

양극산화 기법으로 제조한 TiO₂ 나노튜브의 촉매 도핑 연구 동향

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Research Trends in Doping Methods on TiO₂ Nanotube Arrays Prepared by Electrochemical Anodization

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초 록

전기화학적 양극산화 기법으로 제조한 타이타늄 나노튜브는 타이타늄 특유의 강한 화학내구성 및 나노튜브의 높은 종횡비로 인하여 넓은 범위에 응용된 소재이다. 전해질의 구성 성분과 종류, pH, 전압, 온도 그리고 양극산화 시간이 타이타늄 나노튜브의 성상을 결정짓는 요소들이며 도핑을 통해 촉매능을 부여할 수 있다. 비금속 및 금속 원소 모두 도핑 가능하며 도핑 방법 역시 다양하다. 도핑 방법에는 합금 양극산화, 열처리법, 침전법, 전기도금법 등 다양한 방법들이 이용되며 점차 간단하고 빠른 도핑 방법을 찾는 방향으로 연구가 진행되고 있다. 본 총설에서는 타이타늄 나노튜브의 생성 원리와 상용된 제법들에 관하여 기술하고 도핑과 그 응용 및 최근의 도핑 연구 동향을 다루도록 하겠다.

Abstract

Nanotubular TiO₂ prepared by electrochemical anodization has been significantly used for various applications due to high aspect ratio structures showing a high chemical stability. Morphological properties of nanotubular titanium oxide are easily tailored by adjusting types and compositions of electrolyte, pH value, applied voltage, temperature and anodization time. Since their catalytic properties can be enhanced by doping foreign elements into TiO₂, metal as well as non-metal elements are doped into TiO₂ nanotubes using different methods. For example, single anodization, thermal annealing, precipitation, and electrochemical deposition have been applied to simplify the doping process. In this review, anodization of Ti to produce TiO₂ and doping methods will be discussed in detail.

Keywords: TiO₂ nanotubes, Anodization, Doping, Catalysts

1. Introduction

Anodization has been used for a long time to surface finishing of aluminum in industry, producing a chemically and mechanically stable oxide film from natural oxide on aluminum through electrochemical reaction[1]. Based on successful application of anodic aluminum oxide in various applications, other valve metals such as Ti, Nb, W, Hf have been intensively studied for the last decade[2-7]. Especially, due to unique chemical and physical properties of TiO₂ such as biocompatibility, semiconductor, and catalytic effects, anodization technique of Ti has been developed to produce various morphological features according to expansion of applications. After TiO₂ nanotubular

structures with a thickness of less than 500 nm have been successfully produced in HF based electrolyte in 1984[8], there have been many efforts to develop advanced recipes for producing stable long thickness of nanotubular oxide films. Nowadays, oxide thickness of more than 1000 μm has been reported[3]. Typically, the electrolyte containing F⁻ is used in the anodization of Ti, which allows a relatively low applied voltage to produce homogeneous oxide film with high-aspect-ratio and well-aligned structure at low cost. Because of large surface area, vertically aligned long nanotubular structure, chemical stability, bandgap of 3.0~3.2 eV, reliable biocompatibility, catalytic properties and photocatalytic properties, anodic TiO₂ has attracted much attentions in various applications such as solar cell electrodes, chemical/bio sensors, functional separator membranes, implants and so on[2,9-13]. It is clear that anodic TiO₂ itself is very useful materials for various applications. However, the bandgap is high, which is not able to absorb a visible light and conductivity of oxide is low, which require high overpotential during electrochemical reaction. Doping of foreign elements into TiO₂

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has been studied recently in order to reduce the bandgap and over-potential in electrochemical reaction[11-13]. In this review, recently developed methods for the preparation of anodic TiO₂ and foreign element doping will be discussed. More detailed review for the fabrication and applications of anodic Al₂O₃ and TiO₂ can be found in other literatures[14,15].

