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Abstract

In the present review, we provide an overview of the research trend of anodic TiO$_2$ nanostructures. To date, most anodic TiO$_2$ nanostructure formation has focused on the fluoride ion electrolyte system to form nanotube layers. Recently, a novel approach that describes the formation of thick, self-organized TiO$_2$ nanostructures was reported. These layers can be prepared on Ti metal by anodization in a hot organic/K$_2$HPO$_4$ electrolyte. This nanostructure consists of a strongly interlinked network of nano-sized TiO$_2$, and thus provides a considerably higher specific surface area than that of using anodic TiO$_2$ nanotubes. This review describes the formation mechanism and novel properties of the new nanostructures, and introduces potential applications.

Keywords: TiO$_2$ nanostructure, porous structure, anodization, phosphate/glycerol electrolyte

1. Introduction

Over the past decades, many different strategies to synthesize TiO$_2$ nanostructures have been investigated[1-6]. Since TiO$_2$ has a high degree of geometrical functionality, electrical advantages, and high chemical stability, it is suitable for use in applications like solar energy conversion systems[7], photocatalysis[8], ion-insertion batteries[9,10], biomedical applications[11] and sensing devices[12]. Synthesis of TiO$_2$ nanostructures can be achieved via various routes including sol-gel methods[13], template-assisted methods[14], hydro/solvolothermal approaches[15], and electrochemical methods[3,5-6,16]. Among these routes, the most simple, inexpensive, and straightforward approach of fabricating TiO$_2$ nanostructures is the self-organizing anodization of Ti-metal substrates under specific electrochemical conditions, namely anodization[3,5-6,16].

Anodization is a classic approach in industry to form a compact (namely, barrier-type) or porous oxide layer on the surface of a metal substrate. It is typically carried out in an electrochemical cell containing a suitable electrolyte, a counter electrode (platinum), and a working electrode composed of the metal of interest (valve metal). By applying a certain anodic potential to the metal of interest, M, it is oxidized to M$^{+}$ (Eq. 1), which either forms a metal oxide, MO$_{2+x}$ (Eq. 2), or is
In 1998, a new anodization approach, carried out in a hot phosphate-containing glycerol electrolyte (~200 °C), was suggested by Melody et al.[20]. The authors were interested in using this electrolyte to form thick tantalum oxide layers for application in capacitor electrodes[21]. Following this study, Habazaki et al., reported that nanostructures of Al2O3, Nb2O5, and Ta2O5 could also be formed by anodization approaches[22-24].

In 2009, Schmuki et al. reported the first successful formation of TiO2 mesoporous structures via Ti anodization[25]. In the report, the anodization was performed in 10 wt% K2HPO4/glycerol electrolyte at 180 °C. Later, other types of TiO2 nanostructures (namely, fishbone and nanochannel structures) were formed by optimizing the anodization conditions[26-28]. Considerable empirical work with similar high-temperature electrolytes and salts has revealed that the combination of glycerol and phosphate uniquely forms these types of self-organized oxide structures[26-29]. In this review, we will overview the various properties and possible application of these nanostructures.

2. Properties of TiO2 Nanostructures

2.1. Geometrical Properties

Figure 1(a)-(c) shows representative cross-sectional SEM images of TiO2 nanostructures (mesoporous or nanosponge, channel, and fishbone) formed by anodization in K2HPO4/glycerol at 180 °C, at different potentials. The nanostructure morphology is significantly dependent on the applied anodization voltage (Figure 1(d)). Figure 1(a) shows the sponge-type nanostructure that is normally formed by anodization at a “low” voltage (1-6 V) or with voltage ramping[26,27]. Irregular nanoscopic channels are formed that typically have a preferred orientation perpendicular to the Ti metal grain surface, with a width in the range of 5-10 nm. This layer was modified by chemical etching to a regular mesoporous oxide layer. A very regular mesoporous morphology is obtained over the entire sample thickness with typical TiO2 feature sizes in the range of 5-10 nm and pores that regularly widen to approximately 10 nm. Figure 1(b) shows the channel-type nanostructure formed by anodization at a “medium” voltage (7-20 V)[27]. The very regular channels are typically oriented perpendicular to the Ti substrate, with a width in the range of 10-60 nm over the entire sample thickness. The channels include several nanometer-sized particle-like structures. Figure 1(c) shows the “fishbone”-type (geometrically similar to “fine tree” or “dendrite”) nanostructure formed by anodization at “high” voltage (20-80 V)[27].

