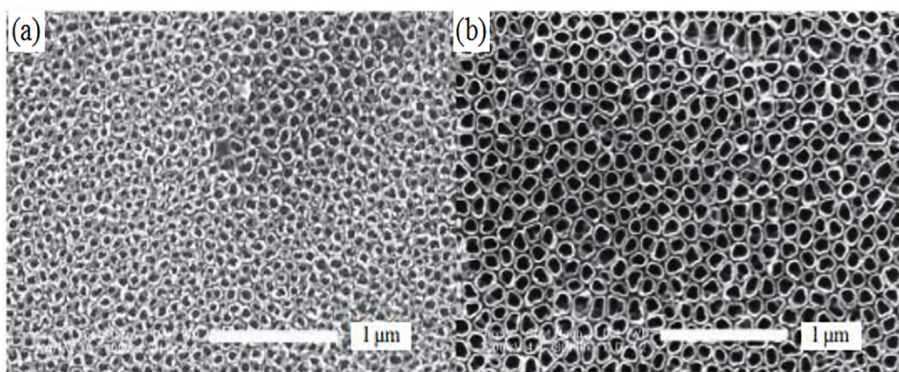
	10 °C	35 nm (porous)	No	No	
	25 °C	125 nm	250 nm	30 nm	
	30 °C	175 nm	-	27 nm	
	50 °C	190 nm	-	22 nm	
	70 °C	200 nm	-	20 nm	
NH ₄ F content	0.1 wt%	45.1 nm	4.479 μm	94.1 nm	
	0.3 wt%	50.2 nm	4.243 μm	65.75 nm	28
	0.5 wt%	49.4 nm	4.421 μm	47.2 nm	
Stirrer rate	No	60 nm	0.66 μm	6.7 nm	
	150 rpm	62 nm	0.75 μm	13.3 nm	
	300 rpm	62 nm	0.71 μm	6.7 nm	95
	600 rpm	61 nm	0.67 μm	6.7 nm	

1 - means that this data is not available in the references

2 **2.4 Anodizing steps**

3 The multiple oxidation of TiO₂ is to form ordered hexagonal depressions on the Ti
4 substrate through the first anodic oxidation, which serves as a template for the further
5 growth of TiO₂ nanotubes. The first anodic oxidation is actually the surface pre-
6 treatment of Ti foil and the first anodic oxidation could provide ordered marks. TiO₂
7 nanotube arrays with more uniform diameter and arrangement order can be obtained by
8 multiple anodic oxidation methods.⁹⁸ However, due to the active nature of the Ti
9 substrate, an excessively thick oxide film may form before the sunken substrate reacts
10 again. Thus, multiple anodization may deteriorate the morphology of nanotubes.

1 TiO₂ nanotubes grown in the second step of anodization are obviously superior to
2 TiO₂ nanotubes prepared by conventional one-step Ti anodization in terms of size
3 uniformity and arrangement order. By adjusting the experimental parameters in the
4 second step of anodization, two new types of TiO₂ nanostructures are obtained: lotus
5 root-like nanostructures, double-layer nanotube arrays with bamboo-like upper part and
6 smooth wall lower part.⁹⁹ The TiO₂ nanotube array constructed by the third anodization
7 shows more regular structure than the sample constructed by the conventional single
8 anodization.¹⁰⁰ In addition, as anodic oxidation moves from the first, second and third
9 steps, the diameter of the inner pores of TiO₂ nanotubes increases, but the wall thickness
10 of TiO₂ nanotubes gradually decreases.¹⁰¹ By carefully studying the influence of
11 multiple anodizing on the morphology and geometric properties of TiO₂ nanotubes, it is
12 found that the length of TiO₂ nanotubes increased sharply by two-step anodizing, which
13 is from 2 μm in one-step anodizing to 4 μm in two-step anodizing. In addition, it also
14 has high roughness factor, surface area and aspect ratio, as well as very orderly structure
15 and clear opening (Fig. 8).^{102, 103}