2. Anodization of Ti

In 1999, Zwillig reopened the stable oxide formation on Ti by anodization in HF based electrolyte[16], which allows the production of vertically-aligned nanotubular TiO₂ with a thickness of less than 500 nm. Afterwards, various electrochemical conditions were reported to increase the thickness of oxide by many research groups[9-13,15,17-19]. Unlike thickness of porous aluminum oxide is mainly determined by anodization time, the thickness of TiO₂ is limited not by the anodization time but by electrolyte bath. It is due to that the formed oxide structure is dissolved in the electrolyte containing F. When dissolution rate equals to the formation rate at a certain time, the length of nanotubes is determined in the case of anodization of Ti. Based on Grimes' book, anodization of Ti can be classified to four generations based on the morphology and thickness of nanotubes[13]. In the first generation, electrolyte of HF with a small amount of acid was used for anodization of Ti, which allowed the formation of nanotubes with a thickness of less than 500 nm. The applied potential was optimized to 20~30V depending on the electrolyte. In the second generation, it was found that pH value is the very important factor to determine the length of nanotubes. Acidic condition led to produce short nanotubes and longer nanotubes were formed when the pH value reached to neutral. Thus, in the second generation, acidic HF was substituted by neutral salts such as NaF and NH₄F, which allowed formation of nanotubes with the maximum thickness of 7 μm. In order to remove H⁺ effects from water, non-aqueous electrolytes such as glycerol and ethylene glycol (EG) was used instead of aqueous electrolyte (the third generation). In this generation, the thickness of nanotubes was dramatically increased. For example, more than 1000 μm thick nanotubes were reported in EG containing NH₄F and small amount of water. In the fourth generation, F⁻ based electrolyte was substituted by non-fluoride electrolyte such as HCl and H₂O₂ since fluoride electrolyte is very corrosive and toxic. However, the obtained results showed that the nanotubes are not homogeneously formed overall the surface of Ti. Instead, clump and bundle of nanotubes at very local areas were formed. In this review, we discussed the doping of foreign element to TiO₂ nanotubes, which is prepared in fluoride based electrolyte.

2.1. Mechanism of formation of TiO₂ nanotubes and important factors

Anodic oxide can be produced by either potentiostatic or galvanostatic method. From industrial point of view, the galvanostatic method is frequently used since it is easy to exactly control the thickness of oxides via anodization time. On the other hands, the cell size, pore (or nanotube) size, pore-pore (nanotube-nanotube) distance are strongly in-

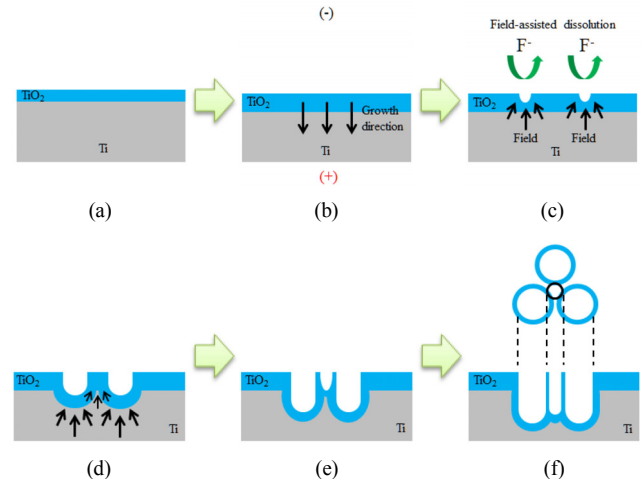


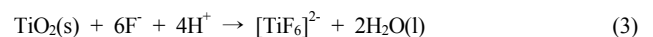
Figure 1. Mechanism of TiO₂ nanotubes formation by potentiostatic method.

fluenced by applied voltage. More highly-arranged nanotubular structures can be obtained by a constant voltage mode (potentiostatic method)[13]. It is due to that the formation mechanism relies on the field-assisted oxide dissolution mechanism. Thus, constant applied voltage is very important factor to prepare homogenous nanotubular TiO₂. In the formation of TiO₂ nanotubes, the following stages were roughly suggested :

- (1) Growth of the barrier-type oxide from natural oxide at initial stage (Figure 1 (a) and (b)).
- (2) Formation of nano-pits on oxide surface by attack of F⁻ ions (Figure 1 (c)).
- (3) The growth of nanotubes from the nano-pits through the electric field concentrated at nano-pits (Figure 1 (d)-(f)).