Figure 2 shows the morphological difference between classic TiO2 nanotubes and nanosponge structures. In the figures, one of the remarkable features of the TiO2 nanostructures formed by anodization in a hot K2HPO4/glycerol electrolyte is that no volume expansion of the oxide layer occurs during anodization[28,30]. This result is in contrast to that observed in general anodic metal oxide structures, for example, TiO2 nanotubes grown in fluoride ion-containing electrolyte.

Under high electric field, Ti is oxidized at the metal-native oxide interface that leads to Ti4+ ion migration outwards. In the same time, O2− ion formed in electrolytes is incorporated in the oxide layer and migrate towards the metal oxide interface.

In certain condition, for example fluoride ion for Ti anodization, F− ion can chemically dissolve titanium oxide layer slightly to form [TiF6]2− complex. In this situation, the small size of F− ion can compete with O2− ion inward migration through oxide layer. For this reason, F− ion can accumulate at the metal/oxide interface. Extended Ti anodization in fluoride containing electrolyte, the oxide layers are push up due to plastic flow mechanism that leads 1D nanoporous structures. In the
2.2. Crystallographic Properties

Generally, as-formed anodic TiO$_2$ nanostructures, in particular nanotube layers, are amorphous. However, for most applications, anatase or rutile phases are desired because these phases have high electron mobility and biocompatibility[5-6]. In order for TiO$_2$ nanotubes to form the desired crystal phase, annealing processes are performed[5-6]. Typically, the annealing process is carried out in a furnace or using rapid thermal annealing equipment. The degree of crystallinity and anatase/rutile ratio can be confirmed by X-ray diffraction (XRD) analysis.

In contrast, anodic TiO$_2$ nanostructures formed in a hot phosphate-containing glycerol electrolyte are already partially crystallized during anodization (Figure 3). Low incidence angle (1°) XRD investigations show the crystallinity of the TiO$_2$ nanostructure after anodization (Figure 3). The XRD patterns shown in Figure 3(a)-(d) illustrate that at low voltage (the sponge or mesoporous-type layer formed at 1 V), amorphous (or nanocrystalline) material is present (Figure 3(a)), and that at high voltage (nanochannel and fishbone structures), increasingly more anatase is formed (Figure 3(b)-(d))[27-29]. It is remarkable that the preferred anatase orientation in the channel structure is (101), whereas at high voltage (when the fishbone structure is formed), the preferred orientation is (004)[26,27,29].

In other words, the nanostructure crystallinity depends strongly on the applied voltage (Figure 3). This could possibly be related to the thermal and electrical energy during anodization. When anodized at higher potentials (e.g. 50 V), the temperature of the electrolyte increases to ~250 °C during the beginning stage of anodization[29]. Under these conditions, the surface temperature should be much higher than that of the electrolyte due to the electrical resistance of the surface and convection to the electrolyte. Such temperatures are sufficiently high to crystallize the TiO$_2$[32], enabling nucleation of crystalline TiO$_2$ structures.

 FIGURE 2. (a) Typical current density transient during anodization of evaporated Ti metal on FTO substrate. Inset shows evaporated metal on FTO glass. (b)-(c) anodic TiO$_2$ nanostructures formed by anodization in electrolytes composed of (b) 10 wt% K$_2$HPO$_4$/glycerol and (c) 0.15 M NH$_4$F-containing ethylene glycol with 3 vol% H$_2$O. Reproduced with permission from[30]. Copyright 2012 Elsevier B.V.