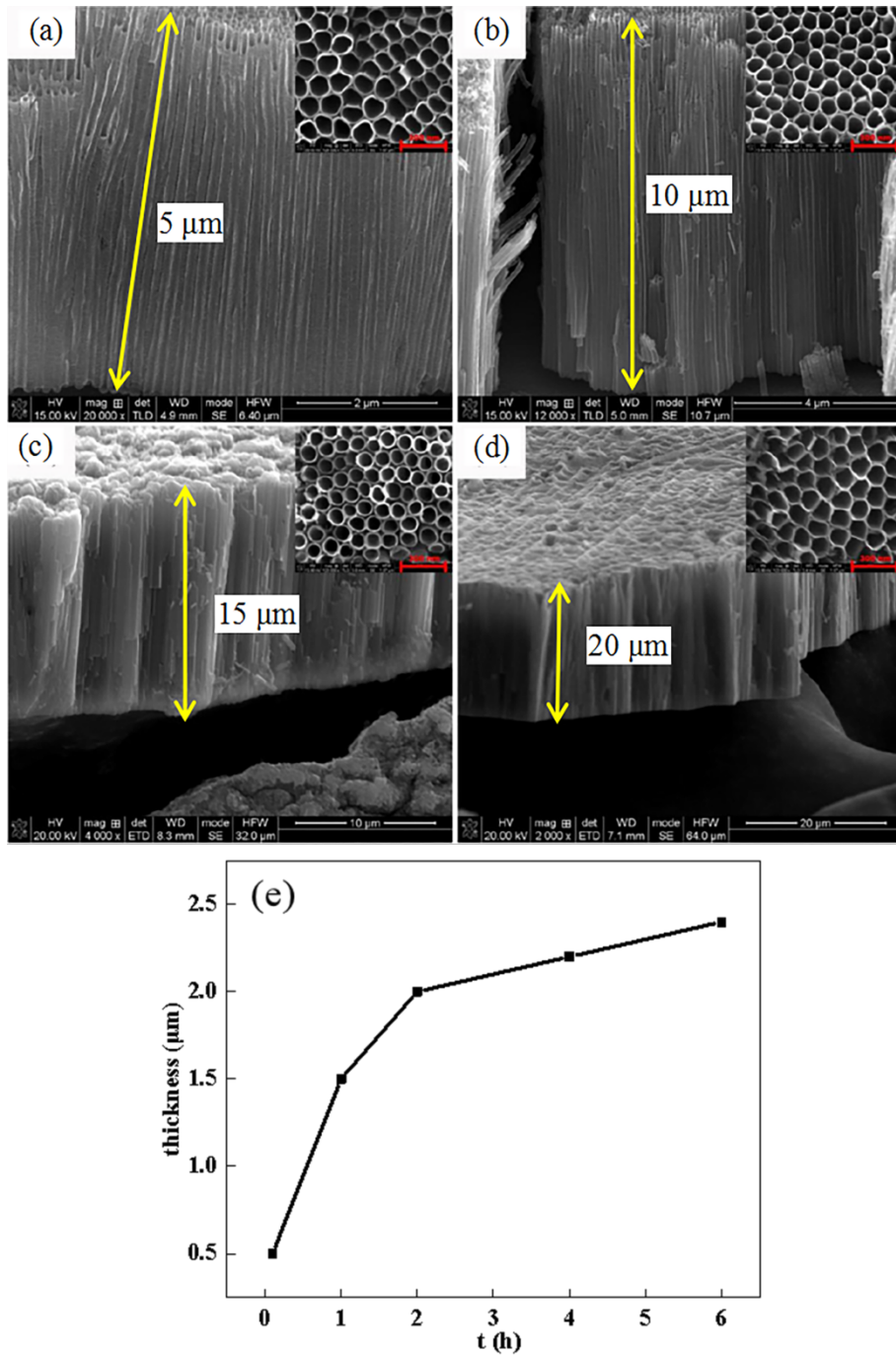


16
17 **Fig. 8** SEM images of TiO₂ nanotubes under different anodizing steps (a) one-step
18 oxidation and (b) two-step oxidation.¹⁰³

19 **2.5 Oxidation Time**

20 When the TiO₂ porous oxide film is formed, the tube length of TiO₂ nanotubes

1 gradually increases with the increasing oxidation time. In addition, with the further
2 extension of oxidation time, the diameter of TiO₂ nanotubes increases similarly.¹⁰⁴ For
3 NH₄F solution organic system, as the solution has a certain viscosity, ion transport is
4 slow and oxidation time is long (usually as long as several hours).^{105, 106} If the oxidation
5 time is short, only TiO₂ porous oxide film can be formed without TiO₂ array.¹⁰⁷ With
6 the increase of anodizing time, the diameter of nanotubes may increase linearly (Fig. 9a,
7 b, c, d),¹⁰⁸ or increases and decreases repeatedly, but eventually increases.¹⁰⁹ However,
8 with the increasing oxide film thickness, the migration rate of H⁺ and F⁻ plasma
9 decreases, the increase of tube length gradually slows down, and finally reaches
10 stability(Fig. 9e).¹¹⁰



1
 2 **Fig. 9** Surface morphology of TiO₂ nanotubes under different oxidation time (a) 1 h, (b) 3 h, (c) 5 h,
 3 (d) 7 h¹⁰⁸ and (e) wall thickness of TiO₂ nanotubes under different oxidation time.¹¹⁰

4 **2.6 In-situ radiation**

5 In recent years, in-situ radiation has been used to adjust the structure of TiO₂ nanotubes.
 6 For example, when the TiO₂ nanotubes are prepared by anodic oxidation under
 7 ultraviolet-visible(UV-vis) radiation, because of the photooxidation of water by

1 nanotubes, the concentration of H^+ is higher at the bottom, the nanotubes with larger
2 diameter and thicker wall are produced after irradiation, and the length of nanotubes
3 remains unchanged compared with that without UV-vis radiation.¹¹¹ In addition, the
4 thickness of the inner wall and outer wall of the double-walled TiO_2 nanotube prepared
5 with UV assistance can be changed by altering the power of UV light.¹¹² Aliabadi et al.
6 carefully studied the influence of UV irradiation time on geometric characteristics, and
7 the results showed that the UV irradiation has a significant impact on geometric
8 characteristics in the two-step anodic oxidation process. After irradiation for 120
9 minutes, the size of TiO_2 nanotubes was increased, meanwhile, the surface area,
10 roughness and aspect ratio were also significantly improved.¹¹³

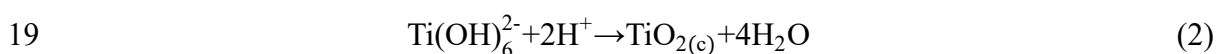
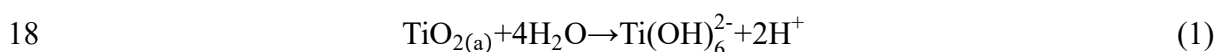
11 In summary, the structure of TiO_2 nanotubes is affected by oxidation voltage,
12 electrolyte, oxidation times and other parameters. The three stages of the oxidation
13 process could be coordinated with each other to obtain TiO_2 nanotubes with desirable
14 structure by adopting appropriate preparation conditions. Albu et al. prepared TiO_2
15 nanotubes with a length of more than 250 μm and a significantly higher aspect ratio in
16 HF acid system for the first time by comprehensively adjusting the voltage, HF acid
17 concentration and oxidation time.¹¹⁴ The high voltage may break through the Ti plate,
18 which is not conducive to the formation of TiO_2 nanotubes. However, by optimizing the
19 NH_4F content under different voltages, a uniform thin film without any oxide
20 breakdown can be obtained, and ordered TiO_2 nanotubes with high aspect ratio can be
21 rapidly prepared in a few minutes under the high anodic oxidation voltage of 220 V, and
22 the fastest growth rate is 2.45 $\mu m/min$.¹¹⁵

23 ***2.7 Heat treatment and water-assisted treatment***

24 Except for some special cases,¹¹⁶ TiO_2 nanotubes prepared by anodic oxidation are

1 amorphous. In order to change them into stable crystalline phase, there are currently two
2 methods: heat treatment and water-assisted treatment. The research shows that the
3 amorphous tube layer is obviously transformed into anatase at about 280 °C.¹¹⁷ At about
4 500 °C, rutile phase begins to appear. As the temperature further increases, anatase
5 phase disappears and completely transforms into rutile phase.¹¹⁸ In nanoscale, anatase is
6 relatively stable, while rutile is thermodynamically considered as the most stable bulk
7 phase. However, with the increasing temperature, the morphology of nanotubes will be
8 worse and worse. When Roy annealed nanotubes at 450 °C, cracks appeared in the tube
9 wall(Fig. 10a).¹¹⁹ Moreover, with the increasing temperature, the grain size becomes
10 larger, which is the main reason for tube collapse. Tube collapse will significantly affect
11 the specific surface area of TiO₂ nanotubes.

