Review Article

Fabrication, Modification, and Emerging Applications of TiO₂ Nanotube Arrays by Electrochemical Synthesis: A Review

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Received 9 July 2013; Accepted 30 July 2013

Academic Editor: Jiaguo Yu

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Titania nanotube arrays (TNAs) as a hot nanomaterial have a unique highly ordered array structure and good mechanical and chemical stability, as well as excellent anticorrosion, biocompatible, and photocatalytic performance. It has been fabricated by a facile electrochemical anodization in electrolytes containing small amounts of fluorine ions. In combination with our research work, we review the recent progress of the new research achievements of TNAs on the preparation processes, forming mechanism, and modification. In addition, we will review the potential and significant applications in the photocatalytic degradation of pollutants, solar cells, water splitting, and other aspects. Finally, the existing problems and further prospects of this nascent and rapidly developing field are also briefly addressed and discussed.

1. Introduction

Nanostructured materials with peculiar properties are not expected in bulk phase and have already led to a breakthrough in various fields of science and technology. Moreover, much of the current interest in one-dimensional nanostructures, such as nanotube, nanowire, nanorod, and nanobelts, was initiated by the discovery of carbon nanotubes by Iijima et al. in 1991 [1]. Within these nanostructure materials, TiO₂-based nanotubes attracted engrossing interest and intensive researches due to their merits of high specific surface area, ion-changeable ability, and photocatalytic ability. Over the past decades, nanostructured materials derived from TiO₂ have extensively been investigated for many promising applications, including solar cells/batteries, self-cleaning coatings, electroluminescent hybrid devices, and photocatalysis, owing to their peculiar chemical and physical behaviors. Currently, developed methods of fabricating TiO₂-based nanotubes comprise the assisted-template method [2, 3], hydrothermal treatment [4–6], and electrochemical anodic oxidation [7–10]. Each fabrication method has unique

advantages and functional features and comparisons among these approaches. Regarding the template-assisted method, anodic aluminum oxide (AAO) nanoporous membrane, which consists of an array of parallel straight nanopores with controllable diameter and length, is usually used as template. However, the template-assisted method often encounters difficulties of prefabrication and postremoval of the previous templates and usually results in impurities. Concerning hydrothermal treatment, the self-assembled TiO₂ nanotubes are based on the treatment of Ti foils or TiO₂ powders in a tightly closed vessel containing highly concentrated NaOH solution (5–10 M) to obtain TiO₂ nanotube layer or TiO₂-based powder [6, 11]. These methods, other than the electrochemical anodic oxidation, are either not suitable for rapid production or notable to yield uniform TiO₂ nanotubes with vertical alignment. The demonstrated architecture of TiO₂ nanotube arrays (TNAs) by a facile electrochemical anodizing process is capable of an ordered alignment with high aspect ratio and establishment of pure-phase TiO₂ structure in one step under ambient environment. More importantly, the electrochemical anodization technique allows the growth

FIGURE 1: SEM images of TNA layers grown with different electrolytes. (a) Typical morphology obtained in acidic fluoride or HF electrolytes, (b) glycerol/fluoride electrolytes, and (c) ethylene glycol/fluoride electrolytes containing small amount of water. The insets show top views, bottom views, and side walls in detail. (d) Fluoride ions free electrolyte; these tubes grow in disordered bundles within seconds at comparably high anodic potentials. (e) Morphology of new type TNAs with time.

of other oxides with self-ordering nanostructures for several transitional and valve metals, such as Al, Zr, Hf, Nb, Ta, W, and Fe and their alloys TiAl, TiZr, TiNb, Ti₆Al₄V, and so on [8, 10].

In 1999, Zwilling et al. firstly reported the self-ordered TiO₂ nanostructures by a simple electrochemical anodizing process in a fluoride electrolyte [12]. Since then, several anodizing approaches, mainly focused on finding the optimal electrolyte and experimental parameters, have been explored to efficiently achieve high quality self-organized TNAs (Figure 1) [13–18], such as short and rough TNAs [13], tapered and conical-shaped TNAs [18], smooth and high-aspect-ratio TNAs [16, 17], transparent TNAs [19, 20], free-standing and

open-ended TNAs [21, 22], highly ordered TNAs by multistep anodization [23, 24], and TNAs with a submicrometer size in diameter [25, 26]. These results demonstrated that structure and morphology of TNAs, including tube diameter, length, wall thickness, and crystallinity, can be controlled by adjusting key parameters such as composition/shape of Ti substrate, electrolyte, pH, temperature, anodization voltage, current, and anodization time. It is, therefore, essential to understand the various factors influencing the characterizations of as-prepared amorphous TNAs. Also, it should be noted that either the annealing posttreatment or the modification of TiO₂-based nanotubes would dominate the corresponding features and the performance of TiO₂-based devices. The aim

FIGURE 2: The number of articles (a) published on TNAs formed by electrochemical anodization and corresponding aggregated citations (b). (Statistics analysis was obtained from web of science database on May 30, 2013). Topic: TiO_2 nanotube, with the exclusion of nanotube formed by hydrothermal, sol-gel, and template or carbon nanotube.

is to make the material more suitable for various applications that rely on specific electrical, optical, or chemical properties. In view of electronic properties, annealing to a crystalline structure mainly changes the conductivity and lifetime of charge carriers, while modification with active doping or band gap engineering by introducing other elements targets for the decreasing of the optical band gap, thus enabling a visible-light photoresponse [27].