 FIGURE 3. XRD spectra of (a) mesoporous, (b)-(c) nanochannel, and (d) fishbone structures. The anodization was performed in 10 wt% K$_2$HPO$_4$ in glycerol at 180 °C. The inset shows the SAED patterns of each layer. The peaks have been annotated as anatase (A) and Ti (T). Reproduced with permission from[27]. Copyright 2011 The Royal Society of Chemistry.

 FIGURE 4. (a)-(d) Optical microscope images of samples after a bending test. Flexibility and stability of the (a) TiO$_2$ mesoporous layer before and after annealing, (b) as-formed nanotubes and (d) fishbone structures. (c) and (e) adherent test of (c) TiO$_2$ nanotubes and (e) mesoporous TiO$_2$ on FTO glass. The tests were performed with Scotch tape. Insets show the transparent layer after the tape was pressed on. After the tape is ripped off, the mesoporous layer (c) remains intact, while the tube layer (e) shows cracks and fissures. Reproduced with permission from [25,26], and [27]. Copyright 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Copyright 2010 American Chemical Society, and Copyright 2012 The Royal Society of Chemistry.

2.3. Mechanical Stability

Another remarkable property of the TiO2 nanostructures formed by anodization in a hot K2HPO4/glycerol electrolyte is their mechanical stability. The mechanical stability was investigated by a simple bending test of TiO2 nanostructures on a metal substrate (Figure 4(a), (b), (d))[25,26]. Figure 4((a), (d)) shows the layers are well-adhered to the surface. The TiO2 nanostructure layers on the metal substrate not only remain intact after intense bending, but also after other intense mechanical treatments[25,26,30].

Moreover, the adherent test was also performed on Ti nanostructures on fluorine-doped tin oxide (FTO) glass. Adhesive tape was pressed on the surface of the anodized structures (Figure 4(c), (e)) and ripped off. The mesoporous layers are well adhered and stable, homogeneous and crack-free on FTO glass (Figure 4(e)). In contrast, TiO2 nanotube layers (Figure 4(b)) show many crack fissures and, in some cases, entire flakes of nanotube layers can be lifted off[28].

This is in contrast to TiO2 nanotube layers formed by anodization in fluoride-containing electrolytes (Figure 4(b), (c)). It is noteworthy that the oxide formation mechanisms are obviously different between the two structures. It is already well known that TiO2 nanotube formation relies on the fluoride ion acting as an etchant to partially dissolve the newly formed oxide layer, with the fluoride ion exhibiting a faster migration rate than that of the oxygen ion[5,6,18]. As a result, fluoride ions accumulate at the oxide nanostructure-metal interface, producing a mechanically weak spot. In contrast, phosphate ions are larger than oxygen ions, implying that phosphate ions hardly migrate or diffuse into formed oxide structures. Furthermore, phosphate ions are a relatively weak etchant compared with fluoride ions.

Figure 5 shows different cross-sectional electron backscattering images of mesoporous TiO2 structures formed by anodization in a hot K3HPO4/glycerol electrolyte on a metal substrate (Figure 5(a)) and FTO glass (Figure 5(b)), together with dark-field transmission electron microscopy (TEM) images of fishbone TiO2 structures (Figure 5(c))[29]. Morphological analysis shows that the bulk and evaporated metal substrates have different grain sizes. The TiO2 structures are formed along the grain boundary of bulk Ti metal, and the oxide layers are interdigitated with the non-oxidized metal substrate. This is another reason for the high mechanical stability of such nanostructures[29].

Moreover, the microscopic images are characteristic of the nanostructure formation mechanism. Oxidation is allowed along the grain boundary following electric field-assisted etching of the oxidized face [28,30]. This is in contrast to nanotube structures that are formed by plastic flow mechanism[33].

3. Applications

3.1. Photocatalyst

Since the first report by Fujishima and Honda, the photocatalytic potential of TiO2 has attracted an increasing research community[8]. UV-stimulated production of electron-hole pairs and resulting OH radicals and peroxides on the TiO2 surface are not only exploited to decompose organic pollutants[33], but also to adjust surface wettability [34,35], establish anti-fogging properties[36] and induce payload release by chain scission of attached monolayers[37-38].