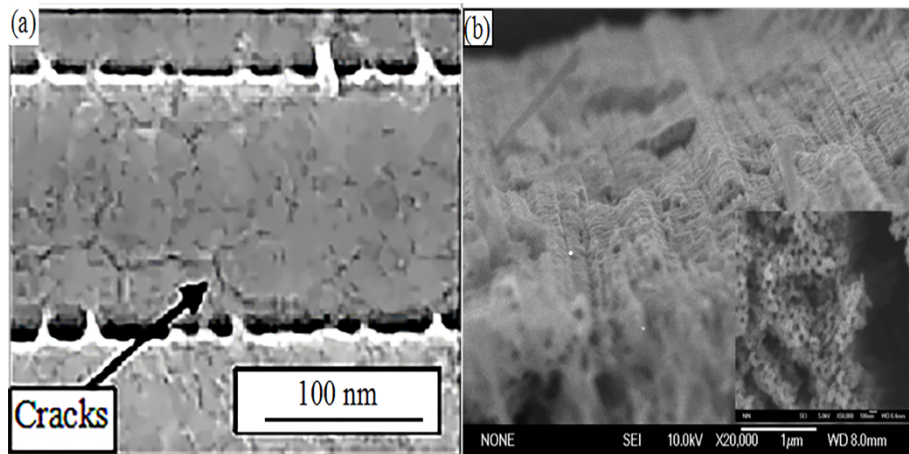
12 Another method is water-assisted treatment. In 2011, Liao et al. used deionized
13 water to place amorphous TiO₂ nanotubes at room temperature for 3-4 days, and the
14 amorphous nanotubes were transformed into stable anatase phase,¹²⁰ and part of TiO₂
15 nanoparticles would be deposited on the surface and side of nanotubes(Fig. 10b), which
16 significantly increased the specific surface area of TiO₂ nanotubes. The mechanism of
17 water-assisted crystallization is as follows:¹²¹



20 Here, TiO_{2(a)} is amorphous TiO₂ nanotube. TiO_{2(c)} is anatase TiO₂ nanotube.

21 After that, researches on water-assisted crystallization of TiO₂ nanotubes have
22 emerged one after another.¹²²⁻¹²⁴ The mixed phase of anatase and rutile can be obtained
23 by adding dilute HCl or HNO₃ into deionized water.¹²⁵ However, the crystallization
24 cycle of water-assisted TiO₂ nanotubes is longer, and the crystallinity is much lower
25 than that of heat-treated TiO₂ nanotubes. So, for TiO₂ applications requiring higher

1 crystallinity, such as dye-sensitized solar cells, water-assisted TiO₂ nanotube
2 crystallization can't replace heat-treated TiO₂ nanotubes,¹²⁶ which also limits the
3 application of water-assisted TiO₂ nanotube crystallization. Therefore, heat treatment is
4 generally adopted at present.^{127, 128}

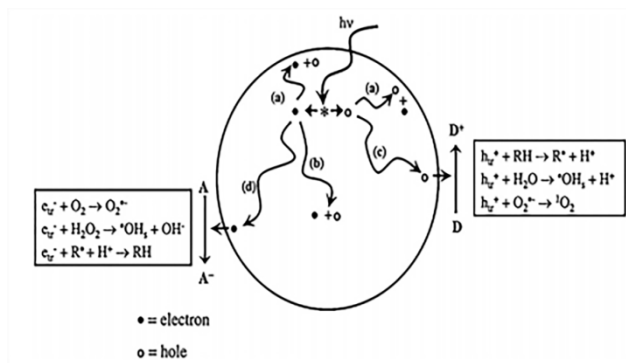
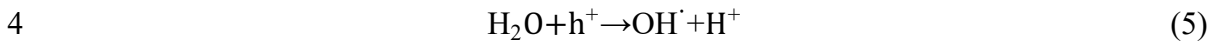
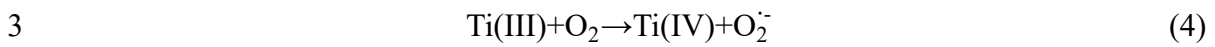
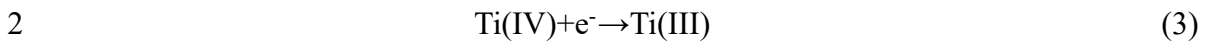


5
6 **Fig. 10** (a) After annealing at 450 °C, TiO₂ nanotubes with cracks in the tube wall,¹¹⁹ and (b) Water-
7 assisted treatment of side and surface morphology of TiO₂ nanotubes.¹²⁰