Based on extensive literatures with regard to self-ordered TNAs, the authors have categorized three broad groups, preparation and formation mechanism, modifications, and applications, which are further subdivided according to their pertinent studies. First, the formation mechanisms and phenomenon of the electrochemical formation of nanopores and nanotubes by a self-ordering process are explained. Among the aforementioned experimental parameters, both electrolyte and anodizing voltage will be focused on and discussed. Then properties and modification of the TNA materials are addressed briefly, including technique examples of doping, noble metal decoration, and semiconductor composite which are to be discussed. Finally, the current stage of knowledge and recent studies on their potential applications, such as photocatalysis, solar cell, water splitting, and other aspects are introduced. Analysis of the physicochemical properties and recent advances in their modification and applications allow the identification of gaps in our knowledge and highlight the need for critical studies in the area of TNAs.

2. Electrochemical Anodization of TNAs

This section presents recent developments on preparation of self-ordered TiO_2 nanoporous and nanotubular, focused primarily on TNAs by electrochemical synthesis. First, the related statistics of the paper about TNAs and phenomenon of the electrochemical formation of nanoporous TiO_2 materials

by a self-organization process is introduced. Then some experimental parameters of synthesis, which are responsible for regulation of the morphology of TiO_2 nanostructures, are considered. Finally, the formation mechanisms of TNA materials fabricated by electrochemical anodization are presented.

The progressively increasing research interest in the TNA layers formed by electrochemical oxidation can be easily seen from publication statistics (see Figure 2). Publication number and corresponding aggregated citations increased several times from the first work by Zwilling et al. [12], where only a tube length of a few hundred nanometers with a rough and high degree of disorder morphology could be obtained, to nowadays, where smooth and almost ideally hexagonally ordered arrays can be produced with individual nanotube lengths of hundreds of micrometers [22]. In other words, by controlling the electrochemical anodization parameters of Ti (temperature, potential ramping speed, applied potential, electrolyte species, electrolyte pH, viscosity, aqueous or organic electrolyte, etc.), one can obtain different titanium oxide structures such as a flat compact oxide, a disordered porous layer, a highly self-organized porous layer, or finally a highly self-organized nanotube layer (schematically shown in Figure 3(a)).

2.1. Effects of Fabrication Factors on TNAs

2.1.1. Electrolyte. Hydrofluoric acid (HF) is the firstly and most widely studied electrolyte in titanium anodization to produce TiO_2 nanostructures. Since then, several optimized electrolytes of diverse acid/HF mixed electrolytes are put forward to successful fabrication of TiO_2 nanostructures [14]. A brief summary of various synthesis generations of TNAs is given in Table 1. However, the nanotube length in this first synthesis generation is limited to a few hundred nanometers. This second generation of TNAs was obtained with a remarkably high aspect ratio, in a neutral

TABLE 1: Brief summary of various synthesis generations of TNAs.

Generation	Electrolyte type	Potential	Anodized time	Morphology	Main Factor	Reference
<i>First generation:</i> inorganic aqueous electrolytes (HF-based electrolyte)	0.5 wt% HF	10–23 V	≥20 min	Short nanotubes Length: 200–500 nm Diameter: 10–100 nm Wall thickness: 13–27 nm	Potential, electrolyte	[13]
	0.3–0.5 wt% HF + 1 M H ₃ PO ₄	1–25 V	2 h	Length: 20–1000 nm Diameter: 15–120 nm Wall thickness: 20 nm		[32]
<i>Second generation:</i> buffered electrolytes (F [−] -based electrolytes)	1 M Na ₂ SO ₄ + 0.1–1.0 wt% NaF	20 V	10 min–6 h	Roughwall with rings Length: 0.5–2.4 μm Diameter: 100 nm Wall thickness: 12 ± 2 nm	Potential, pH, time	[28]
	1 M (NH ₄) ₂ SO ₄ + 0.5 wt% NH ₄ F	20 V	15–30 min	Length: 0.5–1.0 μm Diameter: 90–110 nm		[33]
<i>Third generation:</i> organic electrolyte containing F [−] ions	0.5 wt% NH ₄ F + 0–5 wt% H ₂ O in glycerol	20 V	13 h	Smooth tube Length: 7.0 μm Diameter: ≈40 nm Wall thickness: 12 ± 2 nm	Potential, water content, time	[17]
	0.1–0.7 wt% NH ₄ F + 2–3.5 wt% H ₂ O in ethylene glycol	60 V	216 h	Ultra-long tube Length: 1000 μm Diameter: 120 ± 10 nm		[22]
<i>Fourth generation:</i> fluoride-free electrolytes	0.01–3 M HClO ₄	1 min	15–60 V	Disordered tubes Length: 30 μm Diameter: 20–40 nm Wall thickness: 10 nm	Electrolyte, time	[30]

type of electrolyte containing fluoride ions, for example, Na₂SO₄/NaF, (NH₄)₂SO₄/NH₄F [28, 29]. The reason for the tube-length increase is the limited dissolution on the top of nanotubes in the neutral electrolyte. The nanotubes by the above inorganic electrolyte were always accompanied with a rough external structure, that is, “rings” or “ripples”, due to current oscillations along the anodization process. The third-generation electrolyte, organic electrolytes with additions of fluoride salts, allows the construction of smooth and much taller TNAs to the regime of hundreds of micrometers. To date, the highest tube lengths can be up to 1000 μm in organic viscous electrolytes [22]. The pH of the electrolyte and the amount of water greatly influence the morphology, structure, and growth rate of the as-formed TiO₂ nanotube. Recent synthesis development of TNAs by using fluoride-free electrolytes is commonly considered as the fourth generation. The results of this rapid breakdown anodization (RBA) are also bundles of disordered nanotubes that grow within very short times (several minutes) [30, 31]. Depending on electrolyte nature, each electrolyte provides a unique geometrical feature of the nanotubes and consequently varying surface properties; thereby, a selection of electrolyte medium for the TNA fabrication is a primary concern.