In order to achieve overall high photocatalytic efficiency, typically a high TiO2 surface area is desired. The anodic nanostructures have several unique features that provide the following advantages for photocatalytic applications.

i) The anodic nanostructures have much higher specific surface area than other nanostructures (Degussa P25 = 50 m2/g, nanotubes = 20-30 m2/g, and mesoporous = 70-90 m2/g[26]).

ii) In comparison with nanoparticles, the mesoporous structures are well networked, which enables fast electron transport and reduces the number of recombination sites. In contrast, nanoparticle layers often represent a considerable challenge, frequently resulting in nonideally interlinked particles. From a comparison of photocatalytic activity, the anodic nanostructures show the highest photocatalytic performance among comparable nanostructures, for example, nanoparticle (Degussa P25) and nanotubes (3-µm-thick).

iii) As-formed crystallized nanostructures already consist of a mixture of anatase and rutile. The crystallinity and preferred orientations strongly depend on the applied anodization potential[26]. The crystallographic features can be confirmed by XRD analysis, selected area electron diffraction (SAED) patterns and high-resolution TEM (HRTEM) analysis[25-27]. The comparison of photocatalytic performance shows that the as-formed nanostructures already exhibit higher photocatalytic performance than the as-formed nanotubes, which are almost inactive. Furthermore, the anodic nanostructures exhibit significantly improved photocatalytic performance after annealing, since this process promotes...
additional anatase formation and growth of anatase grain size. Large grain structures are considered to provide fast electron mobility.

iv) Another important advantage for practical application is that the anodic nanostructures provide high mechanical adhesion to the substrate; they are robust and flexible[25,26]. The flexibility and robustness have been demonstrated by simple bending experiments that confirm that the layers are well adhered to the substrate. The novel mechanical properties will aid the development of embedded and immobilization techniques for practical application of anodic TiO2 nanostructures.

Figure 6 shows degradation of a model pollutant (an azo dye, Acid Orange 7) with different TiO2 structure types; namely, nanotubes, fishbone (FB), and fishbone (FB) produced by different methods. The straight lines are fits to a first-order rate law, and the corresponding rate constants are provided in the figure. Reproduced with permission from[26]. Copyright 2010 American Chemical Society.

Figure 6. Comparison of photocatalytic decomposition rates of Acid Orange 7 with TiO2 nanostructures (P25, nanotubes (NT), and fishbone (FB)) produced by different methods. The straight lines are fits to a first-order rate law, and the corresponding rate constants are provided in the figure. Reproduced with permission from[26]. Copyright 2010 American Chemical Society.

3.2. Dye-Sensitized Solar Cells

One of the most promising applications of TiO2 nanotubes is in energy conversion device such as dye-sensitized solar cells (DSSCs). The first report of DSSCs was the observation of the photovoltaic effect on sensitized silver halide in the 1870s[39,40]. In 1985, Grätzel et al. reported an efficient photovoltaic system using TiO2 nanoparticles and a Ru(bpy)32+ complex[41] that showed a quantum efficiency of 80% under visible light irradiation[42]. Later on, Grätzel and O’Regan reported the most significant achievement in this field; namely, the first report of fully fabricated DSSCs[7]. The solar cells consist of a nanocrystalline mesoporous TiO2 thin-film electrode, a Ru-bipyridyl complex and an iodine redox electrolyte that show a conversion efficiency of 11%[7,43]. The working principle is based on excitation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of sensitized dye molecules on the TiO2 surface. Excited electrons are rapidly injected into the metal oxide conduction band (femto- to picoseconds) and oxidized dye molecules are reduced by the electrolyte redox reaction (nanoseconds). However, the electron transport rate in TiO2 and the electrolyte diffusion rate are quite slow (micro to milliseconds). For this reason, the overall cell efficiency is determined by the electron transport rate and the electrolyte diffusion rate[44]. The electron transport rate and electrolyte diffusion rate compete with the electron recombination rate. Generally, the electron transport rate in TiO2 nanoparticles is considerably slow due to the surface state defects and grain boundaries, which play roles as electron trapping and recombination sites[45-49]. In order to overcome the drawback of TiO2 nanoparticles, one-dimensional TiO2 nanostructures, such as nanorods, nanowires and nanotubes, have been considered for use in the photoanode of DSSCs.