In the more detailed mechanism;

- (a) O²⁻ and/or OH⁻ in electrolyte are attracted to positively-biased Ti electrode, and react with metal ions (Ti⁴⁺) at the interface of metal and electrolyte, which forms the metal oxide layer such as TiO₂ (the barrier oxide formation).
- (b) Ti⁴⁺ in TiO₂ is dissolved into electrolyte by electric field, continuously being supplied from the Ti metal.
- (c) TiO₂ reacts with F⁻ in acidic environment to form [TiF₆]²⁻, which is very easily dissolved in water. This allows the formation of nanotubular structures[9-13,15].



The growth mechanism of TiO₂ nanotubes is depicted in Figure 1. The applied potential influences on the thickness of wall of nanotubes[9-13,15]. As the applied potential increases, thickness of the barrier oxide increases, which allows the thick wall of nanotubes (Figure

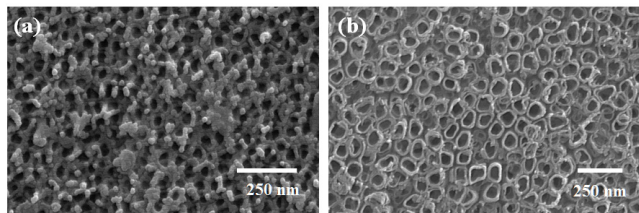


Figure 2. SEM images of titanium nanotubes prepared in (a) H₂SO₄/HF solution at 20 V for 1 h and (b) H₃PO₄/NaOH/HF electrolyte at 20 V for 4 h.

l (a) and (b)). In addition, nanotube-nanotube distance typically increases as the applied potential increases up to 60 V. At applied potential higher than 60 V, there is no more linear relationship. The maximum nanotube-nanotube distance was reported to less than 150 nm.

As mentioned earlier, type and composition of electrolyte are the very important factor to determine the length of nanotubes. In the reaction 3, suppression of evolution of H⁺ is the critical step to avoid the formation of [TiF₆]²⁻, which is the key factor to determine the length of nanotubes. If concentration of F⁻ is too low, reaction for the formation of nanotubes is too slow, reducing the diameters of nanotubes as well as voids between nanotubes. Thus, the final morphology is more-likely nanoporous structure instead of nanotubes. It was reported that the length of structure prepared at a low concentration of F⁻ is higher than that prepared at a higher concentration. On the other hand, large diameter and thin wall of nanotubes are formed in a high concentration of F⁻ ions. If the concentration is too high, the anodic oxide film is completely dissolved.

The length of nanotubes is strongly influenced by pH value. In general, nanotubes can be formed at weak acid or less than 7. It was believed that nanotubular structure is not formed at a basic pH value.

If the pH is less than 1, nanotubes with a thickness of less than 500 nm is prepared even though anodization time is elongated. Until pH value of 2, the thickness does not increase significantly. However, length of nanotubes linearly increases in terms of anodization time above pH value of 2. Up to pH value of 6, the maximum obtainable length of nanotubes is linearly proportional to pH value[9,11,19].