2.1.2. Voltage. The anodization voltage influences the morphology of formed nanostructures [34]: pores instead of tubes grow at low voltages of 5 V (Figure 3(b1)), while, at voltages higher than 8 V, the diameter of the TiO₂ nanotubes is also influenced linearly by the applied voltage (Figure 3(b2)).

However, at high anodization voltages (>50 V), breakdown events can be observed inside the nanotube resulting in formation of sponge-like structures (Figure 3(b3)). At even higher anodization voltages (>80 V), electropolishing of the samples would take place at a high current density (>100 mA cm^{−2}) in this electrolyte. Therefore, the retardation of breakdown events taking place is vital for the creation of a larger tube diameter. Yin et al. reported that TNAs with larger diameter about 600 nm can be obtained in ethylene glycol electrolytes containing 0.09 M ammonium fluoride and 10 vol% water [35]. Albu and Schmuki further increase the tube diameter to reach 800 nm. However, these tubes are not highly organized and seem loosely assembled in a mesoporous matrix rather than in a neatly defined nanotube array [36]. Recently, Ni et al. successfully demonstrated well-defined, large diameter (680–750 nm) TNAs, with the most uniform and clean morphology by using a higher voltage regime of up to 225 V [25].

2.1.3. Other Factors. In addition to the vital factor of the electrolyte and voltage to the high aspect ratio of the as-prepared nanotube, anodizing time and step, fluoride concentration, and pH and temperature also have a great synergistic effect on the morphology, structure, growth rate, crystallization, and even photoelectrochemical properties of the as-prepared TNAs [8, 37–42]. For example, the transition from porous TiO₂ to a nanotubular structure is not only dependent on water content [43, 44] but also depends on the anodization voltage. The applied voltage directly determines the tube

FIGURE 3: The electrochemical anodization process and typical morphologies: (a) (I) metal electropolishing, (II) formation of compact anodic oxides, (III) self-ordered oxides (nanotubes or nanopores), (IV) ordered nanoporous layers, and (V) rapid (disorganized) oxide nanotube formation. Examples of morphologies of obtained structures: (b) classical ordered TiO_2 nanopores (b1), nanotubes (b2), sponge-like nanoporous structures (b3) anodized in F^- ions containing electrolyte, and (c) disordered TiO_2 nanotubes growing in bundles anodized in F^- ions free electrolyte.

diameters but also strongly influences the rate of TNAs growth, length, and crystallization.

2.2. Growth Mechanism of Anodized TNAs. Self-organized oxide tube arrays or pore arrays can be obtained by an anodization process of a suitable metal, such as transition-metal and valve metal. When metals are exposed to a sufficiently anodic voltage in an electrochemical configuration, an oxidation process will be initiated. Depending mainly on the electrolyte and the particular anodization parameters, essentially three possibilities for reactions exist (see illustration of Figure 3(a)): (I) the metal is continuously dissolved (metal corrosion, or electropolishing), (II) the metal titanium ions (M^{n+}) formed react with O^{2-} (provided by H_2O in the electrolyte) and form a compact oxide layer, and (III) under some electrochemical conditions, competition between dissolution and oxide formation is established leading to porous structures. Under even more specific experimental conditions, a situation is established where self-organized growth of TNAs, formation of thick self-organized mesoporous layers ((IV) in Figure 3(a)), or disordered rapid-breakdown anodization (RBA) of nanotube bundles ((V) in Figures 3(a) and 3(c)) can be observed [10].

In general, it can be concluded that all investigated organized oxide structures grown by anodization in fluoride-containing electrolytes on different metals or alloys seem to follow the same growth mechanism and influence by key factors [7, 8, 10]. Ti was firstly oxidized to form a thin barrier oxide layer of TiO_2 due to interaction of the metal with O^{2-} or OH^- ions. Then, the presence of electric field and fluoride ion led to the creation of random pits and small pores. Finally, self-ordered TNAs formed resulted from the allowance of optimal pores to grow continuously and thicker wall to split by chemical dissolution. The tube diameter is determined by the anodization voltage, etching of the tubes (and thus the achievable length of the tubes) depends on the chemical resistance of the oxide against fluoride etching (in a particular electrolyte), and water plays the key role for providing the oxygen source for tube growth, splits pores into tubes, and is responsible for sidewall rings formation. Obviously, anodization techniques in fluoride-containing electrolytes allow the fabrication of nanostructured oxide layers on an extremely wide range of valve metals and alloys that enable the controllable fabrication of mixed nanostructured oxides with virtually endless possibilities to create enhanced properties and therefore have also a very high and widely unexplored technological potential.

3. Modification of TNA

TiO_2 semiconductor material plays the most important role owing to its excellent chemical and physical properties. However, the higher band gap of the annealed TiO_2 between the valence band (VB) and conduction band (CB) makes them inactive under visible irradiation (Figure 4(a)). In this regard, great efforts have been made to extend the absorption of the wavelength range into the visible light range via the modification of its electronic and optical properties.