Figure 7 shows the J-V characteristics of DSSCs fabricated with several TiO2 nanostructure types (nanotubes, nanochannel, mesoporous, fishbone) that are formed by different anodization conditions. Among the different structures, the mesoporous (sponge) structure has the highest open-circuit potential and fill factor (Voc = 0.68 V, FF = 0.57), but the smallest short-circuit current density. The channel structure has the highest short-circuit current density (Jsc = 14.54 mA/cm2), which is a crucial factor to achieve the highest efficiency (5.02%) of DSSCs, which is 10% higher than that of either the nanotube or fishbone structure (Figure 7). The nanochannel structure provides a high surface area and direct electron path as a result of its highly ordered perpendicular structure and the small particulate granules within its channels[27]. Furthermore, the nanochannel structure presented here not only shows a higher efficiency than comparable nanotube layers, but it is also mechanically much more robust than the anodic TiO2 nanotubes[26]. The mechanical weakness of the interface between the metal substrate/oxide...
of fabricating front-side illuminated DSSCs with TiO$_2$ nanostructures is in the range of 20-50% (Figure 8)[30]. The most straightforward method for illuminating solar cells are noticeably higher than those under back-side illumination. As expected, the conversion efficiencies of the front-side illuminated configurations with TiO$_2$ nanostructures is estimated to be in [49,31]. The cell-efficiency difference between front- and back-side illumination is noticeable, especially in terms of light absorption by the electrolyte and reflection by the Pt-coated electrolyte. This cell configuration causes some loss of efficiency from light absorption compared with particle-based solar cells. This can be explained by two key factors: the specific surface area and the cell construction configuration. Moreover, research into optimized dopant composition and application of anodic TiO$_2$ nanostructures were presented in this review. Furthermore, the approaches taken to incorporate the attractive nanostructures into available photoelectrochemical systems have been detailed. The findings shown here indicate that anodic TiO$_2$ layers formed in a hot phosphate/glycerol electrolyte are highly promising as a result of their chemical, physical, electrical and optical properties. The characteristics and properties of new geometries can be readily controlled by various electrochemical techniques outlined herein. While the overall conversion efficiency of anodic nanostructures in comparison with particle-based solar cells may seem low, the layer thicknesses are still lower than optimum conditions (10-15 µm) and further additives or treatments (TiCl$_4$, buffer layer under oxide structure etc.) have not been performed in these studies. In other words, the development of anodic nanostructures still has room for considerable improvement[52].

4. Summary

The significant research efforts regarding the synthesis, properties, and applications of anodic TiO$_2$ nanostructures were presented in this review. Furthermore, the approaches taken to incorporate the attractive nanostructures into available photoelectrochemical systems have been detailed. The findings shown here indicate that anodic TiO$_2$ layers formed in a hot phosphate/glycerol electrolyte are highly promising as a result of their chemical, physical, electrical and optical properties. The characteristics and properties of new geometries can be readily controlled by various electrochemical techniques outlined herein. However, further studies on the TiO$_2$ nanostructures formed by anodization are needed to find an advanced geometry, which will enable the unique properties to be explored in a tremendous range of applications. A major future research area is the development of the anodization process to prepare advanced and tailored nanostructures, which are acceptable in their target applications, with parameter-screening of their key factors. Moreover, research into optimized dopant composition and doping strategies combining anodization processes (e.g. anodization of Ti-based alloys) must be dedicated to the improvement and development of anodic TiO$_2$ nanostructures.

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