8 **3 Factors Affecting Photocatalytic Activity of TiO₂ Nanotubes**

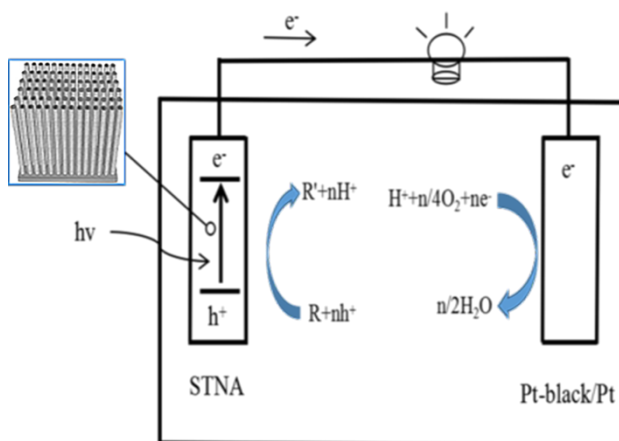
9 The photocatalytic mechanism of TiO₂ is shown in Fig. 11. After absorption of TiO₂
10 nanoparticles, photons with energy is equal to or higher than their band gap collide, and
11 electrons are excited from the valence band (VB) into the unoccupied conduction band
12 (CB), resulting in excited electrons in the conduction band and positive holes in the
13 valence band. These charge carriers can be recombined nonradiatively or radiatively
14 (dissipating input energy as heat), or captured and reacted with electron donors or
15 receptors adsorbed on the surface of the photocatalyst.¹²⁹ At the same time, electrons in
16 the CB usually participate in the reduction process. The reduction process usually reacts
17 with molecular oxygen in air to generate superoxide radical anion (O²⁻), O²⁻ and H⁺
18 form H₂O₂, which is further converted into OH⁻.¹³⁰ These free radicals can oxidize
19 macromolecular pollutants to form non-polluting inorganic small molecules, such as

1 CO₂ and water. The overall mechanism can be summarized as the following steps.¹³¹



7
8 **Fig. 11** Process occurring on bare TiO₂ particles after ultraviolet excitation.¹³⁰

9 Many researchers have developed photocatalytic fuel systems that can not only
10 degrade organic pollutants in water under visible light, but also make full use of their
11 chemical energy for power generation, thus greatly improving the utilization rate of
12 polluted water (Fig. 12).^{132, 133}



13
14 **Fig. 12** Schematic diagram of working principle of PFC system based on STNA wherein R and R'
15 are organic compounds and oxidation products thereof.¹³³

1 The ideal photocatalyst should exhibit the following characteristics: well chemical
2 corrosion resistance, good light corrosion resistance, ability of absorbing a wide range
3 of UV, vis and even infrared light, and effective charge separation. In addition, the
4 photocatalyst should be made of the elements which are rich in earth, cost-effective,
5 suitable for cheap synthesis methods, and can be used on a large scale.¹³⁴ As a common
6 photocatalyst, there are some disadvantages for TiO₂. Firstly, TiO₂ is a semiconductor
7 with a large forbidden band, which has photocatalytic activity only under UV irradiation.
8 Thus, the utilization rate of solar energy is low. Secondly, the photo-generated hole-
9 electron pair excited by TiO₂ is easy to recombine, which will obviously weaken the
10 photocatalytic activity of TiO₂. In order to solve these issues, effective improvement
11 methods include: 1) improving nanotube structure and morphology, 2) introducing other
12 elements, and 3) surface modification.

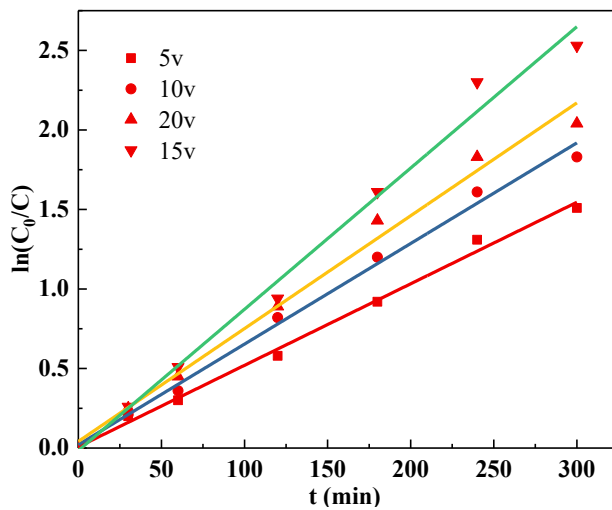
13 ***3.1 Structure and morphology of TiO₂ nanotubes***

14 *3.1.1 Morphology of TiO₂ Nanotubes*

15 Compared with these modifications introduced with foreign substances, it is also
16 remarkable to enhance the photocatalytic activity by improving the structure and
17 morphology of TiO₂ nanotubes.^{135, 136} As the unique aspect ratio structure of TiO₂
18 nanotubes, it is easy to separate the photo-generated carriers. Thus, the preparation of
19 TiO₂ nanotubes with higher aspect ratio is a way to improve their catalytic
20 performance.¹³⁷ With the increasing oxidation voltage and time, the diameter, length
21 and surface area of TiO₂ nanotubes are further increased, and the surface reaction rate
22 constant is linearly related to the surface area.¹³⁸ TiO₂ nanotubes grown on Ti substrate
23 are selectively dissolved at the bottom, and then HF acid is used to dissolve the oxide
24 film on the top of the nanotubes. TiO₂ nanotube arrays with open ends are prepared,

1 which have better permeability and photocatalytic performance.^{139, 140} Alternatively,
2 double-walled TiO₂ nanotube arrays can be prepared by imprint technology, and then
3 highly hexagonal ordered single-walled TiO₂ nanotube arrays can be obtained after
4 optimizing chemical treatment in piranha solution, and its catalytic activity is higher
5 than that of classic self-ordered TiO₂ nanotubes.¹⁴¹ TiO₂ nanotubes with nano grating
6 structure can be prepared by oxidation in fluorine-containing electrolyte, which
7 accelerates electron-hole separation and also provided lower recombination rate.¹⁴² The
8 performance of TiO₂ nanotubes is greatly improved even through simple surface
9 treatment.¹⁴³

10 The regularity and uniformity of TiO₂ nanotubes and their photocatalytic activity
11 increase with the increasing oxidation voltage. However, if the voltage is excessively
12 high, the regularity will be destroyed and the catalytic activity will be reduced.
13 Therefore, when the oxidation voltage increases to a certain value, the catalytic activity
14 of TiO₂ nanotubes reaches an extreme value (Fig. 13).¹⁴⁴