Over the past decade, considerable effort has gone into the modification of TiO_2 to exploit the solar spectrum much better. For example, dye sensitization and doping TiO_2 using either nonmetal anions or metal cations is one of the typical approaches that have been largely applied (Figure 4(b)). Coupling TiO_2 with a narrow band gap semiconductor represents another approach (Figure 4(c)). Decoration of noble metal particles with surface plasmon effects allows for more efficient charge transfer (Figure 4(d)). In all of these cases, essentially three beneficial effects are expected: (1) to promote the photogenerated separation between the electron hole (e^-/h^+) and to prevent their recombination, (2) surface plasmon effects, leading to field enhancement in the vicinity of noble metal particles and thus allowing more efficient charge transfer and effective visible light absorption, and (3) heterojunction formation that either changes the band bending (metal clusters on semiconductor) or provides suitable energy levels for synergic absorption and charge separation for enhanced utilization of solar energy.

3.1. Doping. Doping or sensitizing pure TiO_2 by introducing a secondary electronically active species into the lattice for sensitizing TiO_2 to visible light, which promotes the harness of the main range of the solar spectrum and also can ensure the charge trapping for effective photogenerated carries separation (Figure 4(b)). Asahi et al. firstly reported that the nitrogen doping on TiO_2 by sputtering in nitrogen containing gas mixture improves the photoelectrochemical reactivity under visible light irradiation [45]. In the following years, other doping species, such as a number of nonmetals like carbon [46], fluorine [47], sulphur [48], and boron [49], have been introduced into TiO_2 by using various techniques. The results indicated that the visible light absorption and photoelectrochemical activities of these doped crystallized TNAs were not only influenced by the energy gaps and the distributions of impurity states but were also affected by the locations of Femi levels and the energies of band gap edges [50, 51]. Among all these anions, the doping of TNAs with nitrogen or carbon has been found to receive significant attention [52–59]. Highly promising N-doping approach for TNAs includes one-step direct electrochemical anodization of a TiN alloy or growing TNAs in a solution containing doping species [59]. High-energy ion implantation or sputtering in an atmosphere of doping species following an annealing process has been verified to be an effective doping method [60, 61]. However, these methods require special high energy accelerators be operated in a high vacuum environment and the doping depth be limited to several micrometers. Thermal treatment of TNAs in gas atmospheres of the doping species is regarded as a facile one-step doping technique [62, 63]. Moreover, such surface-modified nanotubes shows a significant photoresponse in the visible range compared to nonmodified nanotubes.

At the same time, TiO_2 doped with transition metal cations (e.g., Fe, V, Cr, and Mn) [64–66] have also been reported to widen visible light absorption range, increase the redox potential of the photogenerated radicals, and enhance the conversion efficiency by extending the life of photogenerated electrons and holes. Although the metal cation doping of

FIGURE 4: Schematic of energy level of pure TiO_2 (a) and corresponding modification ((b)–(d)). (b) Doping or dye-sensitization, semiconductors (c), and noble metals (d) coupling.

TiO_2 improves the visible light absorption of the host material to increase photocatalytic activity, a large amount of research also concluded that, when the doping content is excessively high, extra defects can also act as recombination centers to decrease the photocatalytic activity. This adverse effect could be avoided by a suitable doping amount or annealing the doped TiO_2 .

3.2. Semiconductor Composites. In the past decade, many efforts have been devoted to extend the light absorption range of TNAs and to alleviate the charge carrier recombination, such as formation of semiconductor heterostructures with visible light excited narrow band gap semiconductors (Figure 4(c)), for example, CdS , CdSe , and so forth [67–69]. However, it must be expected that the stability of many applied narrow band gap semiconductors fails quickly, not only due to corrosion or photocorrosion, but also due to instability of some of the materials under applied voltage [70].

TNAs essentially provide a very versatile tool to fill or decorate other semiconductors to form composite electrode [71–73]. One of the most followed-up schemes to establishing p-n heterojunctions for high efficient photoelectrocatalytic devices is the direct deposition of p-type

semiconductor onto TNAs [74, 75]. For example, Wang et al. prepared $\text{Cu}_2\text{O}/\text{TiO}_2$ p-n heterojunction photoelectrodes by depositing p-type Cu_2O nanoparticles on n-type TiO_2 nanotube arrays via an ultrasonication-assisted sequential chemical bath deposition (Figures 5(A)–5(D)) [76]. The largely improved separation of photogenerated electrons and holes was revealed by photocurrent measurements. Consequently, p-n $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunction photoelectrodes exhibited a more effective photoconversion capability than single TiO_2 nanotubes (Figure 5(E)). Furthermore, $\text{Cu}_2\text{O}/\text{TiO}_2$ composite photoelectrodes also possessed superior photoelectrocatalytic activity and stability in rhodamine B degradation with a synergistic effect between electricity and visible light irradiation (Figures 5(F)–5(H)).

TiO_2 nanoparticle decoration on TNAs can be obtained by slow hydrolysis of TiCl_4 precursors [20]. In DSSCs, the TNAs decorated with TiO_2 nanoparticles show higher solar cell efficiency in comparison to pure TNAs. The TiO_2 nanoparticles can be deposited inside as well as outside of the tube wall by hydrolysis of a TiCl_4 solution, which significantly increases the surface area and thereby improves the solar-cell efficiency [77].