2.2. Electrochemical conditions for the preparation of TiO₂ nanotubes

In 1999, Zwilling et al. showed the anodic oxide formation of pure Ti and Ti6V substrates in mixture electrolyte of H₂CrO₄ and HF at 5 V and 10 V[16]. They did not claim that the prepared structure is nanotubular morphology. However, it clearly showed initial stage of nanotubes, which is generally produced by anodization for a short time. In 2001, Grimes's group reported TiO₂ nanotubes by anodization at 0.5 wt% HF at 3, 5, 10 V, and 20 V, respectively, for 45 min, showing that oxide film consisting of granular structure is obtained at less than 10V whereas nanotubes with a thickness of 500 nm is obtained at higher than 10V. The diameters of nanotubes prepared at 10 V and 20 V were measured as 50 nm and 100 nm, respectively, indicating that diameter of TiO₂ nanotube is significantly influenced by the applied voltage. It was well known that the anodic TiO₂ nanotubes

prepared at the same voltage show a similar diameter and wall thickness[17,18]. Longer length of nanotubes is obtained in the mixture of HF and H₃PO₄ (or H₂SO₄), compared to that prepared at a single HF electrolyte since H₃PO₄ (or H₂SO₄) helps maintaining a local pH in nanotubes and suppress the dissolution of the formed oxide through anion-competition reaction[13,20]. Figure 2 (a) shows nanotubes prepared in the mixture of H₂SO₄ and HF.

As mentioned, longer length of nanotubes can be produced by increasing the pH value up to pH of 5~6 through neutralization reaction by the addition of NaOH. Figure 2 (b) shows TiO₂ nanotubes with a thickness of 1 μm, which is prepared by anodization at 20 V for 4 h in the mixture of 1M H₃PO₄, 1 M NaOH, and 0.5 mL HF (pH = 4.5). If the pH increases up to 5.6~6, nanotubes with a thickness of more than 4.4 μm are prepared by anodization for 20 h[11,13]. Diameter of nanotubes is not changed as anodization time increases, unless the applied voltage is not changed[6]. Table 1 shows the mostly-used electrochemical conditions for anodization in aqueous electrolyte. Instead of HF, NH₄F is mostly used in non-aqueous electrolyte. Non-aqueous electrolyte allows the formation of nanotubes with significant long length. Even though there were several attempts to anodize Ti in the mixture of ethylene glycol containing H₃PO₄ and NH₄F, the maximum obtainable length was 2.4 μm[21]. In 2006, Grimes's group showed that anodic nanotubes with a length of 70 μm can be produced in formamide containing a small amount of water, triggering study on formation of anodic the high-aspect-ratio nanotubes. Later on, TiO₂ nanotubes with a thickness of 93 μm was successfully produced in DMSO (dimethyl sulfoxide) containing 2 wt% HF at 60 V for 70 h[18]. Based on the suppression of reaction 3, TiO₂ nanotubes with a length of 1000 μm was prepared in the mixture of ethylene glycol and NH₄F by Grimes's group[22]. Schmuki's group showed the nanotubes with high-aspect-ratio of 150 in the same electrolyte[23]. There are two main problems in the formation of anodic TiO₂ when non-aqueous electrolyte is used. The first, adhesion of Ti nanotubes on a Ti substrate is not good enough. The second, the top of TiO₂ nanotubes, where is exposed in the aggressive electrolyte for the longest time, is dissolved during anodization. It leads to destroy the nanotubular morphology on the top (so-called bamboo-splitting mode). In the bamboo-splitting mode, several parameters such as a high voltage, long anodization time, and small amount of water, enhance the dissolution of the top surface of TiO₂ nanotubes, leading to split the nanotubes to nanowires[24,25]. Figure 3 shows the bamboo-splitting mode and normal TiO₂ nanotubes, respectively. There are several methods to avoid the bamboo-splitting mode. The most frequently used way is to employ ultrasonic immediately after anodization.

3. Catalysts Introducing on TiO₂ Nanotube Arrays

TiO₂ nanotubes are very favorable material to be used for catalysts because of its very high aspect-ratio and chemical stability. Nevertheless, because of a low conductivity of the metal oxide, unnecessary overpotential is required in electrochemical and photoelectrochemical reactions. Uniformly doping of catalysts in TiO₂ nano

Table 1. The Results of Size of Nanotubes Depending on Electrolyte pH, Composition, Anodization Condition[13]