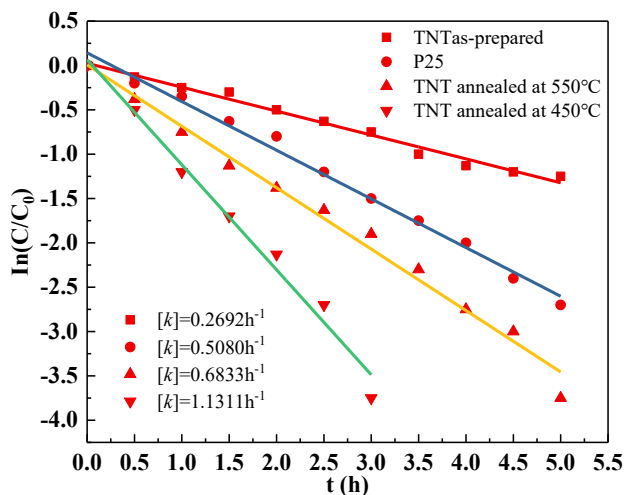


15
16 **Fig. 13** Photocatalytic activity of TiO₂ nanotubes under different voltages.¹⁴⁴

17 *3.1.2 Crystalline phase of TiO₂ Nanotubes*

18 Anatase phase is the main photocatalytic phase, and its catalytic activity is better than

1 that of amorphous and rutile TiO₂ nanotubes. Early studies have shown that the activity
 2 of pure anatase was higher than that of mixed phase.^{145, 146} Macak et al.¹⁴⁷ believed that
 3 the decrease of anatase is the reason for the decrease in photocatalytic activity (Fig. 14).



4
 5 **Fig. 14** Photocatalytic degradation rate of AO7 with different crystal phase structures (▼-anatase
 6 phase. ▲-mixed crystal structure of anatase and rutile).¹⁴⁷

7 However, recent studies have shown that the catalytic activity of the mixed crystal
 8 structure of anatase and rutile is higher than that of pure anatase phase.^{148, 149} According
 9 to the corresponding research, Li et al. showed that when it is annealed at about 500 °C,
 10 anatase and rutile can be obtained in a special layered mixed crystal phase. TiO₂ with
 11 mixed crystal structures can effectively inhibit the photogenerated hole-electron
 12 recombination, thus having higher catalytic activity.¹⁵⁰ The main photocatalytic phase is
 13 the anatase which distributes at the top of the nanotube. However, rutile phase at the
 14 bottom of the nanotube may form an internal electric field to promote effective
 15 separation of the photo-generated carriers, thus improving the activity. TiO₂ nanotubes
 16 prepared in acidic electrolyte can be annealed at 650 °C for 30 minutes to obtain a
 17 mixed phase of anatase and rutile with the highest crystallinity and also obtain the best
 18 catalytic degradation effect on methyl orange.¹³⁶

1 **3.3 Doping Modification**

2 *3.3.1 Non-metallic doping*

3 Non-metallic ion doping modification is a key area in the research of TiO₂ nanotubes,
4 and the doping ions are widely distributed, such as non-metallic cations (I⁵⁺, Si⁴⁺, etc.),
5 and anions (N, C, etc.). However, the B ion is special, which can replace Ti⁴⁺ in the
6 crystal lattice in the form of B³⁺, or replace O²⁻ in the crystal lattice in the form of B²⁻.¹⁵¹
7 Until now, the most successful research is N doping, which can narrow the optical gap
8 and improve the visible light catalytic activity.¹⁵²⁻¹⁵⁴ Because N has the atomic size
9 equivalent to oxygen, small ionization energy, formation and stability of metastable
10 center, so it is easier to dope into TiO₂ crystal lattice. Since Asahi et al. successfully
11 doped N in TiO₂ for the first time,¹⁵² the research on the mechanism of enhancing the
12 photocatalytic activity of TiO₂ nanotubes by N doping has become increasingly perfect.
13 ¹⁵⁵After doping, N may also serve as the recombination center of photo-generated
14 carriers, reducing the photocatalytic activity under UV light.¹⁵⁶The effect of C doping is
15 similar to N doping. It is generally believed that C doping can improve the adsorption of
16 organic molecules and the conductivity of TiO₂.¹⁵⁷ Therefore, C doped TiO₂ nanotubes
17 show better activity than TiO₂ nanotubes under UV light. C doped TiO₂ nanotubes can
18 be prepared by calcining the amorphous TiO₂ nanotubes in air and natural gas
19 atmosphere successively, which reduces the band gap of TiO₂ nanotubes and has higher
20 activity under visible light.¹⁵⁸ However, when the C doping amount is extremely high, C
21 will become the recombination center of electrons and holes, and the catalytic
22 performance will be reduced.¹⁵⁹

23 Many studies demonstrated that C doping is the substitution of C for O²⁻, thus
24 forming TiO_{2-x}C_x type C doped TiO₂ nanotubes,¹⁶⁰ while, according to Valentin et al's
25 theory, C was preferred to replace O under anoxic conditions, and was conducive to

1 replace Ti under oxygen-enriched conditions.¹⁶¹ The diameter of C doped TiO₂
2 nanotubes could be adjusted by changing the flow rate of carrier gas. The optical band
3 gap (2.72 eV) after doping was much smaller than that of anatase TiO₂ (3.20 eV).¹⁶²