FIGURE 5: SEM image of TNAs (A, B) and $\text{Cu}_2\text{O}/\text{TiO}_2$ NTAs (C). TEM image of $\text{Cu}_2\text{O}/\text{TiO}_2$ NTAs (D). (E) Photoresponse of $\text{Cu}_2\text{O}/\text{TiO}_2$ NTAs (a, c) and TNAs (b, d) with (a, b) or without (c, d) a bias potential of 0.5 V (versus SCE) under one sun visible light irradiation. (F) Comparison of photocatalytic, electrocatalytic, and photoelectrocatalytic degradation of RhB under visible light irradiation for $\text{Cu}_2\text{O}/\text{TiO}_2$ NTAs. (G) Schematic illustration of photoelectrocatalytic degradation of RhB under visible light irradiation. (H) Comparison of RhB degradation efficiency using $\text{Cu}_2\text{O}/\text{TiO}_2$ NTAs in the process of photoelectrocatalysis (right) with the sum of photocatalysis and electrolysis (left).

3.3. Noble Metal Nanoparticles Decoration. Another approach related to TiO_2 modification is the decoration of TiO_2 surfaces with noble metal nanoparticles (such as, Ag, Au, Pt, Pd, or alloys). Noble metal loading is proved to be an effective way to restrain the recombination of photogenerated electron/hole pairs resulting in photoelectrocatalytic activity enhancement (Figure 4(d)) [78–83]. Moreover, recent study reveals that noble metal nanoparticles can improve the photoresponse ability of TiO_2 in the visible region based on

the surface plasmon resonance (SPR) [84, 85]. It is known that the free electrons of metal can collectively oscillate induced by light irradiation; when the oscillation frequency of light electromagnetic field is in accordance with the free electrons, the SPR effect is generated and light energy is coupled to the metal nanoparticles in the meantime. For example, Ag nanoparticles can be deposited on the tube wall by a photocatalytically reducing process on a TiO_2 surface with UV illumination [86]. Other metal nanoparticles

are preferably deposited by UHV evaporation, sputtering, or chemical/electrochemical deposition techniques [78, 87]. Pt/TiO₂ or Pd/TiO₂ nanotubes also shows a significantly higher photocatalytic activity and water splitting performance compared with plain nanotubes [79, 80].

3.4. Other Aspects. More recent work deals with decoration with graphene [88, 89], Ag/AgCl [85], or AgBr [90] onto TiO₂ to enhance their photocatalytic activity. Amorphous nanotubes synthesized by room-temperature electrochemical anodization are also reported to be annealed in oxygen-rich (O₂), oxygen-deficient (Ar, N), and reducing (H₂) environments, to modify TiO₂ crystal structure, morphology, and electronic properties.

4. Applications of TNA Materials

Porous and tubular titanium dioxide nanostructures have attracted great interest because of their applications in photocatalysis, photovoltaic cells (solar cell), water splitting, biomedical scaffold, wetting template, and other aspects. This porous TiO₂ material is desirable for these applications because of its multifunctional semiconductor properties that are based on its excellent physical and chemical behavior, along with its specific nanostructured architecture that owns it high surface area, high surface activity and fast carries transfer path.

4.1. Photocatalyst. One of the most practical applications of TiO₂ today is in photocatalytic toxic pollutant decomposing. After Fujishima and Honda reported for the first time on light-induced water electrochemical photolysis on TiO₂ surfaces, this functional semiconductor material has been intensively investigated for applications in heterogeneous catalysis [91]. Since then, TiO₂ has shown to be an excellent photocatalyst due to the fact that the material has a set of good properties of long-term stability, low-cost preparation, and a strong enough oxidizing power to be useful for the decomposition of unwanted organic compounds [92–96].

The basic principles involved in the photocatalytic mechanism are shown in Figure 6. UV light promotes electrons excited from the valence band to the conduction band, and then separated holes and electrons will be transported to the semiconductor-environment interface and react with adsorbed molecules. In aqueous solution, highly reactive $\cdot\text{OH}$ radicals are generated by charge exchange at the valence band ($\text{H}_2\text{O} + \text{h}^+ \rightarrow \cdot\text{OH}$), whereas excited electrons at the conduction band mainly reduce dissolved molecular oxygen to super-oxide anions ($\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$). These $\cdot\text{OH}$ radicals and O_2^- ions are able to virtually oxidize all organic materials to CO₂ and H₂O.

Among many TiO₂ nanotubes preparation strategies, the electrochemical anodization process as a simple, cheap, and rapid growth method has been widely utilized to large-scaled preparation of TiO₂ nanotubes with controllable size and morphology [13, 15, 28]. However, smooth surface, relative low surface area, and the amorphous structure of the obtained anodic TiO₂ nanotubes result in low light utilization efficiency and photogenerated charges separation efficiency,

thus leading to the poor photocatalytic activity [92]. Many efforts have been made to enhance the photocatalytic activity of the anodic TiO₂ nanotubes. For example, annealing of anodic TiO₂ nanotubes in conventional air environment contributes to converting the amorphous TiO₂ into anatase, which can efficiently enhance the photocatalytic performance [93]. In order to achieve maximal decomposition efficiency, in addition to crystallized TNAs with adequate band edge positions, rapid charge separation, and high quantum yield, a large area of the catalyst is desired. Crystallized TNAs with suitable posttreatment processes fit these requirements comparably well [92–94, 97]. In previous work, we used anatase TNAs as the photoanode and verified that such novel TNAs showed higher efficiencies than common TiO₂ nanoparticle photocatalysts (Figures 6(b)–6(d)) [93]. Moreover, the annealing temperature has also greatly influenced the crystal structure and photocatalytic activity of TNAs [96, 98, 99].