No.	Electrolyte			pH	V (V)	t (h)	D (nm)	L (μ m)	Results
	SO ₄ ²⁻	PO ₄ ³⁻	Citric acid						
1	1.0	-	-	< 1	5	1	10 \pm 2	-	No NT
2	1.0	-	-	< 1	10	1	40 \pm 5	0.28 \pm 0.02	NT
3	1.0	-	-	< 1	15	1	80 \pm 9	-	NT
4	1.0	-	-	< 1	20	1	100 \pm 11	0.48 \pm 0.03	NT
5	1.0	-	-	< 1	25	1	110 \pm 12	0.56 \pm 0.04	NT
6	1.0	-	-	< 1	30	1	-	-	No NT
7	1.0	-	0.2	1.3	10	20	30 \pm 5	0.32 \pm 0.03	NT
8	1.0	-	0.2	2.8	15	20	50 \pm 5	1.00 \pm 0.05	NT
9	1.0	-	0.2	2.8	25	20	115 \pm 10	1.50 \pm 0.04	NT
10	1.0	-	0.2	3.8	10	20	30 \pm 5	0.80 \pm 0.06	NT
11	1.0	-	0.2	3.8	10	90	30 \pm 5	2.30 \pm 0.08	NT
12	1.0	-	0.2	4.5	25	20	115 \pm 5	4.40 \pm 0.10	NT
13	1.0	-	0.2	5.0	10	20	30 \pm 5	1.40 \pm 0.06	NT
14	1.0	-	0.2	5.0	25	20	115 \pm 5	6.00 \pm 0.40	NT
15	1.0	0.1	0.2	6.4	10	24	-	-	No NT
16	2.0	-	-	< 1	10	24	-	-	No NT

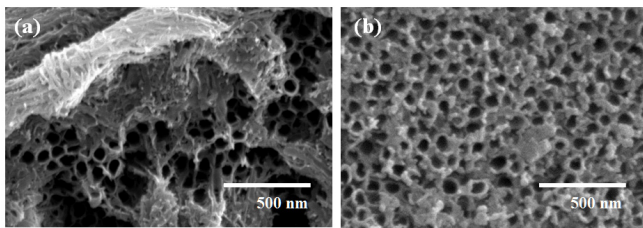


Figure 3. Pore-closed TiO₂ nanotubes by bamboo-splitting mode, which is prepared in EG (ethylene glycol)/NH₄F at 40 V for 19 h (a) and (b) mechanically stable TiO₂ nanotubes containing RuO₂, which is prepared in EG/NH₄F/KRuO₄ for 19 h.

tube arrays has been intensively studied to solve the problems. In general, complicate and delicate processes consisting of several steps are involved to incorporate foreign elements to the TiO₂ because uniform doping is the most difficult task in the high-aspect-ratio structure.

3.1. Conventional doping method and application

Dopants consisting of non-metal elements like N, P, F, B and S are mainly employed for tailoring the bandgap of TiO₂ in the application for photocatalysts[26-31]. Nobel metals such as Ag and Au are frequently doped into TiO₂ in order to increase the sensitivity of gas/bio sensing[32,33] and the others such as Si, CdS, Zr, Cr, Ni, Ru, W, etc. are classified as the catalysts for electrochemical or photoelectrochemical activator[25,34-46].

For example, Wei and co-workers prepared (Ru_{0.3}Ti_{0.34}Sn_{0.3}Sb_{0.06})O₂ catalyst based on RuO₂ on TiO₂ nanotubes for achieving ion selectivity of CER(Chlorine Evolution Reaction)[47,48]. As a precursor, RuCl₃, C₁₆H₃₆O₄Ti, SnCl₄ and SbCl₃ were dissolved in iso-propanol with a proper ratio and subsequently it was brushed on as-prepared TiO₂

nanotube electrodes evenly. Solvent was perfectly evaporated in 100 °C and the samples were annealed in 500 °C during 10 minutes. These procedures were conducted 10 times repeatedly. After the procedure is completed, final single annealing for 1 h at 550 °C was followed[35]. The electrodes showed very high sensitivity and selectivity for CER. However, the main problem was too inconvenient and time-consuming processes required for doping.