4 *3.3.2 Metal doping*

5 The metal doping of TiO₂ nanotubes can be divided into three categories: transition
6 metal ions, rare earth metal ions and noble metal ions. Metal ions are doped into TiO₂
7 lattice to replace Ti⁴⁺ ions, thus affecting energy band structure and reducing the light
8 absorption edge energy of TiO₂. Karvinen et al. studied the doping effect of various
9 transition metal ions (V³⁺, Cr³⁺, Fe³⁺, etc.) on anatase and rutile, and found that the
10 doping of these ions can obviously reduce the band gap of anatase, but has no effect on
11 the rutile.¹⁶³ Rare earth elements have unique 4f orbitals and 5d orbitals, which can
12 reduce the recombination rate of electron-hole pairs. In addition, rare earth elements can
13 effectively prevent grain growth after doping. Compared with other rare earth ions, Gd
14 ion has the smallest energy band gap and grain size after doping, the largest specific
15 surface area and highest photocatalytic activity.¹⁶⁴ Mazierski et al. studied the
16 lanthanide doped TiO₂ nanotubes, and got different conclusions. Under visible light, Ho
17 doped TiO₂ nanotubes had the highest photocatalytic activity, and they thought that the
18 photocatalytic activity under visible light irradiation was not caused by oxygen center,
19 but by other forms of active oxygen (O₂^{·-}, HO₂[·], H₂O₂).¹⁶⁵ Noble metal deposition is
20 also one of the most effective methods to improve the photocatalytic performance of
21 TiO₂ nanotubes.¹⁶⁵ Noble metals such as (Ag, Au, etc.) can induce charge carriers by
22 light, thus realizing the effective separation of electron-hole pairs and improving the
23 photocatalytic activity.^{166, 167} It is generally believed that uniform doping can promote
24 the performance of element-doped TiO₂ nanotubes,¹⁶⁸ while non-uniform doping is

1 detrimental to the performance, because it may lead to partial aggregation of doped
2 elements and become the recombination center of carriers. However, Zhang et al. found
3 that non-uniform doping can form "platinum island" and interface separation effect in
4 Au-doped TiO₂ nanotubes, which is beneficial to isolate photogenerated electrons and
5 holes, so the photocatalytic activity of non-uniform Au-doped TiO₂ is enhanced
6 compared with uniform Au-doped TiO₂ nanotubes.¹⁶⁹ Although metal ions can
7 effectively reduce the band gap of TiO₂, metal ions can easily become the
8 recombination center of electron-hole pairs, which will reduce the photocatalytic
9 activity.¹⁷⁰

10 *3.3.3 Co-doping of Multiple Elements*

11 Although the doping of single element makes the photocatalytic performance of TiO₂
12 nanotubes better than that of un-doped TiO₂ nanotubes, there is still much room for
13 improvement in photocatalytic activity under visible light. In recent years, many
14 literatures show that the performance of multi-element co-doped TiO₂ nanotubes is
15 obviously higher than that of single-element doped TiO₂ nanotubes due to their
16 synergistic effect.^{171, 172}

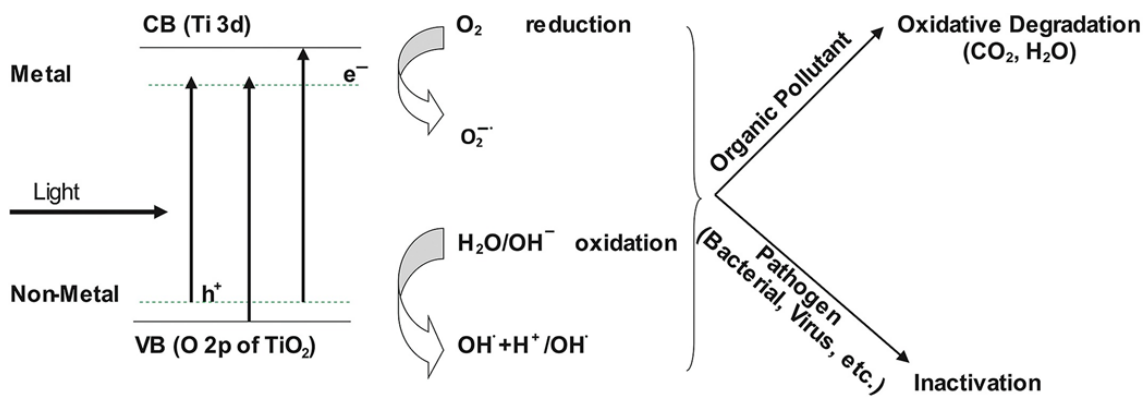
17 Multi-element co-doping includes metal-metal co-doping, metal-non-metal co-
18 doping, and non-metal-non-metal co-doping. For example, Lanthanum, gallium co-
19 doped TiO₂ nanotubes can accelerate the electron capture and dye adsorption. This is
20 because La³⁺ and Gd³⁺ replace Ti⁴⁺, resulting in a large number of oxygen vacancies
21 and surface defects. Thereby accelerating the separation of photo-generated electron-
22 hole pairs and promoting photocatalytic degradation.¹⁷³ Co-doping Ti³⁺ and Ni changes
23 the band structure of TiO₂ nanotubes, narrows the band gap to 2.84 eV, and enhances
24 the light absorption. Ni doping widens the VB of TiO₂, which can promote the

1 separation and transmission process of charge carriers. The performance is about 10
2 times larger than that of un-doped TiO₂ nanotubes.¹⁷⁴ When metallic element Zr is co-
3 doped with non-metallic element N, and the element ratio of Zr to N is 2:1, the
4 recombination of electron-hole pairs can be effectively inhibited due to the joint action
5 of metal and non-metal, so that TiO₂ nanotubes have higher photocatalytic activity
6 under visible light.¹⁷⁵ Non-metallic element B and metallic element Co are successfully
7 doped into TiO₂ nanotubes for the first time. Because the surface hydroxyl groups have
8 obvious advantages in different current densities, pH values, initial degradation
9 concentrations and degradations of different types of pollutants, the doping of Co
10 significantly enhances the stability of TiO₂ nanotubes, although it is detrimental to
11 photocatalytic activity.¹⁷⁶

12 Doping with various of non-metallic elements, such as N and F co-doping, will
13 lead to wormhole-like mesopores, which are beneficial to capture more photons for
14 stimulating the formation of photo-generated carriers, as well as larger surface area and
15 enhanced light absorption, thus having enhanced photocatalytic activity.¹⁷⁷ In addition,
16 the band gap of TiO₂ nanotubes is shortened from 3.2 eV to 3.04 eV by co-doping with
17 three or more non-metallic elements such as C, N, and F. Among all doped non-metallic
18 elements, C, N doping improves the visible light absorption of TiO₂, while F doping
19 leads to the formation of oxygen vacancy. In addition, C doping can also improve the
20 specific surface area of TiO₂ nanotubes, thus having good photocatalytic activity under
21 sunlight.¹⁷⁸