Up to today, many posttreatment methods for the construction of high efficient TNAs photocatalyst, such as annealing in specific gas atmosphere [100, 101], hydrothermal treatment [102, 103], and vapor-thermal treatment [104], have been generally used to synthesize special crystallized TNAs with high devices performance. Annealing the anodic TNAs through a derivative annealing method in a sealed container with specific environments, such as oxygen-rich (O₂), oxygen-deficient (Ar, N), and other reducing (H₂) gas, can modify the TNAs crystal structure, morphology, and electronic properties and influence the photocatalytic performance [105–107]. However, this method is expensive and has high energy consumption. Recently, considerable efforts have been shifted to the construction of hierarchical architectures based on the 1D TNA nanostructure templates. For example, a simple hydrothermal treatment was adopted to reduce the heat treatment temperature for the construction of anatase TiO₂ nanostructure due to a dissolution-recrystallization transformation of amorphous anodic TNAs, and the resultant hierarchical TiO₂ structures decorated with TiO₂ nanoparticles possess a higher surface area than that of smooth TNAs, which showed enhanced photocatalytic performance [103]. Compared to the heteroelement doping (e.g., N, F, and C) of TNAs, very recently, in situ self-doping with homospecies (e.g., Ti^{3+} , and H^+) by an electrochemical reduction treatment has been emerging as a rational solution to enhance TiO₂ photoactivity within both UV and visible light regions [105]. Despite the great efforts contributed by many groups, well-designed posttreatment strategies for constructing desired crystalline structures with high surface area and anatase phase for highly efficient pollutant degradation have still been an attractive ongoing task.

In addition to many posttreatment methods of the anodic TNAs, the direct decoration of noble metal or semiconductor nanoparticles on crystallized TNAs is also verified to be beneficial for photocatalytic activity enhancement [78, 86, 97, 108, 109]. For example, we reported that a pulse current deposition of Ag nanoparticles modified TNAs was used as the photoanode for photoelectrocatalytic decomposition of methyl orange (MO) pollutant [108]. In this case, we found

FIGURE 6: (a) Scheme of photo-induced processes at a TiO_2 semiconductor/electrolyte interface. Light ($h\nu$) excites valence band electron to conduction band. Electrons and holes react with environment acceptor (A) and/or donor (D). (b) XRD patterns of TNAs film. (c) Comparison of photocatalytic degradation rates of MO for nanoparticle film and two different thicknesses of nanotubes films (A) under the high-pressure mercury lamp illumination. (d) ATR-IR spectra of MO before and after photocatalytic degradation.

that photocatalytic activity of titania nanotube layers can be significantly increased by applying an external bias [108]. Xie et al. performed photocatalytic decomposition of a model organic pollutant (methylene blue) in self-organized TNAs decorated with Ag and CdS nanoparticles. The CdS-Ag- TiO_2 three-component nanotube arrays system exhibited superior synergy effect on both photoelectrochemical and photocatalytic activities compared to those of the pure TiO_2 and Ag or CdS modified TiO_2 systems [109].

4.2. Solar Cells. One of the most promising applications of TiO_2 today is in dye-sensitized solar cells (DSSCs), a concept

introduced by O'Regan and Grätzel in 1991 [110]. The classical DSSCs operate with sintered or compressed nanoparticulate TiO_2 layers as electron harvesting material. Compared to agglomerate TiO_2 nanoparticle layer containing a high number of grain boundaries that can act as recombination sites, the new architecture of TNAs by electrochemical anodization has been verified to be an ideal photoanode in photoelectrocatalytic devices due to its improved charge-collection efficiency and short pathway for the photogenerated excitons along the vertically aligned tubes to the conducting substrate. As such, it may be expected that optimized TNAs can significantly increase the solar energy conversion efficiency.

FIGURE 7: Schematic illustration of front-side illuminated DSSC based on transparent TNAs on FTO substrate (a), backside illuminated DSSC based on TNAs on Ti substrate (b), two light sources illuminated DSSC based on both sides of TNAs on Ti substrate (c), and parallel configuration DSSC with one light source irradiation on double-sided TNAs by using a dielectric mirror (d).

4.2.1. Dye-Sensitized Solar Cells (DSSCs). Owing to well-defined structural parameters and enhanced electronic properties, highly ordered TNAs have been employed to substitute TiO₂ nanoparticles for use in DSSCs [111]. Mor et al. reported the integration of TiO₂ nanoparticles modified transparent nanotube array (360 nm in length) architecture in fluorine-doped tin oxide (FTO) glass for front-side illuminated dye solar cell and displayed a photoconversion efficiency (PCE) of 2.9% (Figure 7(a)) [20]. They also observed that solar cells constructed by longer nanotubes formed from titanium foils (backside illumination) have superior charge transfer efficiency and more dyes absorption in comparison with solar cells fabricated with transparent short nanotubes formed on FTO glass. However, the overall power conversion efficiency of dye-sensitized TNA solar cells remained relatively low as a result of incomplete coverage of dye molecules on the TNAs and insufficient infiltration of electrolyte into nanotubes. For example, backside illuminated N719 DSSC based on 6 μm long TNAs film on titanium substrate shows a PCE of 4.24% under AM 1.5 sunlight source (Figure 7(b)) [112]. To further improve the performance of dye-sensitized TNA solar cells, efforts have been directed toward the improvement of dye loading, charge transport, light absorption, and optimization of TiO₂ nanostructures [77, 111, 113–115]. Recently, Liu and Misra applied double-sided TNAs for bifacial dye-sensitized solar cells and reported that a photocurrent density of such bifacial DSSCs was almost twice that of one-sided illumination (Figure 7(c)) [115]. Sun et al. demonstrated a new

parallel configuration of DSSCs using double-sided TNAs as the photoanode and a dielectric mirror for sunlight to be irradiated on both sides of TNA photoanode (Figure 7(d)) [116]. An average 70% increment in photocurrent and 30% enhancement in PCE were obtained relative to those of the single cells. Zheng et al. constructed a layer-by-layer hierarchical photoanode consisting of TiO₂ particles and free-standing TNAs for DSSCs with a PCE of 8.80%, which exhibited increased light-harvesting efficiency, longer electron lifetimes, and more efficient electron extraction than those in single particle film or nanotube array based devices [117].