Non-metallic elements such as C, B, N and S can be easily introduced by annealing in furnace, which shows an enhanced photocatalytic activity. Schmuki and co-workers prepared TiO₂ nanotubes at Na₂HPO₄/HF electrolyte, which was doped with C in furnace under C₂H₂/N₂ gaseous stream. It led to decrease bandgap of TiO₂, increasing photocatalytic activity[28]. B and N could be employed from the molecules of BF₃ and NH₃. These elements were doped based on modification of the method of Schmuki's group by Tsuchiya and co-workers. Doping of B and N allowed the activation of TiO₂ under light source with a range from 420 to 430 nm. Even though individual dopant could show sufficient performance of photocatalytic properties in UV-VIS, the dramatic performance enhancement was achieved when both of dopants were doped[29]. Li conducted doping experiment on TiO₂ nanotubes by annealing under H₂S gaseous stream to obtain the activation of TiO₂ in the whole range of UV-VIS[30]. Metal element such as Cr could be introduced by a dry process such as ion implantation[39]. The most representative method on wet process was electroplating. Zhang and co-workers showed photoelectrochemically doped Au nano particles in TiO₂ nanotube arrays for the application of immunosensor devices to detect antigen of Parkinson's disease[32]. Zr could be deposited on TiO₂ nanotubes by electroplating for achieving activation in visible light[38].

The single-step anodization was able to incorporate a dopant into Ti

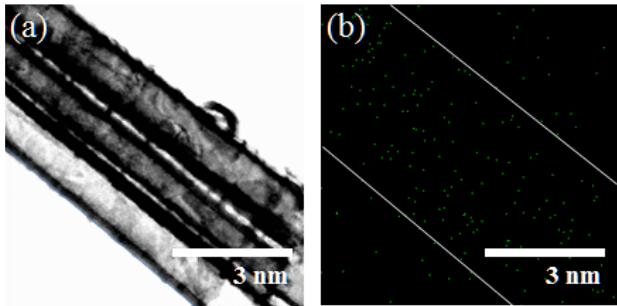


Figure 4. (a) FE-TEM images and (b) EDS mapping result of TiO₂ nanotubes prepared at 40 V for 19 h in 0.25 wt% NH₄F with 0.02M KRuO₄ electrolyte. The green spots demonstrated Ru atoms incorporated in TiO₂ nanotubes. Average atomic percent of Ru was 0.12%.

alloy substrates. For the doping of Ni₂O₃ into TiO₂, Tang and co-worker employed the cast method on NiTi alloy substrates. As a result, Ni₂O₃-TiO₂ nanotubes were successfully prepared, showing biocompatibility and bioactivity[36]. Nb-Ti-O nanotubes were fabricated from NbTi alloy substrates by single-step anodization for the growth of stem cells by Mao and co-workers[37].

3.2. Research trends of doping methods recently

In the techniques of single-step anodization of alloy substrates containing dopants, Cr or CuAl were added in Ti as impurity. By anodizing the alloy substrate, nanotubes with a dopant were successfully prepared. Cr in TiO₂ structure took a role as a activator in UV region under 400 nm wavelength[40]. When Cu and Al were incorporated with TiO₂, antibacterial and human-friendly surface properties were activated. Therefore, the Cu(or Al)-doped TiO₂ was suggested to be used in a novel non-toxic biological material[41].

CdSe or Ag was easily and uniformly doped by immersing method. First, CdSe nanoparticles (NPs) were prepared and then it was deposited on the surface of TiO₂ nanotubes by immersing TiO₂ substrate in the solution containing CdSe NPs. CdSe-TiO₂ interface had the activation in the range from 200 nm to 600 nm wavelength, which is an important light range for solar cell operation[42]. Ag also shows the same effect in visible light region, demonstrating highly-increased performances in solar cells[33].

CdS photoelectrochemical catalysts could be doped by electrochemical deposition. CdS catalysts unusually exhibited the extension of activation region as the doping amount increased. Moshfegh et. al. insisted that it is due to energy trap phenomenon occurred by each CdS particles[43].