22 The general photocatalytic mechanism of doped TiO₂ is shown in Fig. 15. The
23 metal doping produces defect level near the CB of TiO₂, while non-metal doping causes
24 extra defect level above the VB of TiO₂. The defect energy level will shorten the band
25 gap of TiO₂, thus contributing to visible light photoactivity. In co-doped and multi-

1 doped TiO₂, electrons can transition from these defect energy levels or the VB of TiO₂
 2 to metal defect impurity energy levels, or to the highest energy level of CB of TiO₂.
 3 Metal ions in variable oxidation state can be used as electron capture centers. Capture
 4 centers lead to the increase of charge carrier life, thus increasing the photocatalytic
 5 activity of TiO₂.¹⁷⁹ How to select appropriate co-doping elements to exert synergistic
 6 effect and to improve the performance of TiO₂ nanotubes are the theoretical premises of
 7 co-doping modification, because the co-doping of some elements will reduce the
 8 performance of TiO₂ nanotubes.¹⁸⁰



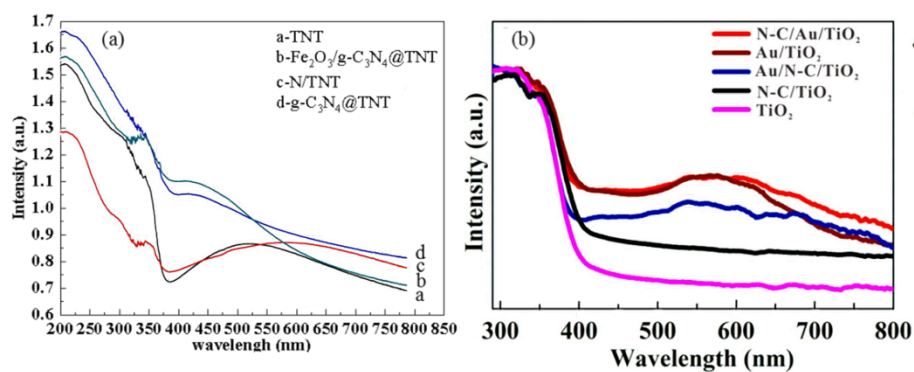
9
 10 **Fig. 15** General photocatalytic mechanism of doped TiO₂.¹⁸¹

11 **3.4 Filling and Surface Modification**

12 Because photo-generated carriers generated by TiO₂ excitation are easy to recombine,
 13 so it is very important to improve the catalytic activity by filling or surface modification
 14 to reduce carrier recombination. The recombination of charges e⁻ and h⁺ is reduced,
 15 more hydroxyl radicals and peroxides (O²⁻) are generated, and the photocatalytic
 16 degradation of organic matters is promoted.¹⁸²

17 It has been reported that many TiO₂ nanotubes are decorated or filled with different
 18 foreign materials.¹⁸³⁻¹⁸⁵ In recent years, the photocatalytic activity of TiO₂ nanotubes
 19 has been enhanced by constructing heterojunction (more than two layers of different
 20 semiconductor thin films are deposited on the same substrate in turn). Fe₂O₃ can form

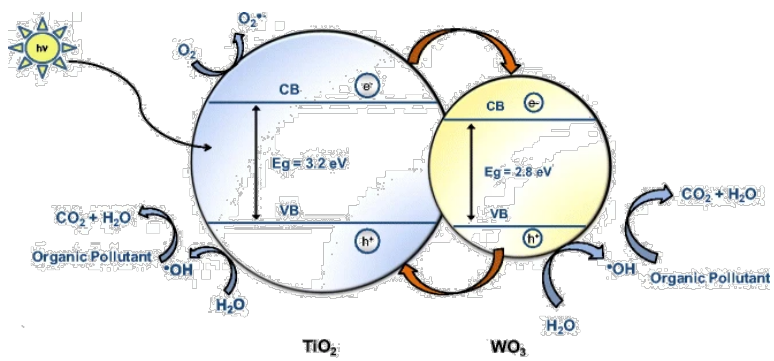
1 the type I heterojunction with TiO₂, which shows enhanced separation of e⁻/h⁺ pairs and
 2 enhanced photocatalytic activity.¹⁸⁶ In addition, similar to co-doping, when multiple
 3 materials with synergistic effect sensitize TiO₂ nanotubes, the performance of TiO₂
 4 nanotubes is higher than that of single material sensitized TiO₂ nanotubes. However,
 5 when materials without synergistic effect are sensitized together, the performance is
 6 reduced.¹⁸⁷ Fe₂O₃ and graphite nitrogen carbide (g-C₃N₄) are loaded on the surface of
 7 N-doped TiO₂ nanotubes, and the excitation energy of TiO₂ nanotubes is reduced due to
 8 the loading of N and Fe₂O₃, thus exhibits a lower E_g value (2.15 eV) than single TiO₂
 9 nanotubes, N-doped TiO₂ nanotubes and g-C₃N₄ loaded N-doped TiO₂ nanotubes. In
 10 addition, g-C₃N₄ can promote charge migration, so it has higher hydroxyl generation
 11 and degradation efficiency (Fig. 16a).¹⁸⁸ This synergistic effect is also applicable to
 12 TiO₂ with other structures (Fig. 16b).¹⁸⁹



13
 14 **Fig. 16** UV-vis diffuse reflectance spectra of different TiO₂ nanotubes¹⁸⁸ and TiO₂ samples.¹⁹⁰

15 WO₃ has a band position matched with TiO₂, which can form the type II
 16 heterojunction (Fig. 17),¹⁹¹ and the separation of electron-hole pairs is enhanced under
 17 visible light.¹⁸⁹ In addition to the WO₃/TiO₂ heterojunction alone, BiVO₄ is selected to
 18 be introduced into WO₃/TiO₂ nanotubes, and oxygen vacancy is also introduced. With
 19 the introduction of BiVO₄, the inherent degradation path dominated by hydroxyl and
 20 hole into the degradation path dominated by oxygen vacancy and hole. The stable
 21 oxygen vacancy is used to construct the separation and transmission of charge carriers