4.2.2. Quantum Dots Sensitized Solar Cells (QDSSCs). Typically, CdX (X = S, Se, and Te) QDs with size-dependent band gaps provide new opportunities for harvesting light energy in the visible and infrared regions of solar light [118]. In addition, through the impact ionization effect, it is possible to generate multiple excitons from single-photon absorption in QDs [119]. In the case of the QDSSCs, excited electrons of CdX nanocrystals are injected into a large band gap semiconductor (e.g., TiO₂ and ZnO), and holes reacted with a redox couple. Recently, Sudhagar et al. prepared the CdS/CdSe coupled TiO₂ nanofibrous electrode with a maximum PCE of 2.69% [120], while Shen et al. fabricated a CdSe QDs-sensitized TNAs photoelectrode with an optimal photovoltaic conversion efficiency of 1.80% [121]. Recently, we report that a PCE of 2.74% is achieved on novel QDSSCs

FIGURE 8: Top view and cross-sectional SEM images of TNAs (a), CdS@TNAs (b), and CdSe/CdS@TNAs (c). (d) Schematic of CdSe/CdS@TNAs for QDSSC. (e) J-V characteristics of corresponding QDSSCs.

based on the CdS/CdSe QDs cosensitized TiO₂ nanocrystal arrays by a sealed annealing process (Figure 8) [67]. We found that such coupled CdS/CdSe QDSSC exhibited a greatly enhanced short-circuit current density (Figure 8(e)) as compared to pure TNAs and single CdS or CdSe QDSSC because the combination of CdS and CdSe QDs has a complementary effect in light harvest and surface area increment, and a stepwise band edge level structure of CdSe/CdS@TNAs benefited for electron injection into TNAs. Sun et al. reported a novel CdS QDs sensitized TNA photoelectrodes by a sequential chemical bath deposition technique and found that the CdS QDs among the TNAs significantly increased the QDSSC efficiency up to 4.15% [122]. These results clearly demonstrate that the unique nanotube structure can facilitate the propagation and kinetic separation of photogenerated charges, suggesting potentially important applications of the inorganic TNA QDSSCs in solar cell applications. However, compared to DSSCs with PCE up to 12%, QDSSCs have not been demonstrated as an efficient inorganic dye than expected. Therefore, great efforts are still needed to inhibit charge recombination at the semiconductor surface for the efficiency improvement of QDSSCs [123].

4.3. Water Splitting. Considering that the principle of photoelectrolysis for water splitting is the same with photocatalysis,

TNAs are considered as good candidates for high efficient water splitting (see Table 2). The photoelectrolysis process using TiO₂ nanotube cells as a photoanode is as follows: when the photoanode is immersed in water and exposed to light irradiation, it absorbs photonic energy over its band gap energy; then, electron-hole pairs are generated in it. The generated holes oxidize O²⁻ ions from absorbed water and produce oxygen gas and an electric current that moves through the external circuit to the conducting cathode in which it reduces H⁺ ions to produce hydrogen gas. Recently, TNAs prepared by anodization of titanium have attracted extensive interest in photocatalytic water splitting. Mor et al. find a hydrogen generation rate of 96 $\mu\text{mol/h/cm}^2$ for the utilization of nanotube array (224 nm in length) for water splitting under a constant voltage bias of -0.4 V (versus Ag/AgCl) [124]. Recently, we reported an enhanced hydrogen generation rate of 150 $\mu\text{mol/h/cm}^2$ by a three-step electrochemical anodized TNAs with a regular porous top layer (Figures 9(a) and 9(b)) [125]. Moreover, we found that palladium quantum dots sensitized TNAs exhibited highly efficient photocatalytic hydrogen production rate of 592 $\mu\text{mol/h/cm}^2$ under 320 mW/cm² irradiation (Figures 9(c)–9(h)) [79]. In general, the hydrogen production rate is greatly depending on the electrolyte, external bias, light intensity, and TiO₂ morphology and structure. Therefore, it is important to

TABLE 2: Summary of TNAs based materials in water splitting.