The outstanding changes in single-step anodization have reported recently. Although P and C can be introduced in the electrolyte of H₃PO₄ and EG[27], it was not agreed widely. In 2012, Cui and co-workers demonstrated that anodization and doping simultaneously occurred when metal anion complex was used as precursor and supporting electrolyte[34].

Our group reported that TiO₂ MAO (micro-arc oxidation) thin film with a doping of IrO₂ and RuO₂ can be prepared by single anodization [44,45]. In addition, we demonstrated that fabrication of RuO₂ doped

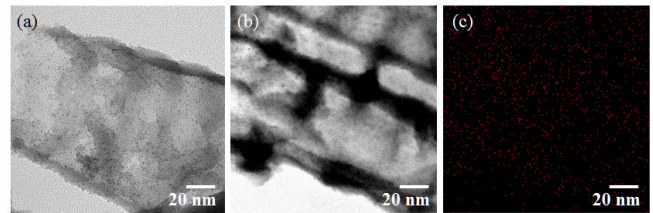


Figure 5. (a) Ru oxide particles doped by potential shock was observed at the surface of nanotubes. Compared to the nanotubes prepared by single-step doping method, Ru oxide phases were clearly observed as spot shape. EDS mapping results of TiO₂ nanotubes prepared by potential shock method were shown in (b) and (c). Ru element entirely and uniformly existed on nanotubes.

TiO₂ nanotubes for DSA (dimensionally stable anode) applications is possible by the same method[25]. EG/NH₄F medium was selected to produce enlarged aspect-ratio of nanotubes and KRuO₄ was dissolved in the electrolyte as a precursor and supporting electrolyte for Ru source. Ru was successfully incorporated in titanium oxide crystal phases as the form of RuO₂ evenly via the potentiostatic anodization at 40 V (Figure 4), showing the dramatic enhanced performance of water splitting with a maximum current density of 85 mA/cm² (at 2 V with Ag/AgCl 3M KCl). Figure 4 demonstrates that the thickness of the walls of nanotubes increase up to around twice when RuO₂ is incorporated into the wall. Thus, the typical nanopore closing problem and bamboo-splitting mode is suppressed[24,25,49].

Because of the minus net charge of RuO₄⁻ in the electrolyte, RuO₄⁻ can be attracted to anode, where is positively biased. Thus, if a high positive potential is imposed on the TiO₂ (so-called potential shock), the RuO₄⁻ can be incorporated into TiO₂ without significant damage of structure. Thus, the 2-step of potential shock is useful method for the doping: the first is fabrication of nanotubes and the second is the doping step by potential shock. Potential shock method was originally developed for the fabrication of through-hole membrane of TiO₂ nanotubes immediately after the fabrication of nanotubes [50]. We found that when the channels of nanotubes at top side is opened clearly, RuO₄⁻ can be introduced into TiO₂ nanotube arrays and be converted to RuO₂ phase evenly (Figure 5)[46]. RuO₂ phase originated from KRuO₄ was doped in TiO₂ nanotubes at 140V of potential shock voltage for 10 s.

4. Concluding Remarks

Recently, the fabrication of TiO₂ nanotubes with high-aspect-ratio has attracted great attention due to unique chemical and physical properties of TiO₂ and cost-effective process on a large scale for various applications. However, because of low conductivity and relative high bandgap, its catalytic and photocatalytic properties are limited to some applications. To increase the conductivity and to reduce bandgap, doping of foreign elements into TiO₂ nanotubes is one of important techniques in anodization of Ti. Various types of catalysts and doping methods can be employed for the proper purposes. In this review, we discussed the fabrication of anodic TiO₂ nanotubes in acid, neutral, and

non-aqueous electrolyte based on the anodic oxide formation mechanism. In addition, various doping elements such as metallic and non-metallic were discussed with their potential applications. Finally, we introduced recently-developed doping protocols: single-step anodization and potential shock.

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