1 in heterogeneous materials, thus realizing the high catalytic performance and stability of
 2 the composite membrane in degrading volatile organic pollutants.¹⁹²

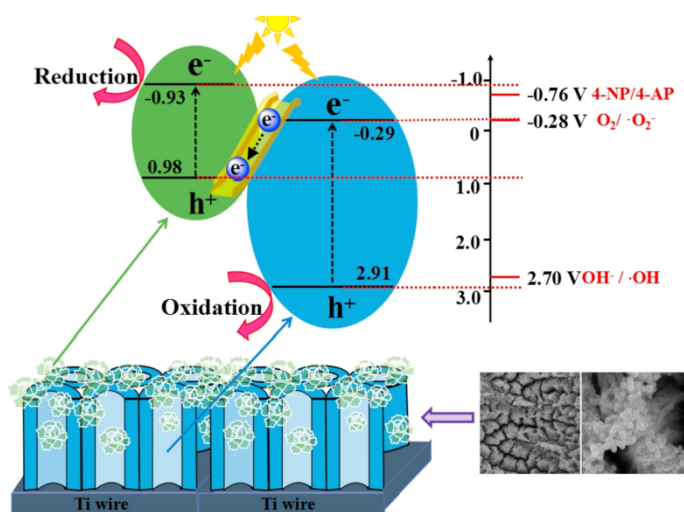


3
 4 **Fig. 17** Mechanisms of degradation proposed for (a) WO_3/TiO_2 and (b) $\text{Fe}_2\text{O}_3/\text{TiO}_2$.¹⁹³

5 Ag_2O is a visible light active photocatalyst with a band gap of 1.2 eV, which forms
 6 a heterojunction with TiO_2 (type III heterojunction).¹⁹¹ Photogenerated electrons in CB
 7 of Ag_2O are transferred into CB of TiO_2 , and react with adsorbed O_2 to form O^{2-} . In
 8 addition, photogenerated h^+ in VB of Ag_2O reacts with OH^- to form $-\text{OH}$, and
 9 participates in degradation.¹⁹⁴

10 In addition, the Z-scheme structure is another connection mode between the above
 11 two semiconductors. Z-scheme structure can reduce the band gap of semiconductor and
 12 make CB potential more negative and VB potential more correct. This structure is a
 13 promising strategy for improving photocatalysts.¹⁹⁵ Compared with the traditional type
 14 II heterostructure, Z-scheme structure can not only realize the effective separation of
 15 photogenerated electrons and holes, but also enhances redox ability.¹⁹⁶ By constructing
 16 the Z-scheme structure of TiO_2 nanotubes-graphene(GR)-CdS quantum dots, the light
 17 absorption range of TiO_2 nanotubes is extended to a wider sunlight area due to the
 18 coupling of TiO_2 nanotubes, GR and CdS quantum dots.¹⁹⁷ The principle of
 19 photocatalytic degradation of 4-nitrophenol (4-NP) by the direct Z-scheme structure
 20 formed by MoSe_2 and TiO_2 nanotubes is shown in Fig. 18, the electrons (-0.93 V)
 21 stored in the CB of MoSe_2 are mainly captured by 4-NP ions and reduced to form 4-

1 aminophenol. Furthermore, the absorbed water molecules are easily oxidized to free
 2 radicals $\cdot\text{OH}$ by the holes (2.91V) accumulated in high potential TiO_2 VB. Then, the
 3 benzene ring of 4-NP is easily attacked by free radical $\cdot\text{OH}$ and degraded into small
 4 organic molecules. In addition, highly ordered anodic TiO_2 nanotubes are beneficial to
 5 the reaction of transferred free radicals $\cdot\text{OH}$ with adsorbed organic molecules, thus
 6 realizing the effective removal of 4-NP.¹⁹⁸



7
 8 **Fig. 18** Mechanism of photocatalytic degradation of 4-NP by $\text{MoSe}_2@\text{TiO}_2$ nanotubes direct Z-
 9 Scheme composite under sunlight.¹⁹⁸

10 Of course, there are still other types of heterojunctions. By constructing the 0D/1D
 11 heterostructure of GdS quantum dots/ TiO_2 nanotubes, the combination of CdS quantum
 12 dots and TiO_2 nanotubes significantly accelerates the process of trapping electrons in
 13 the heterostructure. Furthermore, the recombination lifetime of electrons at the shallow
 14 and deep traps with holes can be extended to 73.2 ps and 622.6 ps, respectively.¹⁹⁹

15 4 Conclusions

16 In this paper, the preparation and modification of anodized TiO_2 nanotubes in recent
 17 years are briefly reviewed. Due to the novel physical properties of vertically aligned
 18 TiO_2 nanotubes prepared by anodic oxidation, anodic oxidation method is widely used.
 19 However, there are still many problems to be solved, including the lack of clear

1 explanation of many basic mechanisms and the development of TiO₂ nanotubes with
2 significant photocatalytic activity under sunlight. In recent years, the rapid development
3 in the preparation and modification of anodized TiO₂ nanotubes has enabled TiO₂
4 nanotubes to meet the increasingly severe challenges of photocatalysts, so as to cope
5 with the practical application of environmental pollution. However, the inherent wide
6 band gap of TiO₂ nanotubes is the main bottleneck which restricts its wide applications.
7 In order to improve the visible light photocatalytic activity of TiO₂ nanotubes, various
8 means are needed to change the electronic structure and energy band structure of the
9 crystal, or to reduce the recombination rate of electron-hole pairs. Some new
10 modification methods developed in recent years make the practical application of TiO₂
11 nanotubes longer. Facing the increasingly serious environmental pollution problem, the
12 photocatalyst- TiO₂ nanotube is playing an important role in protecting our environment.

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18 **Conflicts of interest**

19 There is no conflict of interest.

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