Photoanode	Light intensity (mW/cm ²)	Electrolyte	Photocurrent (mA/cm ²)	Water splitting (μmol/h/cm ²)	Reference
C-TNAs	N/A; 500 W Xe lamp	0.1 M Na ₂ S + 0.02 M Na ₂ SO ₃	N/A	1.6 (0.040 mL/h/cm ²)	[126]
TNAs	70; 300 W Xe lamp	1 M KOH	0.58@0.6 V versus NHE	71 (0.178 mL/h/cm ²)	[127]
C-TNAs (C-containing TiO ₂ based nanotube arrays)	12.7, 300 W Xe Lamp	1 M KOH	1.96@0 V versus Ag/AgCl	11.28 (0.282 mL/h/cm ²)	[128]
TNAs with etching pretreatment	87, 300 W AM 1.5	1 M KOH	1.78@1.23 V RHE	34.8 (0.87 mL/h/cm ²)	[129]
Ru/TNAs@0.05 at% Ru	100	1 M KOH	1.78@0.4 V versus Ag/AgCl	45 (1.08 mL/h/cm ²)	[130]
TNAs (224 nm length, 34 nm wall thickness)	100	1 M KOH	13.0@0 V versus Ag/AgCl	96 (2.30 mL/h/cm ²)	[124]
TNAs	110	1 M KOH + 0.5 M H ₂ SO ₄	4.95	97 (2.32 mL/h/cm ²)	[131]
TNAs	74	1 M KOH	N/A	140 (3.28 mL/h/cm ²)	[132]
Leaf-like TiO ₂ /TNAs	320	2 M Na ₂ CO ₃ + 0.5 M EGD	16.3@0.9 V versus SCE	150	[125]
Pyrococcus furiosus/TNAs	74	1 M KOH	N/A	234.88	[133]
TNAs	74	1 M KOH	32.8@1.5 V versus Ag/AgCl	250	[134]
TNAs (three-step anodization)	320	2 M Na ₂ CO ₃ + 0.5 M EGD	24@-0.3 V versus SCE	420	[135]
Pt@TNAs	320	2 M Na ₂ CO ₃ + 0.5 M EGD	24.2@-0.3 V versus SCE	495	[80]
Pd@TNAs	320	2 M Na ₂ CO ₃ + 0.5 M EGD	26.8@0.9 V versus SCE	592	[79]

optimize these parameters and fundamentally understand their possible correlations to clarify the approaches toward to construct high efficient cell for hydrogen generation.

4.4. Other Applications. As mentioned above, another special electrochemical feature of TNAs or some other TiO₂ nanotube based materials is its ability to serve as a host for small ions insertion, typically hydrogen ion or lithium ion, into the lattice, leading to the drastic change of electronic and optical properties for potential applications in lithium-battery [4, 136, 137], electrochromic devices [138, 139], and supercapacitor [140, 141]. The kinetics, magnitude, and reversibility of the ion insertion and electrochromic reaction strongly depend on the ion diffusion length and therefore on geometry of the electrode surface. Due to the specific vertical alignment of the TNAs, a very high contrast can be obtained using vertically oriented nanotubes. By deposition of Ag nanoparticles on the TNAs, a material can be created that shows considerable photochromic contrast [142]. Furthermore, the TNA has also been proved to be good support for Pt or Pt/Ru catalysts for enhanced methanol electrooxidation [143, 144].

Other applications of the TNAs for biomedical implant are wetting template, target hydrogen sensing, electrochemical detection, and photogenerated cathode anticorrosion

[145–147]. For instance, the combination of organic modification with a controllable photocatalytic reaction of TiO₂ was used to create microscale patterning surfaces with any desired wettability value. Wetting micropatterns with different physical or chemical properties have frequently acted as templates for fabricating various functional materials in a large scale [148]. Moreover, wetting patterns with tailored and reversible adhesion for microfluidic devices and microdroplet manipulation have also been reported [149]. For example, Ag@TNA micropatterns show not only the high-throughput molecular sensing feature with high sensitive, reproducible performance but also show promising targeted antibacterials properties [148]. For gas sensing, Varghese et al. have shown instant resistance response in order of several magnitudes for the TNA layer upon exposure to 1000 ppm H₂ containing nitrogen atmospheres at room temperature [145].

The applications of TNAs can significantly be expanded if secondary material can successfully be deposited into the tubes. The TNAs can also be converted to other titanates MTiO₃ (M = Sr, Pd, Zr) with specific bioactive, piezoelectric or ferroelectric properties and keep with its original tube structure by a simple hydrothermal process in the corresponding precursor solution or a direct anodizing process in appropriate alloy substrates [150–153].

FIGURE 9: Top and cross-sectional SEM images of pure TNAs ((a), (b)) and Pd QDs@TNAs ((c), (d)). The insets show the corresponding magnified images. TEM images of TNAs coated with Pd QDs. (g) Schematic of TNAs on photoelectrolytic water splitting for hydrogen production. (h) Schematic illustration of TNAs deposited with Pd QDs and the charge transfer process from TiO₂ to Pd (lower right panel).

5. Conclusion

Till now, a large number of fundamental studies and application-oriented researches and developments are extensively carried out by many researchers for this low-dimensional nanomaterial due to the expected various properties of TiO₂ (high surface area and controllable nanotube dimensions, geometries, and surface chemistry). This work has presented the recent progress of preparation and modification on the electrochemically anodized TNA materials. These unique low dimensional nanostructure materials have been shown to have many favourable properties for potential applications, including pollutant photocatalytic decomposition,

photovoltaic cells, biomedical scaffold, and wetting template. On the other hand, extensive challenges to fabricate high quality TNAs and develop various oxide nanotubes have been continued. For instance, rapid and high-efficient synthesis of anatase TNAs and other multicomponent nanotubes under ambient low-temperature conditions have recently been reported [154]. Some other aspects aim to encompass the new progress of TiO₂ for an efficient utilization in photocatalytic or photovoltaic applications under visible light, emphasize the future trends of TiO₂ in the environment and/or energy related fields, and suggest new research directions, including preparation aspects for the development of this promising material [155].

Acknowledgments

The authors thank the Alexander von Humboldt (AvH) Foundation of Germany, the EU Microcare project (FP7-PEOPLE-2009-IRSES/247641), and the Natural Science Foundation of Jiangsu Province of China (Grant no. BK20130313) for the financial support of this work. We also acknowledge support from the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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